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Syntheses of dibenzo[*b*,*e*][1,4]dioxin derivatives via iron complexes, and further functionalizations via directed metallation

Richard C. Cambie, Sally J. Janssen, Peter S. Rutledge and Paul D. Woodgate *
Department of Chemistry, University of Auckland, Private Bag, Auckland (New Zealand)
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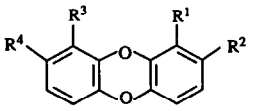
Abstract

Double nucleophilic aromatic substitution reactions between (cyclopentadienyl)(η^6-1,2-dichlorobenzene)iron(1+) salts and substituted 1,2-benzenediols have been carried out under mild conditions to prepare [η^6-dibenzo[*b*,*e*][1,4]dioxin]iron(1+) complexes functionalized in the 1- or 2-position with an alkyl, aldehyde, carboxylic acid, methoxycarbonyl, carboxamide, or hydroxy group. 3-Methyl- and 4-methyl-(η^6-1,2-dichlorobenzene)iron complexes were treated with substituted 1,2-benzenediols to effect functionalization of both aromatic rings of the heterocycle. The dibenzodioxin ligands were liberated routinely by irradiation with ultraviolet light. Directed deprotonation of the free functionalized dibenzodioxins with an alkyllithium reagent followed by quenching with a variety of electrophiles yielded further derivatives, including two new isoindolone systems.

Introduction

Interest in the synthesis of asymmetrically polysubstituted dibenzo[*b*,*e*][1,4]dioxins has been stimulated by the discovery of the potent *in vitro* cytotoxicity and significant *in vivo* antitumour activity of *N*-[2-(dimethylamino)ethyl)]dibenzodioxin-1-carboxamide (**1**) [1]. Two main routes to dibenzodioxins are known, namely the self-condensation of 2-halogenophenols promoted by base [2,3] and the condensation of 1,2-benzenediols with activated chlorobenzenes [4,5]. Significant improvements in the yields obtained from the latter method have been made recently by Lee and Denny [6] using hexamethylphosphoric triamide (HMPT) as the solvent and metallic potassium as the base. Both of these approaches, however, require vigorous experimental conditions which may not be appropriate for the synthesis of polyfunctional dibenzodioxins. Moreover, it would be advantageous practically to use a solvent other than HMPT (use of tetrahydrofuran (THF), dimethylformamide (DMF), or sulpholane gave virtually no dibenzodioxins [6]). The formation of a mixture of regioisomeric dibenzodioxins (often very difficult to separate) when each of the coupling partners is unsymmetrical presents an additional problem. Activation of 1,2-dichlorobenzene by complexation with a tricarbonylchromium moiety [7] and reaction with an excess of the monopotassium salt of 1,2-ben-



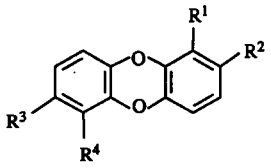
(1; $R^1 = CONH(CH_2)_2NMe_2$, $R^2 = R^3 = R^4 = H$
2; $R^1 = R^2 = R^3 = R^4 = H$
3; $R^2 = Me$, $R^1 = R^3 = R^4 = H$
4; $R^2 = CHO$, $R^1 = R^3 = R^4 = H$
5; $R^2 = (CH_2)_2CO_2H$, $R^1 = R^3 = R^4 = H$
6; $R^1 = OH$, $R^2 = R^3 = R^4 = H$
7; $R^1 = CO_2Me$, $R^2 = R^3 = R^4 = H$
8; $R^1 = R^2 = R^3 = H$, $R^4 = Me$
9; $R^2 = R^4 = Me$, $R^1 = R^3 = H$
10; $R^2 = CHO$, $R^1 = R^3 = H$, $R^4 = Me$
11; $R^2 = CONH(CH_2)_2NMe_2$, $R^1 = R^3 = R^4 = H$
12; $R^2 = CO_2Me$, $R^1 = R^3 = R^4 = H$
13; $R^2 = CO_2H$, $R^1 = R^3 = R^4 = H$
14; $R^2 = CONH(CH_2)_3NMe_2$, $R^1 = R^3 = R^4 = H$
15; $R^1 = CO_2H$, $R^2 = R^3 = R^4 = H$
16; $R^1 = COBu$, $R^2 = R^3 = R^4 = H$
17; $R^1 = CO_2Me$, $R^2 = R^4 = H$, $R^3 = COBu$
18; $R^1 = R^3 = CO_2Me$, $R^2 = R^4 = H$
19; $R^1 = CO_2H$, $R^2 = R^4 = H$, $R^3 = I$
20; $R^1 = COBu$, $R^2 = R^4 = H$, $R^3 = I$
21; $R^1 = CONH(CH_2)_2NMe_2$, $R^2 = R^4 = H$, $R^3 = CHO$
22; $R^1 = CONH(CH_2)_2N^+HMe_2$, $R^2 = R^4 = H$, $R^3 = CO_2^-$
23; $R^1 = CONH(CH_2)_2NMe_2$, $R^2 = R^4 = H$, $R^3 = CO_2Me$
24; $R^1 = CONH(CH_2)_2NMe_2$, $R^2 = R^4 = H$, $R^3 = CONHPh$
25; $R^1 = CONH(CH_2)_2NMe_2$, $R^2 = R^4 = H$, $R^3 = SiMe_3$
26; $R^1 = CON(CH_2)_2N^+HMe_2Cl^-$, $R^2 = R^3 = R^4 = H$
27; $R^1 = CONH(CH_2)_2NMe_2$, $R^2 = SiMe_3$, $R^3 = R^4 = H$
28; $R^1 = CONH(CH_2)_2NMe_2$, $R^2 = R^3 = SiMe_3$, $R^4 = H$
29; $R^1 = CONH(CH_2)_2NMe_2$, $R^2 = t\text{-}BuMe_2Si$, $R^3 = R^4 = H$
30; $R^1 = CONH(CH_2)_2NMe_2$, $R^2 = t\text{-}BuMe_2Si$, $R^3 = CHO$, $R^4 = H$
31; $R^1 = CONH(CH_2)_2NMe_2$, $R^2 = t\text{-}BuMe_2Si$, $R^3 = CO_2H$, $R^4 = H$
32; $R^1 = R^3 = R^4 = H$, $R^2 = Br$
33; $R^1 = R^3 = H$, $R^2 = R^4 = Br$
34; $R^1 = R^3 = R^4 = H$, $R^2 = SiMe_3$
35; $R^1 = R^3 = H$, $R^2 = Bu$, $R^4 = t\text{-}BuMe_2SiO$
36; $R^1 = CH(OH)(CH_2)_3Me$, $R^2 = CONH(CH_2)_2NMe_2$, $R^3 = R^4 = H$
37; $R^1 = CHO$, $R^2 = CON(CHO)$, $R^3 = R^4 = H$
38; $R^1 = R^3 = CONH(CH_2)_2NMe_2$, $R^2 = R^4 = H$)

zenediol gave a good yield of dibenzo[*b*,*e*][1,4]dioxin at relatively low temperature, but HMPT was again the preferred solvent. An alternative method which uses a cationic (cyclopentadienyl)iron complex to activate 1,2-dichlorobenzene towards nucleophilic substitutions has also been reported [8]. We report application of this latter method for the preparation of complexes of 1- and 2-substituted dibenzodioxins from reaction of 3- and 4-substituted 1,2-benzenediols with the substituted (cyclopentadienyl)(η^6-1,2-dichlorobenzene) salts **46**, **47** and **48** under mild conditions. We also report some reactions of the decomplexed dibenzodioxins with an alkyllithium reagent followed by treatment with a variety of electrophiles, leading to further functionalization of the heterocycle.

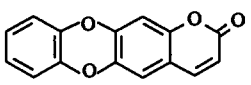
Results and discussion

For spectroscopic comparison purposes the parent dibenzo[*b*,*e*][1,4]dioxin (**2**) was prepared by the classic Ullman-type self-condensation of 2-chlorophenol [9]. Use of the tridentate phase transfer agent tris[2-(2-methoxyethoxy)ethyl]amine [10] and copper(I) chloride as catalysts in this reaction gave **2** in 50% yield, which represents a significant improvement over previous syntheses of this type from 2-chlorophenol (10–20%) [3]. Thermally promoted reaction of **2** with hexacarbonylchromium gave the $Cr(CO)_3$ complex **49** (58%) [7].

Cationic (cyclopentadienyl)iron complexes of 1,2-dichlorobenzene and of substituted 1,2-dichlorobenzenes were prepared by ligand exchange from ferrocene [11,12]. Product dibenzodioxin complexes resulting from reaction of these salts with 1,2-benzenediol and substituted 1,2-benzenediols are given in Table 1, together with the decomplexed dibenzodioxins subsequently obtained. Liberation of



(39; $R^2 = R^3 = Me$, $R^1 = R^4 = H$
40; $R^2 = CHO$, $R^1 = R^4 = H$, $R^3 = Me$
41; $R^1 = CONH(CH_2)_2NMe_2$, $R^2 = t\text{-}BuMe_2Si$, $R^3 = H$, $R^4 = CHO$
42; $R^1 = CONH(CH_2)_2NMe_2$, $R^2 = t\text{-}BuMe_2Si$, $R^3 = H$, $R^4 = CO_2H$
43; $R^1 = R^4 = H$, $R^2 = R^3 = Br$
44; $R^1 = R^4 = H$, $R^2 = Bu$, $R^3 = t\text{-}BuMe_2SiO$)



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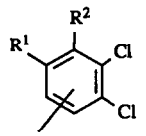


$CpFe^+PF_6^-$

(46; $R^1 = R^2 = H$
47; $R^1 = Me$, $R^2 = H$
48; $R^1 = H$, $R^2 = Me$)

a dibenzodioxin from its η^6-iron(1 +) salt was achieved usually by irradiation [13] through quartz at 300 nm in degassed acetonitrile, although THF or CH_2Cl_2 were used occasionally as solvent and a few photolyses were carried out at 254 nm. Decomplexation could also be effected by pyrolytic sublimation [14] (e.g. **52** afforded **4**, 68%; **66/60** afforded **39/9**, 71%), or by heating with excess *N*-bromosuccinimide (NBS) [15] in THF/MeOH (e.g. **52** afforded **4**, 57%). The double nucleophilic aromatic substitution reactions afforded (η^6-dibenzodioxin)iron(1 +) salts functionalized in the 2-position with methyl (**51**), formyl (**52**), carboxylic acid (**53**) and propanoic (**54**) substituents, and in the 1-position with hydroxy (**55**), carboxylic acid (**56**), methoxycarbonyl (**57**) and *N*-[2-(dimethylamino)ethyl]carboxamide (**58**) [cf. 1] groups. In initial studies potassium carbonate was used as the base and THF [8] was used as the solvent for these coupling reactions. However, it was found that the use of DMF not only increased the rate of reaction considerably, but also resulted in higher yields of (η^6-dibenzodioxin)iron(1 +) complexes. For example, the yield of **50** was 56% after 46.5 h at room temperature in THF, but 74% after only 1.5 h at room temperature in DMF; for the aldehyde **52** the corresponding figures were 32% after 44 h and 44% after 1.5 h. Thus a variety of (η^6-dibenzodioxin)$CpFe^+$ salts could be synthesized in good yield under very mild conditions [cf. 7]. Although in those cases which could lead to the formation of a mixture of regioisomers both coupled complexes were in fact formed (i.e. **66/60**; **61/67**; **62/69**), there was a predictable and potentially exploitable variation in the ratio of the *syn* versus *anti* regioisomer (1.2/1.0; 1.6/1.0; 1.9/1.0, respectively) which reflects initial *ipso* attack preferentially on the more electrophilic chlorine-bearing carbon of the (η^6-1,2-dichlorobenzene)$CpFe^+$ salt by the more nucleophilic phenoxide anion of the substituted 1,2-benzenediol.

Attempts to react the (cyclopentadienyl)iron(1 +) salt of 1,2-dichlorobenzene with 4-(2-aminoethyl)-1,2-benzenediol hydrochloride with the aim of incorporating an amine directly into the dibenzodioxin carboxamide side-chain were less successful, affording an inseparable mixture of **46** and three other cationic complexes [cf. 16] in low combined yield. In the case of 2,3-dihydroxy-*N*-[2-(dimethylamino)ethyl]benzamide as nucleophile a mixture of the unstable (η^6-arene)CpFe$^+$ complex **58** and the free dibenzodioxin-1-carboxamide **1** was formed. Irradiation of this mixture in acetonitrile at 300 nm followed by chromatography afforded the biologically active amide **1** in an overall yield of 32%. This carboxamide was also prepared (89%) by heating methyl dibenzo[*b*,*e*][1,4]dioxin-1-carboxylate (**7**) with an excess of *N*,*N*-dimethyl-1,2-ethanediamine. The corresponding dibenzodioxin-2-carboxamide **11** was prepared indirectly by oxidation of the aldehyde CpFe$^+$ salt **52** to the carboxylic acid complex **53** with Jones reagent and then amidation with *N*,*N*-dimethyl-1,2-ethanediamine using 1,1′-carbonyldiimidazole (CDI) to activate the acid. This sequence afforded the complexed 2-carboxamide **63** as an unstable solid (27%), in addition to the free amide **11**. The latter compound was also prepared from the non-complexed aldehyde **4**, either by conversion (75%) directly [17] into the methyl ester **12** using sodium cyanide and barium manganate [18] in acetic acid/methanol followed by heating the ester with excess $H_2N(CH_2)_2NMe_2$ at 110 °C, or by oxidation to the carboxylic acid (**13**) with Jones reagent (90%) followed by amidation at room temperature with CDI/$H_2N(CH_2)_2NMe_2$ (94%). The corresponding dibenzodioxin **14** with a homologous 2-[*N*-(3-dimethylamino)propyl] side-chain was prepared similarly (94%) by amidation of **13** with CDI/$H_2N(CH_2)_3NMe_2$.

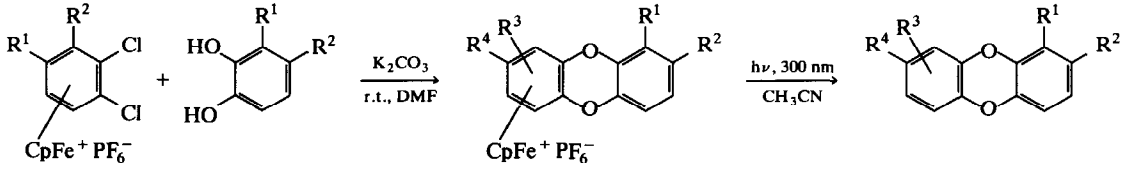
Attempted functionalization of the complexed ring of (η^6-dibenzodioxin)CpFe$^+$ (**50**) by nucleophilic addition of 2-lithiopropanenitrile followed by oxidative aromatization of the putative substituted cyclohexadienyl intermediate with NBS [cf. 15] returned only **50** (45%) and the free ligand (**2**) (19%).

Since the usual method of preparation of (η^6-arene)CpFe$^+$ salts by ligand exchange from ferrocene is catalyzed by $AlCl_3$, one is restricted to the synthesis of complexes from 1,2-dichloroarenes which contain neither an additional electron-withdrawing group (e.g. CO_2R), nor an electron-donating group containing lone pairs of electrons since these interact with the Lewis acid catalyst and thereby deactivate the arene towards formation of the salt. Thus, in order to form dibenzodioxin complexes carrying a methyl substituent on the ring η^6-bound to iron, and hence to provide a locus for further modification leading eventually to heterocycles substituted regioselectively on each aromatic ring, the CpFe$^+$ complexes **47** and **48** of 1,2-dichloro-4-methylbenzene and of 1,2-dichloro-3-methylbenzene were prepared and coupled with 1,2-benzenediol and with 4-methyl-1,2-benzenediol. The salt from reaction of **47** with 4-methyl-1,2-benzenediol was a mixture (1.2 : 1.0) of the *anti* (2,7)- and *syn* (2,8)-isomers **66** and **60** as shown by comparison of the ^1H and ^{13}C NMR spectra of the mixture of decomplexed dibenzodioxins (**39**) and (**9**) with those of a sample of 2,7-dimethyldibenzo[*b*,*e*][1,4]dioxin (**39**) synthesized independently [19].

In order to investigate further functionalization of the decomplexed dibenzodioxins via directed lithiation-quenching sequences, the secondary amides **1**, **11** and **29** as well as selected other derivatives were lithiated and then treated with an electrophile (Table 2). In the case of the parent heterocycle **2** deprotonation by

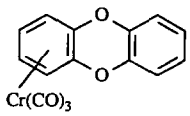
Table 1

Preparation of substituted dibenzo[*b*,*e*][1,4]dioxins



(Dichlorobenzene) $CpFe^+$			1,2-Benzenediol		(η^6-Dibenzodioxin)$FeCp^+$ complex				Dibenzo[*b*,*e*][1,4]dioxin			
	R^1	R^2	R^1	R^2	Time (h)	Product	Yield (%)	m.p. (dec.) (°C)	Time (h)	Product	Yield (%)	m.p. (°C)
46	H	H	H	H	1.75	**50**	74	209–210	3.5	**2**	94	119–120
46	H	H	H	Me	4.5	**51**	69	194–196	4.0	**3**	76	54.5– 55.5
46	H	H	H	CHO	4.0	**52**	75	211–213	2.5	**4**	59	93– 96
46	H	H	H	CO_2H	24.5	**53**	81	226–229	–			
46	H	H	H	$(CH_2)_2CO_2H$	28.0	**54**	75	–	1.25	**5**	45	157–165
46	H	H	OH	H	3.0	**55**	100	Oil	4.0	**6**	26	167–172
46	H	H	CO_2H	H	23.0	**56**	50	Oil	–			
46	H	H	CO_2Me	H	1.5	**57**	87	220–223	3.5	**7**	87	92– 94
46	H	H	$CONH(CH_2)_2NMe_2$	H	6.0	**58**	11	Unstable solid	2.25	**1**	32	101–103
46	H	H	[a]	[a]	2.0	**64**	81	257–261 [c]	1.25	**45**	18	230–270
46	H	H	[b]	[b]	2.5	**65**	55	Unstable solid	–			
47	Me	H	H	H	2.75	**59**	55	163–165	1.5	**8**	69	54.5– 55.5
47	Me	H	H	Me	1.75	**66,60**	52	171–173	3.5	**39,9**	83	81.5– 83.5
47	Me	H	H	CHO	3.0	**61,67**	74	214–216	3.0	**10,40**	60	97 – 99
48	H	Me	H	H	22.0	**68**	13	159.5–160.5	–			
48	H	Me	H	CO_2Me	23.0	**62,69**	25	232.5–234.5 [d]				

[a] 6,7-Dihydroxycoumarin. [b] 2,3-Dihydroxypyridine. [c] Also formed (10%) was a product tentatively identified as **36**. [d] Major isomer **60**.



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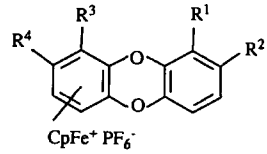
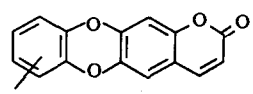
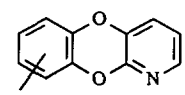


(50; $R^1 = R^2 = R^3 = R^4 = H$
51, $R^2 = Me$, $R^1 = R^3 = R^4 = H$
52; $R^2 = CHO$, $R^1 = R^3 = R^4 = H$
53; $R^2 = CO_2H$, $R^1 = R^3 = R^4 = H$
54; $R^2 = (CH_2)_2CO_2H$, $R^1 = R^3 = R^4 = H$
55; $R^1 = OH$, $R^2 = R^3 = R^4 = H$
56; $R^1 = CO_2H$, $R^2 = R^3 = R^4 = H$
57; $R^1 = CO_2Me$, $R^2 = R^3 = R^4 = H$
58; $R^1 = CONH(CH_2)_2NMe_2$, $R^2 = R^3 = R^4 = H$
59; $R^1 = R^2 = R^3 = H$, $R^4 = Me$
60; $R^2 = R^4 = Me$, $R^1 = R^3 = H$
61; $R^1 = R^3 = H$, $R^2 = CHO$, $R^4 = Me$
62; $R^1 = CO_2Me$, $R^2 = R^4 = H$, $R^3 = Me$
63; $R^1 = R^3 = R^4 = H$, $R^2 = CONH(CH_2)_2NMe_2$)



(64)



(65)

reaction with butyllithium at $-23\,^{\circ}C$ followed by carbonation gave the carboxylic acid **15** (59%), together with the butyl ketone **16** (2%) derived from attack of butyllithium on the carboxylate group formed initially. Lithiation of *N*-[2-(dimethylamino)ethyl]dibenzo[*b*,*e*][1,4]dioxin (**1**) followed by quenching with a variety of electrophiles yielded derivatives functionalized in the 9 position. This regiospecificity reflects lithiation directed by a dioxin oxygen atom and by the amide anion cooperatively to the *peri* site on the distal ring rather than simply *ortho* to the amide. Thus, treatment of **1** with BuLi and then with DMF gave the aldehyde **21**, while quenching with CO_2 gave the zwitterionic acid **22** which gave the ester **23** on treatment with $MeOH/H_2SO_4$. Heating the amide-ester **23** with $H_2N(CH_2)_2NMe_2$ gave the bis 1,9-amide **38** (44%). When the lithiation of **1** was performed in the presence of *N,N,N′,N′*-tetramethyl-1,2-ethanediamine (TMEDA) and the time was extended from 25 min to 2.75 h prior to quenching with DMF, side reactions occurred to give *inter alia* the tetracyclic isoindolone **70** (10%), which is a new ring system. The IR spectrum of **70** contained a hydroxyl band (3375 cm^{-1}) and a carbonyl absorption (1690 cm^{-1}) characteristic of a γ-lactam [20], while both the ^1H and ^{13}C NMR spectra were consistent with the proposed structure. Thus the ^1H NMR spectrum contained a singlet due to an hydroxymethine proton at 5.68 ppm, and two *ortho*-coupled doublets (7.03, 7.09 ppm) attributed to H(5) and H(4) respectively. Moreover, since rotation about the lactam

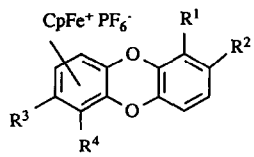
Table 2

Reactions of lithiated dibenzodioxins with electrophiles

Substrate	Lithiation conditions (reagent(s)/ °C)	Time (min)	Electrophile	Product	Yield (%)
2	BuLi/−23	20	CO_2	**15**	59
				76	2
2	^{t}BuLi/−78	60	CO_2	**15**	5
15	BuLi/TMEDA/−78	35	CO_2	**16** [a]	6
				7 [a]	17
				17 [a]	4
15	BuLi/−78	5	CO_2	**16**	9
	then −23	60		**18** [a]	46
15	BuLi/−78	30	I_2	**16,20**	30
				19	38
1	BuLi/−78	25	DMF	**21**	38
1	BuLi/TMEDA/−78	165	DMF	**21**	29
				70	10
1	BuLi/TMEDA/−78	60	DMF	**71**	16
				72	15
				21	15
1	BuLi	30	CO_2	**22**	61
1	BuLi/TMEDA	35	PhNCO	**24**	44
1	BuLi	35	Me_3SiCl	**25**	40
				26	55
1	BuLi/−78 → 20	− [b]	Me_3SiCl	**25**	14
				27	15
1	LiTMP [c]/−78 → 20	− [b]	Me_3SiCl	**27**	60
1	BuLi/TMEDA/−78	15	Me^3SiCl	**28**	9
				27	11
1	BuLi/TMEDA/−78 [d]	15	^{t}BuMe$_2$SiCl	**29**	54
29	^{s}BuLi/TMEDA/−78	75	DMF	**41**	16
				30	31
29	^{t}BuLi/TMEDA/−78	60	CO_2	**31** [e]	32
				42 [e]	21
32 [f]	BuLi/−78	7	Me_3SiCl	**34**	87 [g]
32 [f]	BuLi/−78	7	^{t}BuMe$_2$SiCl	**35** [e]	6
				44 [e]	3
11	BuLi/−78	25	DMF	**73**	54
73	BuLi/−78	30	DMF	**36**	18
14	BuLi/−78	180	DMF	**74**	49

[a] After methylation of the crude material with MeOH/H_2SO_4. [b] Me_3SiCl present before BuLi added [21]. [c] Lithium 2,2,6,6-tetramethylpiperidide. [d] One equivalent BuLi, then ^{t}BuMe$_2$SiCl. [e] Inseparable mixture. [f] Inseparable mixture containing **32**, **2**, **33**, and **43** in the ratio 2.3:1:0.37:0.30. [g] Based on the proportion of 2-bromodibenzodioxin in the starting mixture.

CO–N bond is prohibited, separate signals were observed for each of the four methylene protons [cf. two signals due to the methylene groups (3.53 ppm, q, CH_2CONH; and 2.58, t, CH_2NMe$_2$) in the starting material (**1**)]. The methylene protons adjacent to the lactam nitrogen in (**70**) gave rise to a doublet of doublets of doublets at 3.24 ppm (J = 15.0, 11.0, 2.1 Hz) and to an apparent doublet of doublets at 4.27 ppm (J = 15.0, 3.3 Hz), reflecting not only geminal coupling but also coupling to each of the non-equivalent vicinal protons. The splitting patterns for the methylene protons adjacent to the NMe$_2$ group were not resolved as



(**66**; $R^2 = R^3 = Me$, $R^1 = R^4 = H$

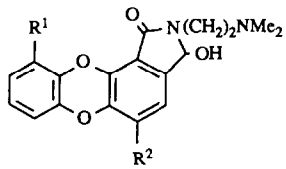
67; $R^1 = R^4 = H$, $R^2 = CHO$, $R^3 = Me$

68; $R^1 = R^2 = R^3 = H$, $R^4 = Me$)

69; $R^1 = CO_2Me$, $R^2 = R^3 = H$, $R^4 = Me$)

(**73**; n = 2

74; n = 3)



(**70**; $R^1 = CH_2OH$, $R^2 = H$

71; $R^1 = CHO$, $R^2 = (CH{=}CH)(CH_2)_2Me$

72; $R^1 = CHO$, $R^2 = H$)

clearly, one proton giving rise to a five-line multiplet centred at 2.78 ppm (J_{obs} = 14.5 Hz). The isoindolone **70** arises as a consequence of cyclization between the newly introduced aldehyde group at C(1) and the nitrogen anion of the carboxamide.

Similarly, treatment of the 2-carboxamide **11** with BuLi at −78 °C and then with excess DMF gave the isomeric isoindolone **73** (54%), also a new ring system. When the lithiation of **11** was carried out at 0 °C prior to the introduction of DMF the C-formyl,N-formyl compound **37** was obtained in addition to the isoindolone **73** (44%). At this temperature intermolecular quenching of the nitrogen anion with DMF is competitive with intramolecular cyclization of the monoanion. This was confirmed by carrying out the lithiation at 0 °C and then cooling the mixture to −78 °C before adding DMF; none of the bis formyl compound **37** was formed, although the yield of the isoindolone **73** decreased to 29%, reflecting the instability of the dianion at 0 °C. Further treatment of the isoindolone **73** with BuLi (2 equiv.) followed by excess DMF did not result in functionalization at C(9), but gave the carboxamide **36** (18%) via deprotonation of the hydroxyl group and ring opening to regenerate the aldehyde and the amide anion. Subsequent nucleophilic attack on the aldehyde by BuLi and protonation during workup would afford the hydroxypentyl side chain.

Treatment of the acid **13** with CDI in either DMF or THF followed by addition of $H_2N(CH_2)_3NMe_2$ afforded the 2-carboxamide **14** (94%). Reaction of the latter compound with BuLi (2 equiv.) for 3 h followed by the addition of DMF (1 equiv.) gave the isoindolone **74** (49%), homologous with **73**.

With a view to subsequent displacement of an aromatic silyl substituent by a carbon electrophile, resulting overall in regiospecific functionalization, chlorotrialkylsilanes were also used as quenching agents. In the case of the dibenzodioxin-1-carboxamide **1** both the 2- and 9-silylated derivatives **27** and **25** were obtained when deprotonation was performed with butyllithium in the presence of chlorotrimethylsilane [21], whereas introduction of the electrophile in the usual manner following a period of metallation afforded only the 9-silyl isomer. These results suggest that C(2) is the site of kinetic deprotonation and that equilibration can occur to generate the thermodynamically more stable C(9) aryllithium. Reaction of **1** with the bulkier electrophile t-butylchlorodimethylsilane gave only the C(2) silylated dibenzodioxin **29**. It is suggested that this compound is formed by initial silylation at the amide nitrogen followed by a 1,4-anionic migration of silicon which traps the C(2) kinetic carbanion efficiently. Indeed, when the amide **1** was *N*-deprotonated with 1 equiv. of BuLi and 1 equiv. of $^tBuMe_2SiCl$ was then added, followed by a second equiv. of BuLi and then excess DMF, no aldehyde-derived products were formed, silane **29** being the only product (59%). Hence the C(2) anion was not present contemporaneously with DMF, indicating that N → C rearrangement of silicon had occurred prior to this. Although 1,4 N → C silyl migration has not been reported, a 1,3 N → C shift of $SiMe_3$ has been proposed [22], and 1,4 O → C and C → C rearrangements are known [23,24]. 1,2-Migration of $^tBuMe_2Si$ from S → C has also been reported [25]. Attempts to prepare the putative $^tBuMe_2Si$–N intermediate in the present case by treatment of the amide **1** with $^tBuMe_2SiCl/Et_3N$ at room temperature returned only **1** after aqueous workup, while N–H deprotonation with NaH at room temperature prior to the addition of $^tBuMe_2SiCl$ at −78 °C gave only the C(2)-silylated derivative **29** in low yield.

In an alternative route to 2-substituted dibenzodioxins, the parent compound **2** was treated with NBS (1.5 equiv.) in DMF as solvent at room temperature. Although this afforded a mixture (2.30 : 1.0 : 0.37 : 0.30) of the 2-bromo derivative **32**, starting material **2**, and the 2,8- and 2,7-dibromides **33** and **43**, metal–halogen exchange followed by addition of Me_3SiCl, workup, and removal of volatile contaminants by sublimation at 70–80 °/0.1 mmHg allowed the isolation of pure 2-trimethylsilyldibenzo[*b*,*e*][1,4]dioxin (**34**). Acyl-desilylation of **34** by treatment with $CH_3COCl/AlCl_3$ gave 2-acetyldibenzodioxin (36%) and **2** (56%).

For all of the compounds reported in this work location of the substituent(s) followed from analyses of NMR spectra and was supported in some cases by derivatization. For example, for the 1-amide aldehyde **21** a doublet of doublets (6.95 ppm), a triplet (7.02 ppm) and a doublet of doublets (7.84 ppm) were observed for the protons of one ring [H(6), H(7) and H(8), respectively] in the ^1H NMR spectrum, ruling out the possibility that the formyl group was located at C(2). The ^{13}C NMR spectrum confirmed formyl substitution on the distal ring, since signals due to C(6)–C(9) (122.2, 127.1, 128.2 and 124.0 ppm) were shifted downfield compared with the corresponding signals in the starting material (116.5, 126.1, 124.8 and 116.3 ppm).

Experimental

For general experimental details see ref. 26. Solvent A for PLC was CH_2Cl_2/EtOH/Et_3N, 100 : 10 : 1.

Dibenzo[b,e][1,4]dioxin (2)

A degassed suspension of 2-chlorophenol (9.24 mL, 90.8 mmol), K_2CO_3 (6.90 g, 49.9 mmol), copper(I) chloride (0.45 g, 4.5 mmol), and tris[2-(2-methoxyethoxy) ethyl]amine [10] (1.45 mL, 4.5 mmol) in unpurified [27] diglyme (10 mL) was heated under reflux under N_2 with vigorous stirring for 19 h. The cooled mixture was filtered through Celite, and the residue was washed with hexanes. The combined filtrate and washings were diluted with CH_2Cl_2 and washed with water. The solvents were removed, and the diglyme solution was adsorbed onto Celite and extracted (Soxhlet) with hot hexanes. The hexanes were removed to give an oil which was chromatographed on alumina (hexanes) to yield dibenzo[*b,e*][1,4]dioxin (1.43 g, 17%) as white crystals, m.p. 119–120 °C (lit. [9] m.p. 119 °C), ν_{max}(KBr) 1490 (aryl C=C), 1290, 1280 (C–O), 740 cm^{-1} (aromatic). δ(O) 90.0 ppm, $\Delta\nu_{h/2}$ 80 Hz, O(5, 10). Correct ^1H NMR [28], ^{13}C NMR [28] and mass spectra [29]. The solid not extracted into hexanes at room temperature was recrystallized from aqueous EtOH to yield further dibenzodioxin (2.78 g, 33%).

Tricarbonyl[(1,2,3,4,4a,10a,-η)-dibenzo[b,e][1,4]dioxin]chromium (49)

A degassed mixture of dibenzodioxin (0.30 g, 1.6 mmol) and hexacarbonylchromium (0.39 g, 1.7 mmol) in dibutyl ether (40 mL) and THF (3.3 mL) was heated under reflux under N_2 for 22 h [30]. The suspension was filtered through Celite, and the residue washed with Et_2O. Solvents were removed, and the solid (0.40 g, 86%) chromatographed (Me_2CO/hexanes, 1:2) to yield tricarbonyl [(1,2,3,4,4a,10a-η)-dibenzo[*b,e*][1,4]dioxin]chromium (**49**) (0.30 g, 58%) as yellow crystals, m.p. 167.5–169.5 ° (dec.). Anal. Found: C, 55.7; H, 3.3. $C_{15}H_8CrO_5$ calc.: C, 56.3; H, 2.5%. ν_{max} ($CHCl_3$) 1975, 1900 (CO), 716 cm^{-1} (aromatic). δ(H) 5.07 (dd, J = 3.0, 4.4 Hz, H(2,3)); 5.42 (dd, J = 2.9, 4.4 Hz, H(1,4)); 6.89 (dd, J_{obs} = 3.8, 3.5, 5.9 Hz, H(7,8)); 7.02 (dd, J = 3.5, 6.1 Hz, H(6.9)) ppm. m/z (8%, M), 264 (10, M – 2CO), 236 (31, 264 – CO), 184 (24, M – $Cr(CO)_3$), 128, (13, 184 – 2CO), 52 (100, Cr).

(Cyclopentadienyl)(dichloroarene)iron(1 +) complexes

(a) From 1,2-dichloro-4-methylbenzene. Complexation of 1,2-dichloro-4-methylbenzene (2.68 mmol) as described for **46** [26] gave a solid (1.12 g, 36%) which was purified by Me_2CO/Et_2O precipitation to yield (η^5-2,4-cyclopentadien-1-yl)(η^6-1,2-dichloro-4-methylbenzene)iron(1 +) hexafluorophosphate(1 –) (**47**) (0.86 g, 30%) as yellow crystals, m.p. 210–213 °C (dec.). Anal. Found: C, 33.9; H, 2.6. $C_{12}H_{11}Cl_2F_6FeP$ calc.: C, 33.8; H, 2.6%. ν_{max}(KBr) 1430, 1422 (aryl C=C), 820, 550 cm^{-1} (PF). δ(H) (CD_3COCD_3) 2.60 (s, CH_3), 5.35 (s, C_5H_5); 6.53 (br, d, $J_{5,6}$ = 6.1 Hz, H(5)); 7.00 (d, $J_{5,6}$ = 6.3 Hz, H(6)); 7.05 (s, H(3)) ppm. δ(C) (CD_3COCD_3) 19.8 (CH_3); 82.3 (C_5H_5); 88.68 (C(5)); 88.74 (C(6)); 90.3 (C(3)); 105.0 (C(4)); 106.4 (C(1)); 107.6 (C(2)) ppm.

(b) From 1,2-dichloro-3-methylbenzene. Complexation of 1,2-dichloro-3-methylbenzene (7 mL, 53.4 mmol), as above in refluxing octane (20 mL, 135 ° C) for 5.5 h followed by workup and precipitation gave a solid (1.28 g, 28%); further product (0.18 g, 4%) was recovered by extraction of the mother liquor with CH_2Cl_2. The combined crude products were purified by Me_2CO/Et_2O precipitation to yield (η^5-2,4-cyclopentadien-1-yl)(η^6-1,2-dichloro-3-methylbenzene)iron(1 +) hexafluorophosphate(1 –) (**48**) (1.17 g, 25%) as a greenish-yellow crystalline solid, m.p.

210–213 °C (dec.). Anal. Found: C, 33.5; H, 2.9. $C_{12}H_{11}Cl_2F_6FeP$ calc.: C, 33.8; H, 2.6%. ν_{max}(KBr) 1450, 1415 (aryl C=C), 830, 551 cm^{-1} (PF). δ(H) (CD_3COCD_3) 2.77 (s, CH_3); 5.29 (s, C_5H_5); 6.47 (t, $J = 6.3$ Hz, H(5)); 6.60 (d, $J_{4,5} = 6.1$ Hz, H(4)); 6.94 (dd, $J_{4,6} = 0.9$, $J_{5,6}$ 6.4 Hz, H(6)) ppm. δ(C) (CD_3COCD_3) 20.4 (CH_3); 8.20 (C_5H_5); 87.2 (C(6)); 88.3 (C(5)); 89.2 (C(4)); 103.8 (C(3)); 107.6 (C(1)); 108.5 (C(2)) ppm.

*2,3-Dihydroxy-*N*-[2-(dimethylamino)ethyl]benzamide*

A mixture of methyl 2,3-dihydroxybenzoate [31] (0.29 g, 1.72 mmol) and *N,N*-dimethyl-1,2-ethanediamine (1.0 mL, 9.11 mmol) was heated under reflux for 20 min. Excess of amine was removed to give an oil which was distilled to yield 2,3-dihydroxy-*N*-[2-(dimethylamino)ethyl]benzamide (0.38 g, 98%) as an unstable yellow oil, b.p. (Kugelrohr) 130–135 °C/0.04 mmHg. Anal. Found: C, 58.6; H, 7.7; N 12.4; $M^{+\cdot}$ 224.1161. $C_{11}H_{16}N_2O_3$ calc.: C, 58.9; H, 7.2; N, 12.5%; $M^{+\cdot}$ 224.1182. ν_{max}($CHCl_3$) 3550 (OH), 3400 (NH), 3100 (OH), 1640 (CO), 1595 (aryl C=C), 1527 (amide II), 1457 (aryl C=C), 1255 (C–O), 730 cm^{-1} (aromatic). δ(H) 2.32 (s, $N(CH_3)_2$; 2.62, apparent t, $J = 5.7$ Hz, $CH_2N(CH_3)_2$); 3.56 (apparent q, $J = 5.0$, 5.3, 4.9 Hz, $CONHCH_2$); 6.59 ($J = 8.0$ Hz, H(5)); 6.91 (dd, $J_{4,6} = 1.3$, $J_{4,5} = 7.9$ Hz, H(4)); 6.96 (dd, $J_{4,6} = 1.3$, $J_{5,6} = 8.1$ Hz, H(6)); 7.52 (s, 3-OH; 8.50, s, 2-OH, NH) ppm. δ(C) 36.6 ($CONHCH_2$); 45.0 ($N(CH_3)_2$); 57.7 (CH_2NMe_2); 114.5 (C(1)); 118.5 (C(6)); 118.8 (C(5)); 146.2 (C(2)); 149.5 (C(3)); 170.3 (CONH) ppm. *m/z* 224 (34, M), 137 (17, M – $NHCH_2CH_2NMe_2$), 109 (7, 137 – CO), 81 (19, 109 – CO), 71 (70, CH_2=$CHNMe_2$), 58 (100 – CH_2NMe_2), 44 (17, NMe_2).

*Reactions of (η^5-2,4-cyclopentadien-1-yl)(η^6-1,2-dichlorobenzene)iron(1 +) hexafluorophosphate(1 −) (**46**)*

(a) With 1,2-benzenediol. A suspension of the complex **46** (92 mg, 0.22 mmol), 1,2-benzenediol (24 mg, 0.22 mmol), and K_2CO_3 [14] (55.5 mg, 0.40 mmol) in degassed DMF [32] (2 mL) was stirred vigorously at room temperature under N_2 in the dark for 1.75 h. The mixture was acidified with 10% HCl and a solution of ammonium hexafluorophosphate (72 mg, 0.44 mmol) in water (*ca* 1 mL) was added with stirring to dissolve a precipitated solid. Water (*ca* 9 mL) was added slowly to precipitate a solid which was purified by CH_2Cl_2/Et_2O precipitation to yield (η^5-2,4-cyclopentadien-1-yl)[1,2,3,4,4a,10a-η)-dibenzo[*b,e*][1,4]dioxin]iron(1 +) hexafluorophosphate(1 −) (**50**) [14] (74 mg, 74%) as yellow crystals, m.p. 209–210 °C (dec.). ν_{max}(KBr) 1520, 1490, 1470 (aryl C=C), 1295, 1285 (C–O), 820 (PF), 755 (aromatic), 550 cm^{-1} (PF). δ(H) (CD_3COCD_3) 5.27 (s, C_5H_5); 6.31 (br s, H(2,3)); 6.54 (br s, H(1,4)); 7.17 (br s, H(7,8)); 7.23 (br s, H(6,9)) ppm. δ(C) (CD_3COCD_3) 76.6 (C(1,4)); 78.9 (C_5H_5); 85.0 (C(2,3)); 118.3 (C(6,9)), 119.0 (C(4a,10a)); 127.3 (C(7,8)); 139.6 (C(5a,9a)) ppm.

Repetition of the reaction in THF under reflux for 22 h gave dibenzo[*b,e*][1,4]dioxin (**2**) (50%) and 2-(2-chlorophenoxy)phenol (36%) [33].

Irradiation of the complex **50** in CH_2Cl_2 under N_2 at 300 nm in a Pyrex test tube [13] for 3.5 h and chromatography (PLC) (CH_2Cl_2/hexanes, 1:1) gave dibenzo[*b,e*][1,4] dioxin (**2**) (94%) (correct ^{1}H NMR spectrum).

(b) With 4-methyl-1,2-benzenediol. The complex **46** (0.50 g, 1.21 mmol) was reacted with 4-methyl-1,2-benzenediol (0.15 g, 1.21 mmol) and K_2CO_3 (0.30 g, 2.19 mmol) in DMF (6 mL) as in (a). Workup after 4.5 h gave a solid (0.39 g, 69%)

which was purified by CH_2Cl_2/Et_2O precipitation to yield (η^5-2,4-cyclopentadien-1-yl)[(5a,6,7,8,9,9a,η)-2-methyldibenzo[*b*,*e*][1,4]dioxin]iron(1 +) hexafluorophosphate(1 −) (**51**) as yellow crystals, m.p. 194–196 °C (dec.). Anal. Found: C, 46.5; H, 3.6. $C_{18}H_{15}F_6FeO_2P$ calc.: C, 46.6; H, 3.3%. ν_{max}(KBr) 1520, 1500, 1470 (aryl C=C), 1295, 1280 (C–O), 875, 860 (aromatic), 820 (PF), 755 (aromatic), 552 cm^{-1} (PF). δ(H) (CD_3COCD_3) 2.34 (s, CH_3); 5.26 (s, C_5H_5); 6.30 (apparent dd, J = 1.7, 4.2 Hz, H(7,8)); 6.53 (apparent dd, J = 3.5, 6.9 Hz, H(6,9)); 7.00 (s, H(1)); 7.05 (s, H(3,4)) ppm. δ(C) (CD_3COCD_3) 20.7 (CH_3); 76.6, (C(6)*); 76.7 (C(9)*); 78.9 (C_5H_5); 84.85 (C(7)**); 84.9 (C(8)**); 117.9 (C(4)); 118.5 (C(1)); 118.9 (C(5a)#); 119.1 (C(9a)#); 127.6 (C(3)); 137.4 (C(2)); 137.5 (C(4a)); 139.2 (C(10a)) ppm.

Irradiation of **51** in acetonitrile through quartz at 254 nm for 4 h yielded 2-methyldibenzo[*b*,*e*][1,4]dioxin (**3**) (76%) as white crystals (correct ^1H NMR spectrum).

(c) With 3,4-dihydroxybenzaldehyde. The complex **46** (2.5 g, 6.06 mmol) was reacted with 3,4-dihydroxybenzaldehyde [34] (0.84 g, 6.06 mmol) and K_2CO_3 (1.51 g, 10.96 mmol) in DMF as in (a). Workup after 4 h gave a yellow solid (2.18 g, 75%) which was purified by Me_2CO/Et_2O precipitation to yield (η^6-2,4-cyclopentadien-1-yl)[(5a,6,7,8,9,9a-η)-dibenzo[*b*,*e*][1,4]dioxin-2-carboxaldehyde]iron(1 +) hexafluorophosphate(1 −) (**52**) as yellow crystals, m.p. 211–213 °C (dec.). Anal. Found: C, 44.9; H, 3.0. $C_{18}H_{13}F_6FeO_3P$ calc.: C, 45.2; H, 2.7%. ν_{max}(KBr) 1695 (CO), 1520, 1500, 1468 (aryl C=C), 1290, 1280 (C–O), 878 (aromatic), 830, 552 cm^{-1} (PF). δ(H) (CD_3COCD_3, 60 MHz) 5.38 (s, C_5H_5); 6.42 (m, H(7,8)); 6.58 (m H(6,9)); 7.38 (d, $J_{3,4}$ = 8.0 Hz, H(4)); 7.63 (d, $J_{1,3}$ = 2.0 Hz, H(1)); 7.83 (dd, $J_{1,3}$ = 2.0 Hz, $J_{3,4}$ = 8.0 Hz, H(3)); 10.03 (s, CHO)) ppm. δ(C) (CD_3COCD_3, 15 MHz) 76.7 (C(6)*); 76.8 (C(9)*); 79.3 (C_5H_5); 85.2 (C(7)**); 85.3 (C(8)**); 118.1 (C(9a)#); 118.3 (C(4)); 118.6 (C(5a)#); 119.2 (C(1); 129.1 (C(3)); 135.7 (C(2)); 140.2 (C(10a)); 144.1 (C(4a)); 190.6 (CHO) ppm.

Irradiation of **52** in acetonitrile for 2.5 h yielded dibenzo[*b*,*e*][1,4]dioxin-2-carboxaldehyde (**4**) (59%) as a cream solid, m.p. 93–96 °C (lit. [35] m.p. 91–92 °C, [36] 101–102 °C). ν_{max}(KBr) 1690 (CO), 1495 (aryl C=C), 1305 (C–O), 750 cm^{-1} (aromatic). δ(H) 6.91 (m, H(6,9)); 6.97 (d, $J_{3,4}$ = 8.2 Hz, H(4)); 7.37 (d, $J_{1,3}$ = 1.9 Hz, H(1)); 7.45 (dd, $J_{3,4}$ = 8.2 Hz, H(3)); 9.82 (s, CHO) ppm. δ(C) (15 MHz) 116.5 (C(4,6)); 116.8 (C(1)); 124.2 (C(7)*); 124.7 (C(8)*); 126.9 (C(3)); 132.8 (C(2)); 141.2 (C(9a)#); 141.5 (C(5a)#); 142.7 (C(10a)); 147.3 (C(4a)); 189.8 (CHO) ppm. m/z 212 (100%, M), 211(55, M − H), 183 (43, 211 − CO), 155 (10, 183 − CO), 127 (25, 155 − CO).

The aldehyde **4** was also formed (48%) by sublimation of the complex **52** at 240 °C/0.06 mmHg in a Kugelrohr oven [14].

(d) With 3,4-dihydroxybenzoic acid. The complex **46** (0.50 g, 1.21 mmol) was reacted with 3,4-dihydroxybenzoic acid [37] (0.24 g, 1.57 mmol) and K_2CO_3 (0.60 g, 4.36 mmol) in DMF (10 mL) as in (a). Workup after 24.5 h gave a yellow solid (0.40 g, 81%) which was purified by Me_2CO/Et_2O precipitation to yield (η^6-2,4-cyclopentadien-1-yl)[5a,6,7,8,9,9a-η)dibenzo[*b*,*e*][1,4]dioxin-2-carboxylic acid]iron(1 +) hexafluorophosphate(1 −) (**53**) as yellow crystals, m.p. 226–229 °C (dec.). Anal. Found: C, 44.1; H, 3.5. $C_{18}H_{13}F_6FeO_4P$ calc.: C, 43.8; H, 2.7%. ν_{max}(KBr) 3425–2575 (OH), 1680 (CO), 1472, 1452 (aryl C=C), 1280 (C–O), 830 (PF), 760 (aromatic), 550 cm^{-1} (PF). δ(H) (CD_3SOCD_3) 5.22 (s, C_5H_5); 6.22 (br, s, H(7,8)); 6.59 (br s, H(6,9)); 7.31 (d, $J_{3,4}$ = 4.2 Hz, H(4)); 7.61 (s, H(1)); 7.78 (d, $J_{3,4}$ = 4.9 Hz,

H(3)) ppm; CO_2H not observed. δ(C) (CD_3SOCD_3) 75.1 (C(9)*); 75.2 (C(6)*); 77.9 (C_5H_5); 83.9 (C(8)#); 84.0 (C(7)#); 116.6 (C(9a)**); 117.0 (C(5a)**); 117.5 (C(4)); 117.9 (C(1)); 127.3 (C(3)); 128.6 (C(2)); 138.1 (C(10a)); 141.7 (C(4a)); 165.6 (CO_2H).

Oxidation of **52** in acetone at 0 °C with Jones reagent gave **53** (100%) (correct IR and ^1H NMR spectra).

(e) With 3,4-dihydroxybenzenepropanoic acid. The complex **46** (25 mg, 0.06 mmol) was reacted with 3,4-dihydroxybenzenepropanoic acid (11 mg, 0.06 mmol) and K_2CO_3 (20 mg, 0.14 mmol) in DMF (0.5 mL) as in (a). Workup after 28 h and trituration with Me_2CO gave a yellow solid which was redissolved in Me_2CO and precipitated with Et_2O to yield (η^5-2,4-cyclopentadien-1-yl)[(5a,6,7,8,9,9a-η)-dibenzo[*b*,*e*][1,4]dioxin-2-propanoic acid]iron(1 +) hexafluorophosphate(1 −) (**54**) (24 mg, 75%) as yellow crystals. ν_{max}(KBr) 3425 (OH), 1695 (CO), 1493 (aryl C=C), 1290, 1280 (C–O), 835 (PF), 744 (aromatic), 550 cm^{-1} (PF). δ(H) (CD_3COCD_3, 60 MHz) 2.82–3.03 (m, $CH_2CH_2CO_2H$); 5.28 (s, C_6H_5); 6.30–6.52 (m, H(6–9); 7.13 (br s, H(1,3,4)) ppm; CO_2H not observed.

Degassed acetonitrile (5 mL) was added to the complex **54** (47 mg), an insoluble white solid was filtered off, and the solution was irradiated at 300 nm in a Pyrex text tube under N_2 for 1.25 h. Removal of solvent and chromatography (PLC) (Et_2O/hexanes, 1 : 1, 3 : 2) yielded dibenzo[*b*,*e*][1,4]dioxin-2-propanoic acid (**5**) [38] (7 mg, 45%) as a white solid, m.p. 157–165 °C Anal Found: $M^{+\cdot}$ 256.0725. $C_{15}H_{12}O_4$ calc.: $M^{+\cdot}$ 256.0736. ν_{max}(KBr) 3500–2550 (OH), 1690 (CO), 1510, 1490 (aryl C=C), 1290, 1280 (C–O), 745 cm^{-1} (aromatic). δ(H) 2.65 (t, J = 7.5 Hz, CH_2CO_2H); 2.85 (t, J = 7.5 Hz, $CH_2CH_2CO_2H$); 6.71 (m, H(1), 0.5 H(3); 6.75, d, $J_{1,3}$ = 1.5 Hz, 0.5H(3)); 6.77 (d, J = 8.0 Hz, H(4)); 6.83 (m, H(7,8); 6.88, m, H(6,9)) ppm; CO_2H not observed. δ(C) 29.8 ($CH_2CH_2CO_2H$); 33.2 ($CH_2CH_2CO_2H$); 116.1 (C(4)); 116.26 (C(6)*); 116.33 (C(9)*, C(1); 123.4 (C(7)#); 123.7 (C(8)#); 123.8 (C(3)); 136.0 (C(2)); 140.6 (C(4a)); 141.7 (C(10a)); 142.0 (C(5a)**); 142.1 C(9a)**); 177.0 (CO_2H) ppm. *m/z* 256 (41, M), 211 (3, M − HO–CO), 210 (5, M − H_2O–CO), 197 (100, M − CH_2CO_2H), 169 (1, 197 − CO), 141 (4, 169 − CO).

(f) With methyl 2,3-dihydroxybenzoate. The complex **46** (0.10 g, 0.24 mmol) was reacted with methyl 2,3-dihydroxybenzoate (41 mg, 0.24 mmol) and K_2CO_3 (60 mg, 0.44 mmol) in DMF (2 mL) as in (a). Workup after 1.5 h gave a yellow solid (0.11 g, 87%) which was purified by Me_2CO/Et_2O precipitation to yield (η^5-2,4-cyclopentadien-1-yl)[methyl (5a,6,7,8,9,9a-η)-dibenzo[*b*,*e*][1,4]dioxin-1-carboxylate]-iron(1 +) hexafluorophosphate(1 −) (**57**) as yellow crystals, m.p. 220–223 °C (dec.). Anal. Found: C, 44.9; H, 3.7. $C_{19}H_{15}F_6FeO_4P$ calc.: C, 44.9; H, 3.0%. ν_{max}(KBr) 1715 (CO), 1527, 1457, 1435 (aryl C=C), 1305, 1280 (C–O), 825 (PF), 750 (aromatic), 555 cm^{-1} (PF). δ(H) (CD_3COCD_3) 3.96 (s, OCH_3); 5.31 (s, C_5H_5); 6.36 (3 lines, J_{obs} = 3.7, 3.0 Hz, H(7,8)); 6.61 (dd, $J_{6,8}$ = 2.8, $J_{6,7}$ = 4.0 Hz, H(6)); 6.64 (dd, $J_{7,9}$ = 2.8, $J_{8,9}$ = 6.8 Hz, H(9)); 7.34 (t, J = 7.9 Hz, H(3)); 7.40 (dd, $J_{2,4}$ = 1.4, $J_{3,4}$ = 8.1 Hz, H(4)); 7.69 (dd, $J_{2,4}$ = 1.4, $J_{2,3}$ = 7.7 Hz, H(2)) ppm. δ(C) (CD_3COCD_3) 52.9 (OCH_3); 76.7 (C(6))*); 77.0 (C(9)*); 79.2 (C_5H_5); 85.21 (C(7)#); 85.24 (C(8)#); 118.4 (C(5a)**); 118.9 (C(9a)**); 121.8 (C(1)); 122.2 (C(4)); 126.5 (C(3)); 128.8 (C(2)); 139.4 (C(4a)); 140.5 (C(10a)); 164.6 (CO_2Me) ppm. *m/z* (DCI^+) 363 (1, $C_{19}H_{15}FeO_4$), 242 (100, 363 − C_5H_5Fe), 211 (81, 242 − CH_3O), 186 (30, $(C_5H_5)_2Fe$), 155 (8, 211 − 2CO), 127 (24, 155 − CO), 121(15, C_5H_5Fe).

Irradiation of **57** in acetonitrile for 2.5 h gave methyl dibenzo[*b*,*e*][1,4]dioxin-1-

carboxylate (**7**) (0.88 g, 87%) which sublimed (Kugelrohr) at 105–120 °C/0.04 mmHg to give a white solid, m.p. 92–94 °C (lit. [39] m.p. 88 °C, [144] 86 °C) Anal. Found: C, 69.6; H, 4.2. $C_{14}H_{10}O_4$ calc.: C, 69.4; H, 4.2%. ν_{max}(KBr) 1720 (CO), 1595, 1460 (aryl C=C), 1280, 1270, 1255 (C–O), 745 cm^{-1} (aromatic). Correct ^1H NMR spectrum [30]. δ(C) 52.3 (OCH_3); 116.1 (C(6)*); 116.9 (C(9)*); 119.3 (C(1)), 120.9 (C(4)); 122.8 (C(3)); 124.1 (C(7)#); 124.4 (C(8)#); 125.8 (C(2)); 141.6 (C(5a)**); 141.8 (C(9a)**); 142.6 (C(4a)); 142.9 (C(10a)); 165.2, (CO_2Me) ppm. *m/z* 242 (100, M), 211 (76, M – CH_3O), 183(33, 211 – CO), 155 (6, 183 – CO), 127 (17, 155 – CO).

(g) With 1,2,3-benzenetriol. The iron complex **46** (0.10 g, 0.24 mmol) was reacted with 1,2,3-benzenetriol (32 mg, 0.24 mmol and K_2CO_3 (77 mg, 0.56 mmol) in DMF (2 mL) as in (a). Workup after 3 h and trituration with Me_2CO followed by precipitation with Et_2O and chromatography (CH_2Cl_2/EtOH, 9:1) yielded (η^5-2,4-cyclopentadien-1-yl)[5a,6,7,8,9,9a-η)dibenzo[*b,e*][1,4]dioxin-1-ol]iron(1 +) hexafluorophosphate(1 –) (**55**) (0.11 g) as an unstable dark oil. δ(H) (CD_3COCD_3, 60 MHz) 5.25 (s, C_5H_5); 6.25–7.03 (m (H2–4,6–9)) ppm.

A degassed solution of the complex **55** (0.11 g) in acetonitrile (12 mL) was irradiated in a Pyrex test tube at 300 nm under N_2 for 4 h. Removal of solvent and chromatography (PLC) (Et_2O/hexanes, 3:2) yielded (i) dibenzo[*b,e*][1,4]dioxin-1-ol (**6**) [40] (12.5 mg, 26%) which crystallized from Me_2CO as white needles, m.p. 167–172 °C. Anal. Found: $M^{+\cdot}$ 200.0470. $C_{12}H_8O_3$ calc.: $M^{+\cdot}$ 200.0473). ν_{max}(KBr) 3350 (OH), 1498, 1484 (aryl C=C), 1308, 1285, 1270, 1240 (C–O), 750 cm^{-1} (aromatic). δ(H) 5.30 (s, OH); 6.44 (dd, $J_{2,4} = 1.3$, $J_{2,3} = 8.2$ Hz, H(2)); 6.60 (dd, $J_{2,4} = 1.3$, $J_{3,4} = 8.3$ Hz, H(4)); 6.79 (t, $J = 8.2$ Hz, H(3)); 6.91 (m, H(6–9)) ppm. δ(C) 102.7 (C(4)); 105.6 (C(2)); 110.9 (C(9)*); 111.3 (C(6)*); 117.9 (C(8)#); 118.5 (C(7)#); 118.9 (C(3)); 124.6 (C(10a)); 136.0 (C(9a)**); 136.5 (C(5a)**); 137.0 (C(1)); 138.7 (C(4a)). *m/z* 200 (100, M), 171 (25, M – CO–H), 144 (11, M – 2CO); and (ii) 2-(2-chlorophenoxy)-1,3-benzenediol or 3-(2-chlorophenoxy)-1,2-benzenediol or a mixture of both isomers as a yellow oil (11 mg, 19%). Anal. Found: $M^{+\cdot}$ 238.0228, 236.0211. $C_{12}H_9ClO_3$ calc.: $M^{+\cdot}$ 238.0211, 236.0240). δ(H) (CD_3COCD_3, 60 MHz) 5.10–7.48 (m) ppm. *m/z* 236 (90, M), 201 (36, M – Cl), 183 (100, M – HCl), 155 (18, 183 – CO).

*(h) With 2,3-dihydroxy-*N*-[2-(dimethylamino)ethyl]benzamide.* The complex **46** (0.22 g, 0.53 mmol) was reacted with 2,3-dihydroxy-*N*-[2-(dimethylamino)ethyl] benzamide (0.12 g, 0.53 mmol) in DMF as in (a). Workup after 6 h, using sufficient 10% HCl to neutralize but not acidify the mixture, gave a brown solid (30.5 mg). The mother liquor was extracted with CH_2Cl_2, and the extract was dried ($MgSO_4$) and concentrated to give a dark oil (0.37 g) which was combined with the solid and chromatographed on alumina (CH_2Cl_2/EtOH, 50:1) to give (i) a mixture (^1H HMR) (0.12 g) of the (dibenzodioxin-1-carboxamide)iron complex **58** and the dibenzodioxin-1-carboxamide **1** as a yellow-brown oil; and (ii) a yellow oil (52 mg) which was purified by Me_2CO/Et_2CO precipitation to yield (η^5-2,4-cyclopentadien-1-yl[5a,6,7,8,9,9a]-*N*-[2-(dimethylamino)ethyl]dibenzo[*b,e*][1,4]dioxin-1-carboxamide]iron(1 +) hexafluorophosphate(1 –) (**58**) (31.5 mg, 11%) as an unstable yellow solid. ν_{max}(KBr) 3425 (NH), 1655 (CO), 1526 (amide II), 1455 (aryl C=C), 1280 (C–O), 825, 550 cm^{-1} (PF). δ(H) 2.39 (s, $N(CH_3)_2$); 2.62 (br, s, CH_2NMe_2); 3.62 (br, s, $CONHCH_2$); 5.17 (s, C_5H_5); 6.29 (3 lines, $J_{obs} = 6.3$, 8.5 Hz, H(7,8); 6.39 (br s, H(6,9)); 7.25 (m, H(3,4)); 7.51 (s, NH); 7.81 (d, $J_{2,3} = 6.5$ Hz,

H(2)) ppm. δ(C) 37.5 ($CONHCH_2$); 45.3 ($N(CH_3)_2$); 57.4 (CH_2NMe_2); 75.8 (C(9)*); 76.0 (C(6)*); 78.4 (C_5H_5); 84.4 (C(8)#); 84.6 (C(7)#); 116.9 (C(9a)**); 117.8 (C(5a)**); 120.2 (C(4)); 124.2 (C(1)); 126.5 (C(2)); 128.3 (C(3)); 136.6 (C(10a)); 138.7 (C(4a)); 162.6 (CONH) ppm.

A degassed solution of the mixture (0.12 g) in acetonitrile (16 mL) was irradiated with stirring in a quartz tube at 300 nm under N_2 for 2.25 h. Removal of solvent and chromatography on alumina (CH_2Cl_2/EtOH, 20:1) yielded *N*-[2-(dimethylamino)ethyl]dibenzo[*b*,*e*][1,4]-dioxin-1-carboxamide (**1**) [1] (50 mg, 32%) as a cream solid, m.p. 101–103 °C. ν_{max}(KBr) 3380 (NH), 1650 (CO), 1520 (amide II), 1495, 1460 (aryl C=C), 1285, 1275 (C–O), 740 cm^{-1} (aromatic). δ(H) 2.36 (s, NMe_2); 2.59 (apparent t, $J = 5.9$ Hz, CH_2NMe_2); 3.59 (apparent q, $J = 6.1$, 4.7, 5.7 Hz, $CONHCH_2$); 6.93 (m, H(3,4,6–9); 7.74 (dd, $J_{2,4} = 3.2$, $J_{2,3} = 6.5$ Hz, H(2)); 8.12 (s, NH) ppm. δ(C) 37.3 ($CONHCH_2$); 45.1 ($N(CH_3)_2$); 57.4 (CH_2NMe_2); 116.3 (C(9)*); 116.5 (C(6)*); 119.4 (C(4)); 121.8 (C(1)); 123.4 (C(2)); 124.0 (C(3)); 124.8 (C(8)#); 126.1 (C(7)#); 140.8 (C10a); 141.3 (C(4a)); 141.8 (C(9a)**); 142.2 (C(5a)**); 167.7 (CONH) ppm. δ(O) 90.8 ($\Delta\nu_{h/2}$ 191 Hz, O(5)); 93.5 (sh, O(10)); 243.7 ($\Delta\nu_{h/2}$ 8862 Hz, CONH) ppm. *m/z* 298 (≤ 1, M), 296 (≤ 1, M – H_2), 211 (8, M – $NHCH_2CH_2NMe_2$), 183 (6, 211 – CO), 155 (2, 183 – CO), 127 (6, 155 – CO), 71 (43, CH_2=$CHNMe_2$), 58 (100, CH_2NMe_2), 44 (8, NMe_2).

Treatment of a mixture of the ester **7** (0.62 g, 2.53 mmol) and *N*,*N*-dimethyl-1,2-ethanediamine (3.1 mL, 28.2 mmol) under reflux for 6.5 h gave the carboxamide **1** (0.67 g, 89%).

(i) With 2,3-dihydroxybenzoic acid. The iron complex **46** (0.50 g, 1.21 mmol) was reacted with 2,3-dihydroxybenzoic acid (0.24 g, 1.57 mmol) and K_2CO_3 (0.60 g, 4.36 mmol) in DMF (10 mL) as in (a). Workup after 23 h by extraction into CH_2Cl_2, washing the organic layer with dilute aqueous NaOH, acidification of the aqueous extract with 10% aqueous HCl, and extraction into EtOAc gave (η^5-2,4-cyclopentadienyl)[(5a,6,7,8,9,9a-η)-dibenzodioxin-1-carboxylic acid]iron(1 +) hexafluorophosphate(1 –) (**56**) (0.30 g, 50%) as an unstable oil. ν_{max}(film) 3600–2500 (OH), 1652 (CO), 1505, 1446 (aryl C=C), 1245 (C–O), 830 (PF), 766 (aromatic), 554 cm^{-1} (PF). δ(H) (CD_3COCD_3, 60 MHz) 5.28 (s, C_5H_5); 6.30 (m, H(6–9)); 6.83–7.35 (m, H(3,4)); 7.58–7.93 (m, H(2)) ppm.

(j) With 6,7-dihydroxycoumarin. The complex **46** (0.10 g, 0.24 mmol) was reacted with 6,7-dihydroxycoumarin (0.43 g, 0.24 mmol) and K_2CO_3 (60 mg, 0.44 mmol) in DMF (2 mL) as in (a). Workup after 2 h gave a yellow solid (0.10 g, 81%) which was recrystallized from CH_3NO_2/Et_2O using the isopiestic method at 4 °C overnight to yield [(6a,7,8,9,10,10a-η)-benzo[*b*][benzopyran-2-ono[7,6-*e*]][1,4]dioxin](η^5-2,4-cyclopentadien-1-yl) iron(1 +) hexafluorophosphate(1 –) (**64**) as yellow crystals, m.p. 257–261 °C (dec.). Anal. Found: C, 46.4; H, 2.4. $C_{20}H_{13}F_6FeO_4P$ calc.: C, 46.4; H, 2.5%. ν_{max}(KBr) 1700 (CO), 1462 (aryl C=C), 1295 (C–O), 836 (aromatic), 825, 550 cm^{-1} (PF). δ(H) (CD_3SOCD_3) 5.22 (s, C_5H_5); 6.23 (br s, H(8,9)); 6.54 (br s H(3)); 6.61 (br s, H(7,10)); 7.39 (s, H(12)); 7.62 (s, H(5)); 8.05 (br s, H(4)) ppm. δ(C) (CD_3SOCD_3) 75.1 (C(7)*); 75.2 (C(10)*); 77.8 (C_5H_5); 83.8 (C(8)#); 84.0 (C(9)#); 105.5 (C(12)); 115.6 (C(3)); 115.8 (C(5)); 116.0 (C(4a)); 116.2 (C(6a)**); 117.0 (C(10a)**); 134.9 (C(5a)); 140.8 (C(11a)); 143.1 (C(4)); 151.1 (C(12a)); 159.4 (C(2)) ppm.

The aqueous mother liquor was extracted with CH_2Cl_2 and the extract was worked up to give a yellow crystalline solid tentatively assigned as (η^5-2,4-cyclo-

pentadien-1-yl)[(5a,6,7,8,9,9a-η)-3-hydroxydibenzo[*b*,*e*][1,4]dioxin-2-propenoic acid] iron(1 +) hexafluorophosphate(1 −) (13 mg, 10%). ν_{max}(KBr) 3425 (OH), 1642 (CO), 1257, 1133 (C–O), 835, 552 cm^{-1} (PF).

Irradiation of the complex **64** in acetonitrile for 1.25 h yielded benzo[*b*]benzopyran-2-ono-[7,6-*e*][1,4]dioxin (**45**) (18%) as a cream solid, m.p. 230–270 °C(dec.). Anal. Found: $M^{+\cdot}$ 252.0410. $C_{15}H_8O_4$ calc.: $M^{+\cdot}$ 252.0423. ν_{max}(KBr) 1725 (CO), 1565, 1498 (aryl C=C), 1300, 1250 cm^{-1} (C–O). *m/z* (100, M), 224 (54, M − CO), 196 (2, 224 − CO), 168 (14, 196 − CO), 140 (3, 168 − CO), 139 (13, 140 − H).

(k) With 2,3-dihydroxypyridine. The complex **46** (0.10 g, 0.24 mmol) was reacted with 2,3-dihydroxypyridine (27 mg, 0.24 mmol) and K_2CO_3 (60 mg, 0.44 mmol) in DMF (2 mL) as in (a). Workup after 2.5 h gave a solid (98 mg, 90%) which was purified by Me_2CO/Et_2O precipitation to yield [5a,6,7,8,9,9a-η)-[1,4]benzodioxino[2,3,*b*]pyridine](η^5-2,4-cyclopentadien)-1-yl)iron(1 +) hexafluorophosphate(1 −) (**65**) [8] as a yellow-brown solid. ν_{max}(KBr) 1445 (aryl C=C), 1280 (C–O), 825, 550 cm^{-1} (PF). Correct ^{1}H NMR spectrum [8]. δ(C) (CD_3COCD_3, 15 MHz) 76.9 (C(6))*); 77.7 (C(9)*); 79.8 (C_5H_5); 85.8 (C(7)#); 85.9 (C(8)#); 118.4 (C(5a)**); 118.8 (C(9a)**); 124.5 (C(3)); 127.5 (C(4)); 135.8 (C(4a)); 144.9 (C(2)); 146.5 (C(10a)) ppm.

Reactions of (η^5-2,4-cyclopentadien-1-yl)(η^6-1,2-dichloro-4-methylbenzene)iron(1 +) hexafluorophosphate(1 −) (47)

(a) With 1,2-benzenediol. The complex **47** (0.10 g, 0.24 mmol) was reacted with 1,2-benzenediol (26 mg, 0.24 mmol) and K_2CO_3 (58 mg, 0.42 mmol) in DMF (2 mL) as above. Workup after 2.75 h gave a solid which was purified by CH_2Cl_2/Et_2O precipitation to yield (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,4a,10a-η)-2-methyldibenzo[*b*,*e*]1,4]dioxin]iron(1 +) hexafluorophosphate(1 −) (**59**) (60 mg, 55%) as yellow crystals, m.p. 163–165 °C. Anal. Found: C, 46.8; H, 3.7. $C_{18}H_{15}F_6FeO_2P$ calc.: C, 46.6; H, 3.3%. ν_{max}(KBr) 1520, 1480 (aryl C=C), 1290, 1270 (C–O), 850, 832 (aromatic), 817 (PF), 750 (aromatic), 546 cm^{-1} (PF). δ(H) (CD_3COCD_3) 2.55 (s, CH_3); 5.24 (s, C_5H_5); 6.24 (br d, $J_{3,4}$ = 6.0 Hz, H(3)); 6.50 (d, $J_{3,4}$ = 6.2 Hz, H(4)); 6.55 (s, H(1)); 7.18 (br s, H(7,8)); 7.25 (3 lines, J_{obs} = 3.4, 5.4 Hz, H(6.9)) ppm. δ(C) (CD_3COCD_3) 19.8 (CH_3); 75.7 (C(4)); 77.3 (C(1)); 79.4 (C_5H_5); 84.9 (C(3)); 101.1 (C(2)); 117.9 (C(4a)); 118.31 (C(6)*); 118.34 (C(9)*); 118.4 (C(10a); 127.3 (C(7,8)); 139.7 (C(5a)#); 139.7 (C(9a)#) ppm.

Irradiation of **59** in CH_2Cl_2 as above for 1.5 h and chromatography (PLC) (CH_2Cl_2/hexanes, 1:8) yielded 2-methyldibenzo[*b*,*e*][1,4]dioxin (**8**) (21 mg, 69%) as white crystals, m.p. 54.5–55.5 °C (lit. [41] m.p. 54 °C). ν_{max}(KBr) 1497 (aryl C=C), 1285 (C–O), 740 cm^{-1} (aromatic). δ(H) 2.23 (s, CH_3); 6.55 (m, H(1), 0.5H(3)); 6.67 (d, $J_{1,3}$ = 1.3 Hz, 0.5H(3)); 6.72 (d, $J_{3,4}$ = 7.9 Hz, H(4)); 6.84 (m, H(6–9)) ppm. δ(C) 20.7 (CH_3); 115.9 (C(4)); 116.30 (C(6)*); 116.34 (C(9)*); 116.8 (C(1); 123.6 (C(7)#); 123.7 (C(8)#); 124.0 (C(3)); 133.6 (C(2)); 139.8 (C(4a)); 141.7 (C(10a)); 142.2 (C(5a)**); 142.3 (C(9a)**) ppm. *m/z* 198 (100, M), 196 (33 (M − H_2), 169 (14, M − H–CO), 141 (12, 169 − CO).

(b) With 4-methyl-1,2-benzenediol. The complex **47** (0.20 g, 0.46 mmol) was reacted with 4-methyl-1,2-benzenediol (58 mg, 0.46 mmol) and K_2CO_3 (0.12 g, 0.84 mmol) in DMF (4 mL) as above. Workup after 1.75 h and precipitation from CH_2Cl_2/Et_2O yielded a mixture (1.2:1) (^{1}H NMR) of (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,4a,10,-η)-2,7-dimethyldibenzo[*b*,*e*][1,4]dioxin]iron(1 +) hexafluorophos-

phate(1 −) (**66**) and (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,4a,10a-η)-2,8-dimethyldibenzo[*b*,*e*][1,4]dioxin]iron(1 +) hexafluorophosphate(1 −) (**60**), as yellow crystals (0.12 g, 52%), m.p. 171–173 °C. Anal. Found: C, 47.1; H, 3.5. $C_{19}H_{17}O_2F_5FeP$ calc.: C, 47.7; H, 3.6%. ν_{max}(KBr) 1500, 1480 (aryl C=C), 1300, 1280 (C–O), 830 (PF), 824 (aromatic), 550 cm^{-1} (PF). δ(H) (CD_3COCD_3) (**66**) 2.31 (s, 7-CH_3); 2.52 (s, 2-CH_3); 5.19 (s, C_5H_5); 6.19 (d, $J_{3,4}$ = 6.2 Hz, H(3)); 6.45 (d, $J_{3,4}$ = 6.4 Hz, H(4)); 6.51 (s, H(1)); 6.98 (s, H(6)); 7.03 (s, H(8,9). (**60**) 2.31 (s, 8-CH_3); 2.52 (s, 2-CH_3); 5.19 (s, C_5H_5); 6.19 (d, $J_{3,4}$ = 6.2 Hz, H(3)); 6.46 (d, $J_{3,4}$ = 6.5 Hz, H(4)); 6.50 (s, H(1)); 6.96 (s, H(9)); 7.03 (s, H(6,7)). δ(C) (CD_3COCD_3) (**66**) 19.7 (2-CH_3); 20.7 (7-CH_3); 75.6 (C(4)); 77.2 (C(1)); 79.2 (C_5H_5); 84.8 (C(3)); 100.9 (C(2)); 117.8 (C(9)); 118.0 (C(4a)); 118.3 (C(10a)); 118.5 (C(6)); 127.5 (C(8)); 137.4 (C(7,9)); 139.2 (C(5a). (**60**) 19.7 (2-CH_3); 20.7 (8-CH_3); 75.7 (C(4)); 77.3 (C(1)); 79.9 (C_5H_5); 84.7 (C(3)); 101.0 (C(2)); 117.8 (C(4a)); 117.9 (C(6)); 118.4 (C(9)); 118.6 (C(10a)); 127.5 (C(7)); 137.4 (C(5a,8)); 139.2 (C(9a)) ppm.

In a further experiment carried out for 3 days the products were (i) a mixture (18%) of **66** and **60**, and (ii) from PLC (Et_2O/hexanes, 1:3) of the mother liquors a mixture (1.2:1) (^{1}H NMR) (25 mg, 25%) of 2,7-dimethyldibenzo[*b*,*e*][1,4]dioxin (**39**) and 2,8-dimethyldibenzo[*b*,*e*][1,4]dioxin (**9**) which crystallized from EtOH as needles, m.p. 83–85 °C. ν_{max}(KBr) 1500 (aryl C=C), 1302, 1226, 1218, 1204 (C–O), 801 cm^{-1} (aromatic). δ(H) (**39**) 2.24 (s, 2xCH_3); 6.65 (m, H[1,6,0.5H(3),0.5H(8)]; 6.67 (m, 0.5H(3,8)); 6.72 (d, J = 8.0 Hz, H(4,9)). (**9**) 2.24 (s, 2xCH_3); 6.65 (m, H[1,9,0.5(H)3]); 6.67 (m, 0.5H(3,7)); 6.71 (d, J = 8.2 Hz, H(4.6)) ppm. δ(C) (**39**) 20.7 (2xCH_3); 115.9 (C(4,9)); 116.8 (C(1,6)); 123.8 (C(3,8)); 133.5 (C(2,7)); 139.8 (C(4a,9a)); 141.8 (C(5a, 10a)). (**9**) 20.7 (2xCH_3); 115.9 (C(4,6)); 116.8 (C(1,9)); 124.0 (C(3,7)); 133.4 (C(2,8)); 140.0 (C(4a,5a)); 141.7 (C(9a,10a)) ppm. *m/z* 212 (100, M), 211 (28, M − H), 197 (4, M − CH_3), 183 (13, 211 − CO), 169 (9, 197 − CO), 155 (3, 183 − CO), 141 (5, 169 − CO).

An authentic sample of **39**, m.p. 109–112 °C (lit. [19] 113 °C) was prepared by the method of Ramsden [19].

Irradiation of the mixture of **66** and **60** in acetonitrile for 3 h gave (83%) a mixture (1.3:1) of **39** and **9**. Sublimation (Kugelrohr) of **66** and **60** at 185 °C/0.02 mmHg for 30 min gave (71%) a mixture **39** and **9**.

(c) With 3,4-dihydroxybenzaldehyde. The complex **47** (94 mg, 0.22 mmol) was reacted with 3,4-dihydroxybenzaldehyde (30.5 mg, 0.22 mmol) and K_2CO_3 (55 mg, 0.40 mmol) in DMF (2 mL) as above. Workup after 3 h gave a yellow solid (88 mg, 81%) which was purified by precipitation from Me_2CO/Et_2O to yield a mixture (1.6:1) (^{13}C NMR) of (η^5-2,4-cyclopentadien-1-yl)[(5a,6,7,8,9,9a-η)-8-methyldibenzo[*b*,*e*][1,4]dioxin-2-carboxaldehyde]iron(1 +) hexafluorophosphate(1 −) (**61**) and (η^5-2,4-cyclopentadien-1-yl)[(5a,6,7,8,9,9a-η)-7-methyldibenzo[*b*,*e*][1,4]dioxin-2-carboxaldehyde]iron(1 +) hexafluorophosphate(1 −) (**67**) as yellow crystals (80 mg, 74%), m.p. 214–216 °C. Anal. Found: C, 46.5; H, 2.9. $C_{19}H_{15}F_6FeO_3P$ calc.: C, 46.4; H, 3.1%. ν_{max}(KBr) 1690 (CO), 1604, 1519, 1500, 1480 (aryl C=C), 1290 (C–O), 870 (aromatic), 825 (PF), 774 (aromatic), 552 cm^{-1} (PF). δ(H) (CD_3COCD_3) (**61**) 2.54 (s, CH_3); 5.27 (s, C_5H_5); 6.25 (br d, $J_{6,7}$ = 6.2 Hz, H(7)); 6.54 (d, $J_{6,7}$ = 6.4 Hz, H(6)); 6.59 (s, H(9)); 7.36 (d, $J_{3,4}$ = 8.2 Hz, H(4)); 7.62 (s, H(1)); 7.80 (d, $J_{3,4}$ = 8.1 Hz, H(3)); 9.00 (s, CHO). (**67**) 2.54 (s, CH_3); 5.27 (s, C_5H_5); 6.25 (br d, $J_{8,9}$ = 6.2 Hz, H(8)); 6.54 (d, $J_{7,8}$ = 6.4 Hz, H(9)); 6.59 (s, H(6)); 7.37 (d, $J_{3,4}$ = 8.2 Hz H(4)); 7.62 (s, H(1)); 7.80 (d, $J_{3,4}$ = 8.2 Hz, H(4)); 7.62 (s, H(1)); 7.80 (d,

$J_{3,4}$ = 8.1 Hz, H(3)); 9.00 (s, CHO) ppm. δ(C) (CD_3COCD_3) (**61**) 19.7 (CH_3); 75.7 (C(6)); 77.2 (C(9)); 79.6 (C_5H_5); 85.1 (C(7)); 101.5 (C(8)); 117.1 (C(5a)); 118.1 (C(9a)); 118.3 (C(4)); 119.2 (C(1)); 129.1 (C(3)); 135.7 (C(2)); 140.2 (C(10a)); 144.1 (C(4a)); 190.8 (CHO). (**67**) 19.7 (CH_3); 75.6 (C(9)); 77.2 (C(6)); 79.6 (C_5H_5); 85.2 (C(8)); 101.4 (C(7)); 117.5 (C(9a)); 117.6 (C(5a)); 118.3 (C(4)); 119.2 (C(1)); 129.1 (C(3)); 135.7 (C(2)); 140.3 (C(10a)); 144.1 ((4a)); 190.8 (CHO) ppm.

Irradiation of **61** and **67** in acetonitrile for 3 h gave a mixture (1.8:1) of 8-methyldibenzo[*b*,*e*][1,4]dioxin-2-carboxaldehyde (**10**) and 7-methyldibenzo[*b*,*e*][1,4]dioxin-2-carboxaldehyde (**40**) as white crystals, m.p. 97–99 °C. Anal. Found: C, 73.9; H, 4.6; $M^{+\cdot}$ 226.0623. $C_{14}H_{10}O_3$ calc.: C, 74.3; H, 4.5%; $M^{+\cdot}$ 226.0630). ν_{max}(KBr) 1688 (CO), 1502 (aryl C=C), 1298 (C–O), 806 cm^{-1} (aromatic). δ(H) (**10**) 2.26 (s, CH_3); 6.70 (d, $J_{7,9}$ = 1.6 Hz, H(9)); 6.73 (dd, J_{obs} = 1.9, 1.6, $J_{6,7}$ = 7.5 Hz, H(7)); 6.76 (d, $J_{6,7}$ = 8.0 Hz, H(6)); 6.95 (d, $J_{3,4}$ = 8.2 Hz, H(4)); 7.35 (d, $J_{1,3}$ = 2.1 Hz, H(1)); 7.4 (dd, J_{13} = 1.8, $J_{3,4}$ = 8.2 Hz, H(3)); 9.81 (s, CHO). (**40**) 2.26 (s, CH_3); 6.70 (d, $J_{6,8}$ = 1.6 Hz, H(6)); 6.73 (dd, J_{obs} = 1.9, 1.6, $J_{8,9}$ = 7.5 Hz H(8)); 6.77 (d, $J_{8,9}$ = 8.2 Hz, H(9)); 6.95 (d, $J_{3,4}$ = 8.2 Hz, H(4)); 7.35 (d, $J_{1,3}$ = 2.3 Hz, H(1)); 7.44 (dd, $J_{1,3}$ = 1.3, $J_{3,4}$ = 8.2 Hz, H(3)); 9.81 (s, CHO) ppm. δ(C) (15 MHz) (**10**) 20.7 (CH_3); 116.1 (C(6)); 116.5 (C(4)); 116.7 (C(9)); 116.9 (C(1)); 124.4 (C(7)); 126.9 (C(3)); 132.6 (C(2)); 134.6 (C(8)); 138.9 (C(5a)); 141.0 (C(9a)); 142.7 (C(10a)); 148.5 (C(4a)); 189.9 (CHO). (**40**) 20.7 (CH_3); 116.1 (C(9)); 116.5 (C(4)); 116.7 (C(6)); 116.9 C(1)); 124.9 (C(8)); 126.8 (C(3)); 132.7 (C(2)); 134.1 (C7)); 139.1 (C(9a)); 140.7 (C(5a)); 142.9 (C(10a)); 147.3 (C(4a)); 189.9 (CHO) ppm. *m/z* (100, M), 225 (60, M – H), 197 (50, 225 – CO), 169 (10, 197 – CO), 141 (10, 169 – CO).

*Reactions of (η^5-2,4-cyclopentadien-1-yl)(η^6-1,2-dichloro-3-methylbenzene)iron(1 +) hexafluorophosphate(1 –) (**48**)*

(a) With 1,2-benzenediol. The complex **48** (0.10 g, 0.23 mmol) was reacted with 1,2-benzenediol (26 mg, 0.23 mmol) and K_2CO_3 (48 mg, 0.42 mmol) in DMF (2 mL) as above. Workup after 22 h and chromatography on alumina (CH_2Cl_2/EtOH, 10:1) gave a yellow oil (64.5 mg). Further chromatography (PLC) (solvent A) yielded (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,4a,10a-η)-1-methyldibenzo[*b*,*e*][1,4]-dioxin]iron(1 +) hexafluorophosphate(1 –) (**68**) (14 mg, 13%) which crystallized from Me_2CO/Et_2O (isopiestic method, 4 °C) as yellow needles, m.p. 159.5–160.5 °C. Anal. Found: C, 46.6; H, 3.1. $C_{18}H_{15}F_6FeO_2P$ calc.: C, 46.6; H, 3.3%. ν_{max}(film) 1490, 1465 (aryl C=C), 1295, 1275 (C–O), 820 (PF), 745 cm^{-1} (aromatic). δ(H) (CD_3COCD_3) 2.62 (s, CH_3); 5.22 (s, C_5H_5); 6.26 (t, *J* = 6.2 Hz, H(3)); 6.33 (d, $J_{2,3}$ = 6.0 Hz, H(2)); 6.48 (dd, $J_{2,4}$ 1.0, $J_{3,4}$ = 6.3 Hz, H(4)); 7.16 (m, H(7,8)); 7.25 (dd, J_{obs} = 3.5, 3.7, 4.8 Hz, H(6,9)) ppm. δ(C) (CD_3COCD_3) 15.1 (CH_3); 54.4 (C(4)); 79.1 (C_5H_5); 83.5 (C(3)); 86.2 (C(2)); 92.4 (C(1)); 117.8 (C(4a)); 118.2 (C(6)*); 118.4 (C(9)*), 118.5 (C(10a)); 127.5 (C(7)#); 127.3 (C(8)#); 139.7 (C(5a)**), 139.9 (C(9a)**).

(b) With methyl 2,3-dihydroxybenzoate. The complex **48** (0.11 g, 0.26 mmol) was reacted with methyl 2,3-dihydroxybenzoate (43 mg, 0.26 mmol) and K_2CO_3 (64 mg, 0.47 mmol) in DMF (2.2 mL) as above. Workup after 23 h and chromatography on alumina (CH_2Cl_2/EtOH, 10:1) gave a yellow oil (99 mg). Further chromatography (PLC) (solvent A) gave a mixture (1.9:1) (^{1}H NMR) of (η^5-2,4-cyclopentadien-1-yl)[methyl (5a,6,7,8,9,9a-η)-9-methyldibenzo[*b*,*e*][1,4]dioxin-1-carboxylate]iron-(1 +)hexafluorophosphate(1 –) (**62**) and (η^5-2,4-cyclopentadien-1-yl)[methyl-

(5a,6,7,8,9,9a-η)-6-methyldibenzo[*b,e*][1,4]dioxin-1-carboxylate]iron(1 +) hexafluorophosphate(1 −) (**69**) as a yellow solid (33.5 mg, 25%). δ(H) (CD_3COCD_3) (**62**) 2.65 (s, CH_3); 3.99 (s, OCH_3); 5.21 (s, C_5H_5); 6.24 (t, J = 6.2 Hz, H(7)); 6.33 (d, $J_{7,8}$ = 6.1 Hz, H(8)); 6.49 (d, $J_{6,7}$ = 6.4 Hz, H(6)); 6.35 (t, J = 7.9 Hz, H(3)); 7.40 (dd, $J_{2,4}$ = 1.7, $J_{3,4}$ = 8.1 Hz, H(4)); 7.74 (dd, $J_{2,4}$ = 1.7, $J_{2,3}$ = 7.7 Hz, H(2)). (**69**) 2.27 (s, CH_3); 3.91 (s, OCH_3); 5.14 (s, C_5H_5); 6.24 (t, J = 6.2 Hz, H(8)); 6.33 (d, $J_{7,8}$ = 6.1 Hz, H(9)); 7.03 (t, J = 7.9 Hz, H(3)); 7.10 (dd, $J_{2,4}$ = 1.8, $J_{3,4}$ = 8.0 Hz, H(4)); 7.44 (dd, $J_{2,4}$ = 1.7, $J_{2,3}$ = 7.8 Hz, H(2)) ppm.

Recrystallization from Me_2CO/Et_2O (isopiestic method, 4 °C) yielded **62** (7 mg, 5%) as yellow needles, m.p. 232.5–234.5 °C (dec.). Anal. Found: C, 46.0; H, 3.6. $C_{20}H_{17}F_6FeO_4P$ calc.: C, 46.0; H, 3.3%. ν_{max}(KBr) 1710 (CO), 1460 (aryl C=C), 1275 (C–O), 820, 552 cm^{-1} (PF). δ(C) (CD_3COCD_3) 15.0 (CH_3); 52.9 (OCH_3); 75.4 (C(6)); 79.3 (C_5H_5); 83.7 (C(7)); 86.3 (C(8)); 93.0 (C(9)); 117.3 (C(5a)); 118.5 (C(9a)); 121.5 (C(1)); 122.2 (C(4)); 126.4 (C(3)); 128.9 (C(2)); 139.8 (C(4a)); 140.6 (C(10a)); 164.7 (CO_2CH_3) ppm.

Amidation of (η^5-2,4-cyclopentadien-1-yl)](5a,6,7,8,9,9a-η)-dibenzo[b,e][1,4]dioxin-2-carboxylic acid]iron(1 +) hexafluorophosphate(1 −) (53)

1,1′-Carbonyldiimidazole (16 mg, 0.10 mmol) was added to a solution of the complex **53** (50 mg, 0.10 mmol) in DMF (0.3 mL) with swirling, causing effervescence and precipitation of a white solid. After 5 min *N,N*-dimethyl-1,2-ethanediamine (12 μL, 0.11 mmol) was added, the mixture was left for 1.75 h, and solvent was removed. Chromatography of the resulting oil on alumina (CH_2Cl_2/EtOH, 10:1) yielded (i) *N*-2-(dimethylamino)ethyl]dibenzo[*b,e*][1,4]dioxin-2-carboxamide (**11**) (5 mg, 17%) which crystallized from hexanes as white crystals, m.p. 117.5–118.5 °C. Anal. Found: C, 68.2; H, 6.0; N, 9.7. $C_{17}H_{18}N_2O_3$ calc.: C, 68.4; H, 6.1; H, 9.4%. ν_{max}(KBr) 3200 (NH), 1645 (CO), 1550 (amide II), 1500, 1490 (aryl C=C), 1300, 1285 (C–O), 730 cm^{-1} (aromatic). δ(H) 2.33 (s, $N(CH_3)_2$); 2.58 (apparent *t*, J = 5.7, 5.9 Hz, CH_2NMe_2); 3.53 (apparent q, J = 5.4, 5.7, 5.3 Hz, $CONHCH_2$); 6.88 (m, H(4,6–9)); 7.02 (s, NH); 7.33 (d, $J_{1,3}$ = 2.0 Hz, H(1)); 7.38 (dd, $J_{1,3}$ = 2.0, $J_{3,4}$ = 8.3 Hz, H(3)) ppm. δ(C) 36.9 ($CONHCH_2$); 45.0 ($N(CH_3)_2$); 57.8 ($CH_2N(CH_3)_2$); 115.5 (C(1)); 116.2 (C(4)); 116.45 (C(9)*); 116.47 (C(6)*); 123.0 (C(3)); 124.1 (C(8)#); 124.3 (C(7)#); 130.2 (C(2)); 141.6 (C(10a)); 141.7 (C(9a)**); 142.0 (C(5a)**); 144.7 C(4a)); 166.1 (CONH) ppm. m/z (< 1, M), 296 (< 1, M − H_2), 254 (< 1, M − NMe_2), 228 (9, M − $CH{=}CHNMe_2$), 211 (9, M − $NHCH_2CH_2NMe_2$), 183 (6, 211 − CO),155 (1,183 − CO), 71 (34, $CH_2{=}CHNMe_2$), 58 (100, CH_2NMe_2), 44 (5, NMe_2); and (ii) (η^5-2,4-cyclopentadien-1-yl)[(5a,6,7,8,9,9a-η)-*N*-[2-(dimethylamino)ethyl]dibenzo[*b,e*][1,4]dioxin-2-carboxamide]iron(1 +) hexafluorophosphate(1 −) (**63**) (15 mg, 27%) as a yellow unstable solid. ν_{max}(KBr) 3430 (NH), 1644 (CO), 1533 (amide II), 1490, 1462 (aryl C=C), 1282 (C–O), 836 (PF), 755 (aromatic), 550 cm^{-1}. δ(H) (CD_3COCD_3, 60 MHz) 2.26 (s, $N(CH_3)_2$); 2.50 (m, CH_2NMe_2); 3.50 (m, $CONHCH_2$); 5.33 (s, C_5H_5); 6.33–7.90 (m, H(1,3,4,6–9) ppm; NH not observed.

Dibenzo[b,e][1,4]dioxin-1-carboxylic acid (15)

A suspension of the ester **7** (0.10 g, 0.41 mmol) in 20% aqueous NaOH (2 mL) was heated under reflux with stirring for 3 h, and worked up to give a solid which crystallized from aqueous EtOH to yield dibenzo[*b,e*][1,4]dioxin-1-carboxylic acid

(**15**) (56 mg, 60%) as white needles, m.p. 212–215 °C (lit. [1] m.p. 207 °C, [39] 210 °C). ν_{max}(KBr) 3600–2100 (OH), 1682 (CO), 1495, 1455 (aryl C=C), 1270 (C–O), 737 cm^{-1} (aromatic). Correct ^1H NMR spectrum [1]. δ(C) (CD_3SOCD_3) 115.0 (C(6))*); 115.5 (C(9)*); 118.5 (C(4)); 119.6 (C(1)); 121.7 (C(7)#); 122.9 (C(8)#); 123.1 (C(3)); 124.7 (C(2)); 140.4 (C(5a)**); 140.5 (C(9a)**), 140.8 (C(4a)); 141.3 (C(10a)); 165.1 (CO_2H) ppm. *m/z* (100, M), 211 (11, M – OH), 183 (11, 211 – CO), 155 (6, 183 – CO), 127 (10, 155 – CO).

*Methyldibenzo[*b,e*][1,4]dioxin-2-carboxylate (12)*

A suspension of the aldehyde **4** (19 mg, 0.09 mmol), barium manganate (0.48 g, 1.89 mmol) [17,18], NaCN (23 mg, 0.48 mmol), and acetic acid (8 μL, 0.14 mmol) in MeOH (10 mL) was stirred vigorously for 19 h, and the mixture was worked up to give a cream solid. Chromatography (Et_2O/hexanes, 1:5) yielded methyl dibenzo[*b,e*][1,4]dioxin-2-carboxylate (**12**) (16 mg, 75%) as a white solid, m.p. 103–107.5 °C (lit. [36] m.p. 102–103 °C). ν_{max}(KBr) 1730 (CO), 1592, 1507, 1495 (aryl C=C), 1320, 1285 (C–O), 750, 722 cm^{-1} (aromatic). δ(H) (60 MHz) 3.90 (s, OCH_3); 6.88 (s, H(4, 6–9)); 7.51 (s, overlapping d, H(1), 0.5 H(3)); 7.66 (d, $J_{1,3} = 2.0$ Hz, 0.5H(3)) ppm. *m/z* 242 (82, M), 211 (100, M – CH_3O), 183 (53, 211 – CO), 155, (9, 183 – CO), 127 (29, 155 – CO).

Treatment of the ester **12** (11 mg, 0.05 mmol) with *N,N*-dimethyl-1,2-ethanediamine (100 μL, 0.91 mmol) in a sealed vial at *ca.* 100 °C for 2.5 h and chromatography of the product on alumina (Et_2O) gave *N*-[2-(dimethylamino) ethyl]dibenzo[*b,e*][1,4]dioxin-2-carboxamide (**11**) (11 mg, 82%). Correct ^1H NMR spectrum.

*Dibenzo[*b,e*][1,4]dioxin-2-carboxylic acid (13)*

The aldehyde **4** (74 mg, 0.35 mmol) in acetone (10 mL) was treated with Jones reagent (2.67 mol L^{-1}, 1.20 mmol), and the mixture was worked up and chromatographed (Et_2O/hexanes, 5:1) to yield dibenzo[*b,e*][1,4]dioxin-2-carboxylic acid (**13**) (72 mg, 90%) as a white solid, m.p. 245.5–247 °C (lit. [36] m.p. 239–241 °C). ν_{max}(KBr) 3500–2550 (OH), 1675 (CO), 1495, 1443 (aryl C=C), 1305 (C–O), 740 cm^{-1} (aromatic). δ(H) ($CDCl_3/CD_3SOCD_3$) 6.89 (m, H(4,6–9)); 7.52 (s, H(1)); 7.62 (d, $J_{3,4} = 7.8$ Hz, H(3)) ppm; CO_2H not observed. δ(C) ($CDCl_3/CD_3SOCD_3$) 115.7 (C(4)); 116.1 (C(6,9)); 117.6 (C(1)); 123.7 (C(8)*); 124.1 (C(7)*); 125.8 (C(3)); 126.5 (C(2)); 141.2 (C(10a)); 141.39 (C(9a)#); 141.42 (C(5a)#); 145.4 (C(4a)); 166.9 (CO_2H) ppm. *m/z* 228 (100, M), 211 (38, M – OH), 183 (31, 211 – CO), 155 (10, 183 – CO), 127 (19, 55 – CO).

Treatment of the acid **13** (0.17 g, 0.75 mmol) with *N,N*-dimethyl-1,2-ethanediamine (90 μL, 0.82 mmol) and CDI (0.12 g, 0.75 mmol) in DMF (0.55 mL) at room temperature gave *N*-[2-(dimethylamino)ethyl]dibenzo[*b,e*][1,4]dioxin-2-carboxamide (**11**) (0.22 g, 94%).

N-*[3-(Dimethylamino)propyl]dibenzo[*b,e*][1,4]dioxin-2-carboxamide (14)*

The acid **13** (0.51 mmol) was treated with *N,N*-dimethyl-1,3-propanediamine (0.51 mmol) and CDI (0.51 mmol) in DMF (1 mL). Workup gave *N*-[3-(dimethylamino)propyl]dibenzo[*b,e*][1,4]dioxin-2-carboxamide (**14**) (0.15 g, 94%) which crystallized from hexanes as white needles, m.p. 101.5–103 °C. Anal. Found: C, 68.8;

H, 6.6; N, 9.0; $M^{+\cdot}$ 312.1478. $C_{18}H_{12}N_2O_3$ calc.: C, 69.2; H, 6.5; N, 9.0%; $M^{+\cdot}$ 312.1474). ν_{max}(KBr) 3325 (NH), 1630 (CO), 1530 (amide II), 1510 (aryl C=C), 1320, 1310 (C–O), 745 cm^{-1} (aromatic). δ(H) 1.75 (quintet, $J = 5.9$ Hz, $CH_2CH_2CH_2$); 2.31 (s, NMe_2); 2.50 (apparent t, $J = 5.8$ Hz, CH_2NMe_2); 3.54 (apparent q, $J = 5.9$, 5.7, 5.0 Hz, $CONHCH_2$); 6.88 m, H(4,6–9)); 7.28 (d, $J_{1,3} = 2.0$ Hz, H(1)); 7.30 (dd, $J_{1,3} = 2.0$, $J_{3,4} = 8.3$ Hz, H(3)); 8.50 (s, NH) ppm. δ(C) 25.1 ($CH_2CH_2CH_2$); 40.8 ($CONHCH_2$); 45.4 ($N(CH_3)_2$); 59.4 (CH_2NMe_2); 115.3 (C(1)); 116.1 (C(4)); 116.4 (C(9)*); 116.5 (C(6)*); 122.5 (C(3)); 124.0 (C(8)*); 124.2 (C(7)*); 130.7 (C(2)); 141.6 (C(10a)); 141.8 (C(9a)**); 141.9 (C(5a)**); 144.4 (C(4a)); 165.6 (CONH) ppm. m/z 312 (7%, M), 211 (16, M – $NHCH_2CH_2CH_2NMe_2$), 183 (9, 211 – CO), 155 (2, 183 – CO), 127 (8, 155 – CO), 72 (20, $CH_2CH_2NMe_2$), 58 (100, CH_2NMe_2), 44 (9, NMe_2).

*Reaction of lithiated dibenzo[*b,e*][1,4]dioxin (2) with carbon dioxide*

(a) Butyllithium (2.13 mol L^{-1} in hexanes, 1.20 mL, 2.56 mmol) was added dropwise with stirring to a solution of **2** (0.43 g, 2.33 mmol) in THF (23 mL) at −23 °C under N_2, and after 20 min, CO_2 was bubbled into the mixture for 15 min. The atmosphere of CO_2 was maintained and the solution was allowed to warm to room temperature. After 2.5 h, the mixture was acidified with dilute H_2SO_4 and solvent was removed to give a solid which was chromatographed (hexanes) to yield (i) dibenzodioxin (**2**) (72 mg, 17%), and on further elution (hexanes/CH_2Cl_2, 1:1) (ii) 1-pentanoyldibenzo[*b,e*][1,4]dioxin (**16**) (11 mg, 2%) as a colourless oil. ν_{max}($CHCl_3$) 1655 (CO), 1595, 1495, 1465 (aryl C=C), 1270 (C–O), 830 cm^{-1} (aromatic). m/z 268 (38%, M), 226 (32, M – C_3H_6), 211 (100, 226 – Me), 183 (27, 211 – CO), 155 (17, 155 – CO). Further elution (solvent A) and chromatography (EtOAc) yielded (iii) dibenzo[*b,e*][1,4]dioxin-1-carboxylic acid (**15**) (0.31 g, 59%).

Esterification of the crude product from (a) in MeOH (50 mL) and concentrated H_2SO_4 (1.25 mL) under reflux for 2.5 h and chromatography (CH_2Cl_2/hexanes, 1:2) gave methyl dibenzo[*b,e*][1,4]dioxin-1-carboxylate (**7**) (0.41 g, 39%).

(b) Use of t-butyllithium (1.1 mol equiv.) and TMEDA (1.1 mol equiv) for 2 h gave the benzodioxin (**2**) (78%) and the acid (**15**) (5%). Esterification of the crude product from (b) and chromatography (CH_2Cl_2/hexanes, 1:2) yielded (i) methyl dibenzo[*b,e*][1,4]dioxin-1-carboxylate (**7**) (93 mg, 9%) and (ii) dimethyl dibenzo[*b,e*][1,4]dioxin-1,9-dicarboxylate (**18**) (0.12 g, 9%) which crystallized from acetone at 4 °C. ν_{max} ($CHCl_3$) 1725 (CO), 1455 (aryl C=C), 1272 (C–O) cm^{-1}. Correct ^1H NMR spectrum [39]. δ(C) 52.3 (2xCH_3O); 119.9 (C(4,6)); 120.1 (C(1,9)); 123.5 (C(3,7)); 126.1 (C(2,8)); 141.7 (C(4a,5a); 142.4 (C(9a,10a)); 165.1 (2xCO_2Me) ppm. m/z 300 (100, M), 269 (61, M – CH_3O), 239 (37, 269 – CH_2O), 211 (9, 239 – CO), 210 (2, 211 – H or M – $2CH_3O$–CO), 183 (7, 211 – CO), 170 (2, 269 – CH_3-3CO), 155 (4, 183 – CO), 127 (6, 155 – CO), 126 (9, 210 – 3CO).

*Reactions of lithiated dibenzo[*b,e*][1,4]dioxin-1-carboxylic acid (15)*

(a) With carbon dioxide. Butyllithium (2.13 mol L^{-1} in hexanes, 0.32 mL, 0.68 mmol) was added dropwise to a stirred solution of the acid **15** (70 mg, 0.31 mmol) and TMEDA (102 μL, 0.68 mmol) in THF (2 mL) at −78 °C under N_2. After 35 min CO_2 was bubbled through the mixture for 15 min, and the mixture was allowed to warm to room temperature. After 1.5 h, the solution was acidified with dilute H_2SO_4, giving a white precipitate, and the solvent was removed. The crude

product, MeOH (20 mL), and concentrated H_2SO_4 (0.5 mL) were heated under reflux for 3 h. Workup and chromatography (PLC) (CH_2Cl_2) yielded (i) 1-pentanoyldibenzo[*b*,*e*][1,4]dioxin (**16**) (5 mg, 6%); (ii) methyl dibenzo[*b*,*e*][1,4]dioxin-1-carboxylate (**7**) (15 mg, 17%); (iii) methyl 9-pentanoyldibenzo[*b*,*e*][1,4]dioxin-1-carboxylate (**17**) (4 mg, 4%) as a white solid. *m/z* 326 (44, M), 284 (35, M − C_3H_6), 269 (100, 284 − CH_3), 252 (44, 284 − CH_3OH), 239 (63, 269 − CH_2O), 211 (35, 239 − CO), 183 (12, 211 − CO), 155 (7, 183 − CO), 127 (9, 155 − CO); and (iv) dimethyl dibenzo[*b*,*e*][1,4]dioxin-1,9-dicarboxylate (**18**) (27 mg, 30%).

(b) With iodine. Butyllithium (1.49 mol L^{-1} in hexanes, 0.27 mL, 0.41 mmol) was added dropwise to a stirred solution of the acid **15** (42 mg, 0.19 mmol) in THF (3 mL) at −78 °C under N_2, and after 30 min a solution of I_2 (0.10 g, 0.41 mmol) in THF (1.5 mL) was added. After 30 min the solution was warmed to room temperature, acidified with dilute HCl, treated with NaCl and extracted into EtOAc. The extract was washed with dilute aqueous $NaHSO_3$ and worked up to give a cream solid. Chromatography (PLC) (solvent A) gave (i) a mixture (MS) (16 mg) of the butyl ketone **16** (the major component) and 9-iodo-1-pentanoyldibenzo[*b*,*e*][1,4]dioxin (**20**) as a pale yellow oil. *m/z* (**16**) 268 (39, M), 226 (31, M − C_3H_6), 211 (100, 226 − CH_3), 183 (26, 211 − CO), 155 (5, 183 − CO), 127 (13, 155 − CO). (**20**) 394 (3, M), 352 (3, M − C_3H_6), 337 (4, 352 − CH_3), 309 (1, 337 − CO); and (ii) 9-iododibenzo[*b*,*e*][1,4]dioxin-1-carboxylic acid (**19**) [25 mg, 38%) which crystallized from CH_2Cl_2/hexanes as white needles, m.p. 223–227 °C. Anal. Found: $M^{+\cdot}$ 353.9415. $C_{13}H_{17}O_4I$ calc.: $M^{+\cdot}$ 353.9389. ν_{max}(KBr) 3500–2400 (OH), 1690 (CO), 1452 (aryl C=C), 1275, 1250 cm^{-1}. δ(H) ($CDCl_3/CD_3SOCD_3$) 6.67 (t, J = 8.0 Hz, H(7)); 6.80 (dd, $J_{6,8}$ = 1.4, $J_{6,7}$ = 8.1 Hz, H(6)); 6.96 (apparent t, J = 7.9, 7.7 Hz, H(3)); 6.99 (dd, $J_{2,4}$ = 0.9, $J_{3,4}$ = 7.6 Hz, H(4)); 7.33 (dd, $J_{6,8}$ = 1.4, $J_{7,8}$ = 8.0 Hz, H(8)); 7.53 (dd, J_{obs} = 1.2, 1.0, $J_{2,3}$ = 7.8 Hz, H(2)) ppm; CO_2H not observed. δ(C) ($CDCl_3/CD_3SOCD_3$) 83.2 (C(9)); 116.3 (C(6)); 119.5 (C(4)); 120.9 (C(1)); 123.5 (C(3)); 125.6 (C(2)); 126.2 (C(7)); 133.7 (C(8)); 141.9 (C(4a)); 142.02 (C(10a)*); 142.04 (C(5a)*); 142.4 (C(9a)); 166.1 (CO_2H) ppm. *m/z* 354 (100, M), 337 (7, M − OH), 309 (4, 337 − CO), 227 (9, M − I), 100 (3, 227 − CO), 171 (2, 199 − CO); and (iii) acid **42** (21 mg, 50%).

Reactions of lithiated N-*[2-(dimethylamino)ethyl]dibenzo[*b,e*][1,4]dioxin-1-carboxamide (1)*

(a) (i) Butyllithium (1.83 mol L^{-1} in hexanes, 0.40 mL, 0.74 mmol) was added dropwise to a stirred solution of **1** (0.10 g, 0.34 mmol) in THF (5 mL) at −78 °C under N_2. After 25 min, DMF (90 μL, 1.12 mmol) was added, and the stirring continued for 1.75 h. The mixture was allowed to warm to room temperature, and after 1.25 h was worked up and chromatographed (PLC) (CH_2Cl_2/EtOH/Et_3N, 100:10:1) to yield **1** (47 mg, 47%) and *N*-[2-(dimethylamino)ethyl]-9-formyldibenzo[*b*,*e*][1,4]dioxin-1-carboxamide (**21**) (38.5 mg, 38%) which crystallized from CH_2Cl_2/hexanes as white crystals, m.p. 199.5–121.5 °C. Anal. Found: C, 66.4; H, 5.4; N, 8.9%; $M^{+\cdot}$ 326.1261. $C_{18}H_{18}N_2O_4$ calc.: C, 66.3, H, 5.6; N, 8.6%; $M^{+\cdot}$ 326.1267. ν_{max}(KBr) 3420 (NH), 1678 (CHO), 1652 (CONH), 1575 (amide II), 1505, 1476, 1448 (aryl C=C), 1290, 1280 cm^{-1} (C–O). δ(H) 2.35 (s, $N(CH_3)_2$); 2.70 (apparent t, J = 6.6 Hz, CH_2NMe_2); 3.74 (apparent q, J = 6.5, 5.9, 6.4 Hz, $CONHCH_2$); 6.95 (dd, $J_{6,8}$ = 1.8, $J_{6,7}$ = 7.9 Hz, H(6)); 7.02 (t, J = 7.9 Hz, H(7)); 7.11 (m, H(3,4)); 7.37 (dd, $J_{2,4}$ = 3.3, $J_{2,3}$ = 6.1 Hz, H(2)); 7.84 (dd, $J_{6,8}$ = 1.7,

$J_{7,8}$ = 7.9 Hz, H(8)); 8.60 (s, NH); 10.05 (s, CHO) ppm. δ(C) 37.9 ($CONHCH_2$); 35.3 (NMe_2); 58.2 (CH_2NMe_2); 119.4 (C(4)); 122.0 (C(1)); 122.2 (C(6)); 124.0 (C(9)); 124.3 (C(2)); 124.5 (C(3)); 127.1 (C(7)); 128.2 (C(8)); 139.7 (C(10a)); 141.1 (C(4a)); 141.4, (C(5a)); 142.3 (C(9a); 163.1 (CONH); 189.5 (CHO) ppm. *m/z* 326 (< 1, M), 324 (< 1, M − H_2), 256 (3, M − CH=$CHNMe_2$), 239 (3, M − $NHCH_2$ CH_2NMe_2), 211 (2, 239 − CO), 183 (1, 211 − CO), 155 (1, 183 − CO), 127 (2, 155 − CO), 71 (25, CH_2=$CHNMe_2$), 58 (100, CH_2NMe_2).

(ii) Repetition of the reaction with the concentration of **1** at 0.20 mol L^{-1}, TMEDA (2.2 molar equiv.), a lithiation period of 2.75 h, and then with DMF (5 molar equiv) for 3 h yielded (i) **1** (6 mg, 26%); (ii) **21** (32 mg, 29%); and (iii) 2-[2-dimethylamino)ethyl]-3-hydroxy-10-hydroxymethyl-1*H*-[[1,4]benzodioxino][2,3-g]isoindol-1-one (**70**) (12 mg, 10%) as a colourless oil. Anal. Found: $M^{+\cdot}$ 356.1369. $C_{19}H_{20}N_2O_5$ calc.: $M^{+\cdot}$ 356.1372). ν_{max}(film) 3375 (OH), 1690 (CO), 1492, 1470 (aryl C=C), 1289 (C–O), 755 cm^{-1} (aromatic). δ(H) 2.43 (s, $N(CH_3)_2$); 2.54 (br d, *J* = 14.5 Hz, (CH_aH_b)NMe_2); 2.78 (5 lines, J_{obs} = 2.5, 2.3, 12.0 Hz, (CH_aCH_b) NMe_2); 3.24 (ddd, J_{obs} = 2.0, 11.0, 15.0 Hz, $N(CH_aH_b)$); 4.27 (apparent dt, *J* = 2.8, 3.8, 15.1 Hz, $N(CH_aH_b)$); 4.74 (d, $J_{H_aH_b}$ = 13.1 Hz, (CH_aH_b)OH); 4.82 (d, $J_{H_aH_b}$ = 13.5 Hz, 5.68, s, CHOH); 6.81 (dd, $J_{7,9}$ = 2.9, $J_{7,8}$ = 6.7 Hz, H(7)); 6.89 (m, H(8,9)); 7.03 (d, $J_{4,5}$ = 8.0 Hz, H(5)); 7.09 (d, $J_{4,5}$ = 8.0 Hz, H(4)) ppm; (C_aH_b)O*H* and CHO*H* not observed. δ(C) 39.2 ($N(CH_aH_b)$); 44.4 ($N(CH_3)_2$); 58.4 ((CH_aH_b)NMe_2); 61.6 ((CH_aH_b)OH); 82.6 (CHOH); 115.9 (C(7)); 118.3 (C(5,11b)); 120.3 (C(9)); 123.8 (C(4)); 124.0 (C(8)); 129.8 (C(10)); 138.9 (C(3a)); 140.0 (C(5a)); 140.3 (C(10a)); 142.1 (C(11a)); 143.3 (C(6a)); 165.4 (CON) ppm. *m/z* 356 (4, M), 338 (1, M − H_2O), 323 (< 1, 338 − Me), 71 (19, CH_2=$CHNMe_2$), 58 (100, CH_2NMe_2).

(iii) Repetition of the reaction using butyllithium (4.4 molar equiv.), a lithiation period of 1 h, and DMF (20 molar equiv.) gave (i) (*Z*)-2-[2-(dimethylamino)ethyl]-10-formyl-3-hydroxy-5-pentenyl-1*H*-[[1,4]benzodioxino][2,3-g]isoindol-1-one (**71**) (30 mg, 16%) as a colourless oil. Anal. Found: $M^{+\cdot}$ 422.1838. $C_{24}H_{26}N_2O_5$ calc.: $M^{+\cdot}$ 422.1842). ν_{max}($CHCl_3$) 3400 (OH), 1697sh, 1682 (CO), 1489, 1462, 1447sh (aryl C=C), 1290 (C–O), 722 cm^{-1} (aromatic). δ(H) 0.98 (t, *J* = 7.4, Hz, CH_2CH_3); 1.53 (sextet, J_{obs} = 7.4, 7.7, 8.0, 7.6, 7.4 Hz, $CH_2CH_2CH_3$); 2.42 (s, $N(CH_3)_2$); 2.46 (m, $CH_2CH_2CH_3$); 2.54 (br d, *J* = 12.2 Hz, (CH_aH_b)NMe_2); 2.78 (apparent dt, *J* = 2.5, 2.8, 3.3, 10.7, 13.8 Hz, (CH_aH_b)NMe_2); 3.25 (ddd, J_{obs} = 2.2, 11.1, 15.4 Hz, $N(CH_aH_b)$); 4.26 (ddd, J_{obs} = 3.3, 5.0, 15.2 Hz, $N(CH_aH_b)$); 5.66 (s, CHOH); 6.88 (dd, $J_{1,9}$ = 1.4, $J_{7,8}$ = 8.1 Hz, H(7)); 6.98 (t, *J* = 8.0 Hz, H(8)); 7.00 (d (sh on upfield side of each component), *J* = 8.0 Hz, CH=$CHCH_2$); 7.08 (d, (sh on upfield side of each component), *J* = 8.0 Hz, CH=$CHCH_2$); 7.12 (dd, $J_{7,9}$ = 1.3, $J_{8,9}$ = 8.1 Hz, H(9)); 7.64 (s, H(4)); 9.70 (CHO) ppm; OH not observed. δ(C) 14.4 ($CH_2CH_2CH_3$); 21.7 ($CH_2CH_2CH_3$); 27.0 (CH_2CH_2); 39.5 ($N(CH_aH_b)$); 44.5 ($N(CH_3)_2$); 58.7 ((CH_aH_b)NMe_2); 81.9 (CHOH); 117.4 (CH=$CHCH_2$); 118.3 (C(11b)); 118.4 (C(4)); 120.1 (C(7)); 123.8 (C(8)); 124.1 (C(9,10)); 138.5 (C(3a)*); 139.7 (C(5)*); 140.5 (C(5a)); 141.7 (CH=$CHCH_2$); 142.0 (C(11a)); 142.5 (C(6a)); 144.4 (C(10a)); 164.8 (CON); 196.0 (CHO) ppm. *m/z* 422 (2%, M), 421 (2, M − H), 71 (10, CH_2=$CHNMe_2$), 58 (100, CH_2NMe_2); and (ii) 2-[2-(dimethylamino)ethyl]-3-hydroxy-10-formyl-1*H*-[[1,4]-benzodioxino][2,3-g]isoindol-1-one (**72**) (25 mg, 15%) as a white solid, m.p. 180–185 °C. Anal. Found: $M^{+\cdot}$ 354.1205. $C_{19}H_{18}N_2O_5$ calc.: $M^{+\cdot}$ 354.1216). ν_{max}($CHCl_3$) 3360 (OH), 1690 (CO), 1472 (aryl C=C), 1285 cm^{-1}

(C–O). δ(H) 2.41 (s, $N(CH_3)_2$) 2.50 (m, $(CH_aH_b)NMe_2$, CHO*H*); 2.75 (apparent dt, $J = 2.5$, 13.4, 10.9 Hz, $(CH_aH_b)NMe_2$); 3.25 (ddd, $J_{obs} = 2.0$, 11.3, 14.9 Hz, $N(CH_aH_b)$); 4.25 (apparent dt $J = 3.1$, 15.1 Hz, $N(CH_aH_b)$); 5.66 (s, C*H*OH; 7.00, t, $J = 7.8$ Hz, H(8)); 7.02 (d, $J_{4,5} = 8.0$ Hz, H(5)); 7.05 (dd, $J_{7,9} = 1.7$, $J_{7,8} = 7.9$ Hz, H(7)); 7.12 (d, $J_{4,5} = 8.0$ Hz, H(4)); 7.47 (dd, $J_{7,9} = 1.7$, $J_{8,9} = 7.7$ Hz, H(9)); 10.6 (s, CHO) ppm. δ(C) 39.6 ($N(CH_aH_b)$); 44.5 ($N(CH_3)_2$; 58.7 ($(CH_aH_b)NMe_2$); 81.8 (CHOH); 118.6 (C(11b)); 118.8 (C(5)); 120.3 (C(7)); 121.8 (C(4)); 122.4 (C(8)); 124.1 (C(9)); 124.6 (C(10)); 137.9 (C(3a)); 140.8 (C(5a)); 142.1 (C(11a)); 142.3 (C(6a)); 144.2 (C(10a)); 164.6 (CON); 187.5 (CHO) ppm. *m/z* 354 (1%, M), 256 (4, M – CH=CHNMe$_2$–CO), 239 (3, 256 – OH), 211 (2, 239 – CO), 71 (29, CH_2=CHNMe$_2$), 58 (100, CH_2NMe_2); and (iii) the aldehyde-amide **49** (22 mg, 15%).

(b) *With CO_2.* Butyllithium (2.0 mol L^{-1} in hexanes, 0.27 mL, 0.54 mmol) was added dropwise to a stirred solution of the amide **1** (73 mg, 0.25 mmol) and TMEDA (0.08 mL, 0.53 mmol) in THF (1.6 mL) at −78 °C under N_2 and after 30 min CO_2 was bubbled into the solution. Workup yielded the zwitterionic form of 9-[*N*-[2-(dimethylamino)ethyl]carboxamide]dibenzo[*b*,*e*][1,4]dioxin-1-carboxylic acid (**22**) (51 mg, 61%) as a white solid, m.p. *ca.* 220 °C. Anal. Found: $M^{+\cdot}$ 342.1186. $C_{18}H_{18}N_2O_5$ calc.: $M^{+\cdot}$ 342.1216). ν_{max}(KBr) 3275 (NH), 1635 (CONH), 1563 (CO_2^-), 1534 (amide (II), 1445 (aryl C=C), 1280 (C–O), 728 cm^{-1} (aromatic). δ(H) 2.84 (s, $^+NH(CH_3)_2$); 3.15 (apparent t, $J = 4.8$, 5.0 Hz, $CH_2NHMe_3^+$); 3.92 (apparent q, $J = 5.3$, 4.7, 5.2 Hz, CONHC*H*$_2$); 6.94 (m, H(3,4,6,7), $^+NHMe_2$); 7.46 (dd, $J_{6,8} = 2.3$, $J_{7,8} = 7.2$ Hz, H(8)); 7.79 (dd, $J_{2,4} = 2.9$, $J_{2,3} = 6.8$ Hz, H(2)); 9.89 (s, CONH) ppm. δ(C) 3.51 (CONH*C*H$_2$); 42.9 ($^+NH(CH_3)_2$); 58.4 ($CH_2NHMe_2^+$); 118.1 (C(6)); 119.5 (C(4)); 120.6 (C(9)); 123.3 (C(8)); 123.8 (C(7)); 125.5 (C(1)); 126.0 (C(3); 126.2, C(2)); 140.3 (C(9a)); 141.2 (C(5a)); 142.1 (C(4a)); 142.3 (C(10a)); 163.8 (CONH); 169.5 (CO_2^-) ppm. *m/z* 342 (1, M), 272 (10, M – CH=CHNMe$_3$), 255, (3, 272 – OH or M – NHCH$_2$CH$_2$NMe$_2$), 227 (2, 255 – CO), 211 (3, 262 – HO–CONH$_2$), 183 (2, 211 – CO), 71 (34, CH_2=CHNMe$_2$), 58 (100, CH_2NMe_2).

A suspension of **22** (48 mg, 0.14 mmol) in DMF (0.42 mL) was heated to 120 °C and CDI (45.5 mg, 0.28 mmol) was added, followed by *N*,*N*-dimethyl-1,2-ethanediamine (68 μL, 0.62 mmol) after 20 min. After 50 min the mixture was worked up and chromatographed (PLC) (solvent A) to give (i) starting material (9 mg, 19%) in non-ionized form, as a cream solid. ν_{max} ($CHCl_3$) 3600–2800 (OH), 3380 (NH), 1696 (CO_2H), 1648 (CONH), 1534 (amide II), 1452 (aryl C=C), 1280 cm^{-1} (C–O). δ(H) (60 MHz) 2.45 (s, $N(CH_3)_2$); 2.87 (m, CH_2NMe_2); 3.76 (m, CONHC*H*$_2$); 6.84–7.35 (m, H(3,4,6–8)); 7.72–7.93 (m, H(2)); 10.08 (s, NH) ppm; CO_2H not observed. *m/z* M not observed, 324 (1, M – H_2O), 256 (6, M – HN=CHCH$_2$NMe$_2$), 239 (5, 256 – HO), 227 (1, M – NHCH$_2$CH$_2$NMe$_2$–CO or 256 – H–CO), 211 (2, 239 – CO), 183 (1, 211 – CO), 155 (1, 183 – CO), 127 (3, 155 – CO), 71 (32, CH_2=CHNMe$_2$), 58 (100, CH_2NMe_2); and (ii) **22** (9 mg, 19%).

A solution of the crude product (0.10 g, 0.34 mmol) in MeOH (20 mL) and concentrated H_2SO_4 (0.5 mL) was heated under reflux for 6.25 h. Workup and chromatography on alumina (CH_2Cl_2/EtOH, 20:1) yielded methyl 9-[*N*-[2-(dimethylamino)ethyl]carboxamido]dibenzo[*b*,*e*][1,4]dioxin-1-carboxylate (**23**) (64 mg, 53%) which crystallized from CH_2Cl_2/hexanes as white crystals, m.p. 122–124 °C. Anal. Found: C, 63.7; H, 5.6; N, 7.9; $M^{+\cdot}$ 356.1356. $C_{19}H_{20}N_2O_5$ calc.: C, 64.0; H, 5.7; N, 7.9%; $M^{+\cdot}$ 356.1372). ν_{max}(KBr) 3225 (NH), 1710 (CO_2Me), 1650 (CONH),

1531 (amide II), 1450 (aryl C=C), 1290, 1265 cm^{-1} (C–O). δ(H) 2.32 (s, $N(CH_3)_2$); 2.65 (apparent t, $J = 7.1$ Hz, CH_2NMe_2); 3.67 (apparent q, $J = 6.8$, 6.6, 6.5 Hz, $CONHCH_2$); 3.87 (s, OCH_3); 6.90 (dd $J_{6,8} = 1.8$, $J_{6,7} = 7.9$ Hz, H(6)); 6.92 (apparent t, $J = 7.0$, 8.0 Hz, H(3)); 6.97 (t, $J = 8.0$ Hz, H(7)); 6.99 (dd, $J_{2,4} = 1.7$, $J_{3,4} = 8.0$ Hz, H(4)); 7.51 (dd $J_{2,4} = 1.7$, $J_{2,3}$ 7.9 Hz, H(2)); 7.84 (dd, $J_{6,8} = 1.7$, $J_{7,8} = 7.9$ Hz, H(8)); 9.03 (apparent t, $J = 5.2$ Hz, NH) ppm. δ(C) 37.9 ($CONHCH_2$); 45.3 ($N(CH_3)_2$); 52.2 (OCH_3); 58.3 (CH_2NMe_2); 117.5 (C(1)); 119.3 (C(6)); 120.9 (C(4)); 121.6 (C(9)); 123.6 (C(3)), 123.8 (C(8)); 125.8 (C(7)); 126.9 (C(2)); 139.9 (C(9a)); 141.3 (C(5a)); 142.0 (C(4a)); 142.3 (C(10a)); 162.9 (CONH); 164.2 (CO_2Me) ppm. m/z 356 (< 1, M), 354 (< 1, M – H_2), 286 (12, M – CH=$CHNMe_2$), 269 (4, 286 – NH_3), 239 (2, 269 – CH_2O), 120 (1, 239 – H–CO, or 269 – CH_3O–CO), 183 (1, 239 – 2CO), 71 (33, CH_2=$CHNMe_2$), 58 (100, CH_2NMe_2).

(c) *With phenyl isocyanate.* Butyllithium (1.83 mol L^{-1} in hexanes, 0.42 mL, 0.77 mmol) was added dropwise to a stirred solution of **1** (70 mg, 0.23 mmol) and TMEDA (0.2 mL, 1.33 mmol) in THF (1 mL) at −78 °C under N_2, and after 35 min, phenyl isocyanate (0.25 mL, 2.35 mmol) was added. Workup after 2.5 days followed by chromatography (PLC) yielded 9-(*N*-phenylcarboxamido)-*N*-[2-(dimethylamino)ethyl]dibenzo[*b*,*e*][1,4]dioxin-1-carboxamide (**24**) (43.5 mg, 44%) as a white solid, m.p. 222–225 °C. Anal. Found: $M^{+\cdot}$ 417.1701. $C_{24}H_{23}N_3O_4$ calc.: $M^{+\cdot}$ 417.1689. ν_{max}(KBr) 3325 (NH), 1642 (CO), 1523 (amide II), 1454 (aryl C=C), 1278 cm^{-1} (C–O). δ(H) (CD_3SOCD_3) 2.49 (s, $N(CH_3)_2$); 2.86 (br s, CH_2NMe_2); 3.38 (br s, $CONHCH_2$); 7.16 (m, H(3,4,4′,6,7)); 7.38 (apparent t, $J = 7.4$, 8.1 Hz, H(3′,5)); 7.42, $J_{2',3'} = 7.7$ Hz, H(2)); 7.47 (d, $J_{5',6'} = 7.3$ Hz, H(6′)); 7.76 (d, $J = 7.5$ Hz, H(2,8)); 8.59 (s, $CONHCH_2$); 10.50 (s, $CONHPh$) ppm. δ(C) (CD_3SOCD_3) 35.3 ($CONHCH_2$); 42.9 ($N(CH_3)_2$); 55.9 (CH_2NMe_2); 119.06 (C(4)*); 119.12 (C(6)*); 120.7 (C(2,6′)); 122.5 (C(1)#); 123.9 (C(9)#); 124.3 (C(2,4′)**); 124.5 (C(8)**); 124.7 (C(3)##); 125.4 (C(7)##); 128.8 (C(3′,5′)); 138.6 (C(1′)); 139.1 (C(10a)⊕); 139.4 (C(9a)⊕); 141.46 (C(4a)*); 141.53 (C(5a)*); 163.3 ($CONHCH_2$‡); 163.4 ($CONHPh$‡) ppm. m/z 417 (1, M), 416 (< 1, M – H), 415 (1, M – H_2), 373 (1, M – NMe_2), 359 (M – CH_2NMe_2), 347 (22, M – CH=$CHNMe_2$), 330 (6, M – $NHCH_2CH_2NMe_2$), 254 (7, 330 – C_6H_4), 236 (4, 254 – H_2O), 210 (6, 236 – CN), 182 (3, 210 – CO), 71 (55, CH_2=$CHNMe_2$), 58 (100, CH_2NMe_2).

(d) (i) *With chlorotrimethylsilane.* (i) Butyllithium (1.83 mol L^{-1} in hexane, 0.4 mL, 0.74 mmol) was added dropwise to a stirred solution of **1** (0.10 g, 0.34 mmol) in THF (5 mL) at −78 °C under N_2, and after 35 min chlorotrimethylsilane (0.21 mL, 1.68 mmol) was added. After 1 h the mixture was allowed to warm to room temperature, MeOH (0.14 mL, 3.35 mmol) was added to react with the excess of chlorotrimethylsilane, and the mixture was worked up. PLC (solvent A) yielded 9-trimethylsilyl-*N*-[2-(dimethylamino)ethyl]dibenzo[*b*,*e*][1,4]dioxin-1-carboxamide (**25**) (49 mg, 40%) which crystallized from Me_2CO/hexane as white needles, m.p. 166–169 °C. Anal. Found: C, 64.6; H, 7.3; N, 7.5. $C_{20}H_{26}N_2O_3Si$ calc.: C, 64.8; H, 7.1; N, 7.6%. ν_{max}(KBr) 3320 (NH), 1640 (CO), 1545 (amide II), 1465, 1425 (aryl C=C), 1270 (C–O), 1235, 830, 750 cm^{-1} ($SiMe_3$). δ(H) 0.34 (s, $Si(CH_3)_3$); 2.35 (s, $N(CH_3)_2$); 2.63 (apparent t, $J = 6.0$ Hz, CH_2NMe_2); 3.59 (apparent q, $J = 5.7$ Hz $CONHCH_2$); 6.65 (NH); 6.86 (dd, $J_{6,8} = 1.5$, $J_{6,7} = 7.8$ Hz, H(6)); 6.92 (m, H(3,4,7)); 6.98 (dd, $J_{7,8} = 7.2$ Hz, H(8)); 7.22 (dd, $J_{2,4} = 2.7$, $J_{2,3} = 6.5$ Hz, H(2)) ppm. δ(C) −1.1 ($Si(CH_3)_3$); 37.2 ($CONHCH_2$); 45.1 ($N(CH_3)_2$); 57.8 (CH_2NMe_2); 117.8 (C(6)); 118.3 (C(4)); 123.5 (C(2)); 123.9 (C(7)); 124.3 (C(3)); 124.6 (C(1)); 127.6

(C(9)); 129.3 (C(8)); 140.1 (C(10a)); 141.4 (C(4a)); 142.4 (C(5a)); 145.7 (C(9a)); 165.6 (CONH) ppm. *m/z* 370 (1%, M), 368 (1%, M − H_2), 355 (1, M − Me), 326 (1, M − NMe_2), 71 (39, CH_2=$CHNMe_2$), 58 (100, CH_2NMe_2); and (ii) *N*-[2-(dimethylamino)ethyl]dibenzo[*b*,*e*][1,4]dioxin-1-carboxamide (**26**) (61 mg, 55%) as a white solid. δ(H) (60 MHz) 2.69 (s, $^+NH(CH_3)_2$); 3.10 (2 lines, J_{obs} = 5.5 Hz, $CH_2NHMe_2^+$); 3.5 (apparent q, *J* = 5.5, 6.0, 5.5 Hz, CONHCH_2); 6.82–6.94 (m, H(3,4,6–9), $^+NHMe_2$); 7.58 (3 lines, J_{obs} = 4.5, 5.0 Hz, H(2)); 8.10 (s, CONH) ppm.

(ii) Chlorotrimethylsilane (23 μL, 0.18 mmol) was added dropwise to a solution of **1** (50 mg, 0.17 mmol) and TMEDA (56 μL, 0.37 mmol in THF (0.8 mL) at room temperature under N_2, the mixture was cooled to −78 °C, and butyllithium (2.0 mol L^{-1} in hexanes, 0.18 mL, 0.37 mmol) added dropwise with stirring. After 1.5 h the mixture was allowed to warm to room temperature for 1.5 h, MeOH (34 μL, 0.84 mmol) was added, followed by water, and then the mixture was shaken with CH_2Cl_2. Workup and chromatography (PLC) (solvent A) gave (i) 2-trimethylsilyl-*N*-2-[dimethylamino)dibenzo[*b*,*e*][1,4]dioxin-1-carboxamide (**27**) (9 mg, 15%) as a pale yellow oil. δ(H) 0.25 (s, $Si(CH_3)_3$); 2.38 (s, $N(CH_3)_2$); 2.68 (m, CH_2NMe_2); 3.60 (m, CONHCH_2); 6.84 (d, $J_{3,4}$ = 8.0 Hz, H(4)); 6.85 (m, H(6–9)); 7.02 (s, NH); 7.10 (d, $J_{3,4}$ = 8.0 Hz, H(3)) ppm. δ(C) 0.2 ($Si(CH_3)_3$); 37.0 (CONHCH_2); 44.9 ($N(CH_3)_2$); 75.5 (CH_2NMe_2); 116.4 (C(4)); 116.5 (C(9)*); 116.8 (C(6)*); 123.9 (C(8)#); 124.2 (C(7)#); 130.4 (C(3)) ppm; quaternary carbons not observed; and (ii) a mixture (^{1}H NMR) (36 mg) of **1** (*ca.* 27 mg, 54%) and **25** (*ca.* 9 mg, 14%) as a white oily solid.

(iii) Butyllithium (1.6 mol L^{-1} in hexanes, 0.18 mL, 0.29 mmol) was added dropwise to a stirred solution of **1** (71 mg, 0.24 mmol) and TMEDA (0.09 mL, 0.57 mmol) in THF (1.25 mL) at −78 °C under N_2 and after 15 min chlorotrimethylsilane (37 μL, 0.29 mmol) was added. A second aliquot of butyllithium was added after 15 min, and the mixture worked up and chromatographed (PLC) (solvent A) to yield 2,9-bis(trimethylsilyl)-*N*-[2-(dimethylamino)ethyl]dibenzo[*b*,*e*][1,4]dioxin-1-carboxamide (**28**) (10 mg, 9%) as a colourless oil. Anal. Found: $M^{+\cdot}$ 442.2104. $C_{23}H_{34}N_2O_3Si_2$ calc.: $M^{+\cdot}$ 442.2108. ν_{max}(film) 3350 (NH), 1650 (CO), 1575 (amide II), 1460 (aryl C=C), 1270 (C–O), 1225, 825, 745 cm^{-1} ($SiMe_3$). δ(H) 0.27 (s, 2-$Si(CH_3)_3$); 0.31 (s, 9-$Si(CH_3)_3$); 2.25 (s, $N(CH_3)_2$); 2.54 (apparent t, *J* = 5.9 Hz, C$H_2(CH_3)_2$; 3.52 (apparent q, *J* = 5.5, 5.5, 5.8 Hz, CONHCH_2); 6.56 (s, NH; 6.81, d, $J_{3,4}$ = 8.0 Hz, H(4)); 6.82 (dd $J_{6,8}$ = 1.9, $J_{6,7}$ = 7.9 Hz, H(6)); 6.87 (t, *J* = 7.5 Hz, H(7)); 6.94 (dd, $J_{6,8}$ = 1.8, $J_{7,8}$ = 7.2 Hz, H(8)); 7.05 (d, $J_{3,4}$ = 8.0 Hz, H(3)) ppm. δ(C) −1.15 (9-$Si(CH_3)_3$); −0.15 (2-$Si(CH_3)_3$); 37.0 (CONHCH_2); 45.0 ($N(CH_3)_2$); 57.0 (CH_2NMe_2); 116.1 (C(4)); 117.5 (C(6)); 123.8 (C(7)); 127.8 (C(9)); 129.9 (C(8)); 130.0 (C(3)); 131.7 (C(1)); 132.9 (C(2)); 139.1 (C(10a)); 141.0 (C(4a)); 142.7 (C(5a)); 146.0 (C(9a)); 167.0 (CONH) ppm. *m/z* 442 (< 1, M), 427 (5, M − CH_3), 71 (21, CH_2=$CHNMe_2$), 58 (100, CH_2NMe_2); and a mixture (^{1}H NMR) (17 mg) of **25** (*ca.* 10 mg, 11%) and **13** (*ca.* 7 mg, 10%).

(iv) Butyllithium (2.0 mol L^{-1} in hexanes, 0.18 mL, 0.37 mmol) was added dropwise with stirring to a solution of 2,2,6,6-tetramethylpiperidine (62 μL, 0.37 mmol) in THF (1.25 mL) at −78 °C under nitrogen. After 30 min, $(CH_3)_3SiCl$ (0.21 mL, 1.68 mmol) was added, followed by a solution of the amide **1** (50 mg, 0.17 mmol) in THF (1.5 mL). The cooling bath was removed after 1 h and the mixture was allowed to warm to room temperature. After 1.25 h, workup gave the 9-silyl derivative **25** (37 mg, 60%) and the starting amide **1** (6.5 mg, 13%).

(e) *With t-butylchlorodimethylsilane.* Butyllithium (2.0 mol L^{-1} in hexanes, 0.18 mL, 0.37 mmol) was added dropwise to a stirred solution of **1** (0.10 g, 0.34 mmol) and TMEDA (0.11 mL, 0.74 mmol) in THF (1.6 mL) at −78 °C under N_2. After 15 min a cooled solution of t-butylchlorodimethylsilane (1.64 mol L^{-1} in THF, 0.22 ml, 0.36 mmol) was added, followed after 15 min by a second aliquot of butyllithium. DMF (0.10 mL, 1.29 mmol) was added after 30 min and after a further 30 min the mixture was worked up. PLC (solvent A) gave (i) 2-(t-butyldimethylsilyl)-*N*-[2-(dimethylamino)ethyl]dibenzo[*b*,*e*][1,4]dioxin-1-carboxamide (**29**) (82 mg, 59%) as a colourless oil, b.p. (Kugelrohr) 145–155 °C/0.07 mmHg. Anal. Found: C, 66.8; H, 7.9; N, 6.8; $M^{+\cdot}$-Me 397.1944. $C_{23}H_{32}N_2O_3Si$ calc.: C, 67.0; H, 7.8; N, 6.8%; $M^{+\cdot}$-Me 397.1947. $\nu_{max}(CHCl_3)$ 3375 (NH), 1655 (CO), 1580 (aryl C=C), 1508 (amide II), 1494, 1467 (aryl C=C), 1285 (C–O), 1250 ($SiMe_2$), 832 (aromatic), 815 cm^{-1} ($SiMe_2$). δ(H) 0.22 (s, $Si(CH_3)_2$); 0.88 (s, $C(CH_3)_3$); 2.22 (s, $N(CH_3)_2$); 2.51 (apparent t, $J = 5.9$ Hz, CH_2NMe_2); 3.49 (apparent q, $J = 5.7$, 6.6, 6.6 Hz, $CONHCH_2$); 6.40 (s, NH); 6.80 (d, $J_{3,4} = 8.0$ Hz, H(4)); 6.81 (m, H(6–9)); 7.03 (d, $J_{3,4} = 8.1$ Hz, H(3)) ppm. δ(C) 4.5 ($Si(CH_3)_2$); 17.5 ($C(CH_3)_3$); 27.1 ($C(CH_3)_3$); 37.1 ($CONHCH_2$); 44.9 ($N(CH_3)_2$); 57.3 (CH_2NMe_2); 115.8 (C(4)); 116.3 (C(9)*, 116.5, C(6)*); 123.86 (C(8)#); 123.92 (C(7)#); 130.9 (C(1)); 131.7 (C(3)); 132.0 (C(2)); 138.7 (C(10a)); 141.8 (C(4a)); 142.1 (C(9a)**); 142.5 (C(5a)**), 166.9 (CONH) ppm. *m/z* M not observed, 410 (< 1, $M - H_2$), 397 (1, $M - CH_3$); 355 (17, $M - C_4H_9$), 269 (13, 355 − $HN{=}CHCH_2NMe_2$), 72 (61, $CH_2CH_2NMe_2$), 58 (100, CH_2NMe_2); and (ii) **2** (13 mg, 13%).

Reaction in the absence of DMF gave the same products.

*Reactions of lithiated 2-(t-butyldimethylsilyl)-*N*-[2-(dimethylamino)ethyl]dibenzo [b,e][1,4]dioxin-1-carboxamide (29)*

(a) *With DMF.* s-Butyllithium (0.95 mol L^{-1}, 0.29 mL, 0.27 mmol) was added dropwise to a stirred solution of **29** (37 mg, 0.09 mmol) and TMEDA (41 μL, 0.27 mmol) in THF (0.65 mL) at −78 °C under N_2. After 1.25 h DMF (70 μL, 0.90 mmol) was added, and after a further 30 min the mixture was worked up. PLC (solvent A) afforded (i) 2-(t-butyldimethylsilyl)-*N*-[2-(dimethylamino)ethyl]-6-formyldibenzo[*b*,*e*][1,4]dioxin-1-carboxamide (**41**) (6 mg, 16%) as a colourless oil. Anal. Found: $M^{+\cdot}$-C_4H_9 383.1390. $C_{24}H_{32}N_2O_4Si$ calc.: $M^{+\cdot}$-C_4H_9 383.1427). $\nu_{max}(CHCl_3)$ 3410 (NH), 1685 (CHO), 1655 (CONH), 1585 (aryl C=C), 1509 (amide II), 1465 (aryl C=C), 1282 (C–O), 1244, 815 cm^{-1} ($SiMe_2$). δ(H) 0.23 (s, $Si(CH_3)_2$); 0.89 (s, $C(CH_3)_3$); 2.32 (s, $N(CH_3)_2$); 2.65 (m, $CH_2N(CH_3)_2$); 3.58 (m, $CONHCH_2$); 6.85 (d, $J_{3,4} = 8.1$ Hz, H(4)); 16.96 (apparent t, $J = 8.0$, 7.3 Hz, H(8)); 7.05 (dd, $J_{obs} = 1.7$, 1.4, $J_{8,9} = 7.9$ Hz, H(9)); 7.12, d, $J_{3,4} = 8.1$ Hz, H(3)); 7.38 (dd $J_{7,9} = 1.6$, $J_{7,8} = 7.8$ Hz, H(7)); 7.50 (s, NH); 10.27 (s, CHO) ppm. *m/z* M not observed, 412 (1, $M - CH_3$), 409 (< 1, $M - CH_3$–3H), 397 (1, 425 − CO), 383 (5, $M - C_4H_9$), 355 (11, 383 − CO), 72 (38, $CH_2CH_2NMe_2$), 58 (100, CH_2NMe_2); and (ii) 2-(t-butyldimethylsilyl)-*N*-[2-(dimethylamino)ethyl]-9-formyldibenzo[*b*,*e*][1,4]dioxin-1-carboxamide (**30**) (12 mg, 31%) as a colourless oil. Anal. Found: 424. $M^{+\cdot}$-CH_3–H 1770; $M^{+\cdot}$-$2CH_3$–H 409.1547. $C_{24}H_{32}N_2O_4Si$ calc.: $M^{+\cdot}$-CH_3–H 424.1818, $M^{+\cdot}$-$2CH_3$–H, 409.1584). $\nu_{max}(CHCl_3)$ 3375 (NH), 1690 (CHO), 1655 (CONH), 1585 (aryl C=C), 1517 (amide II), 1465 (aryl C=C), 1282 (C–O), 1242, 815 cm^{-1} ($SiMe_2$). δ(H) 0.35 (s, $Si(CH_3)_2$); 0.90 (s, $C(CH_3)_3$); 2.40 (s, $N(CH_3)_2$); 2.71 (m, CH_2NMe_2); 3.65 (m, $CONHCH_2$); 6.87 (d, $J_{3,4} = 8.2$ Hz, H(4)); 6.98 (t, $J = 7.9$ Hz, H(7)); 7.06

(dd, $J_{6,8}$ = 1.7, $J_{6,7}$ = 7.9 Hz, H(6)); 7.11 (d, $J_{3,4}$ = 8.2 Hz, H(3)); 7.39 (dd, $J_{6,8}$ = 1.6, $J_{7,8}$ = 7.8 Hz, H(8)); 7.50 (s, NH); 10.23 (s, CHO) ppm. δ(C) −3.3 ($(Si(CH_3)_2$); 19.3 (CMe_3); 26.6 ($C(CH_3)_3$); 36.8 ($CONHCH_2$); 44.9 ($N(CH_3)_2$); 58.1 (CH_2NMe_2); 116.7 (C(4)); 121.9 (C(6)); 123.5 (C(7)); 123.8 (C(8)); 124.1 (C(9)); 130.7 (C(1)); 132.0 (C(3)); 133.3 (C(2)); 138.4 (C(10a)); 142.2 (C(4a)); 142.5 (C(5a)); 144.2 (C(9a)); 167.1 (CONH); 187.8 (CHO) ppm. *m/z* M not observed, 424 (3, M − Me−H)); 142.5 (C(5a)); 144.2 (C(9a)); 167.1 (CONH); 187.8 (CHO) ppm. *m/z* M not observed, 424 (3, M − Me−H), 409 (3, 424 − Me), 354 (15, M − C_4H_9−H−CO), 71 (20, CH_2=$CHNMe_2$), 58 (100, CH_2NMe_2).

(b) *With CO_2.* t-Butyllithium (1.03 mol L^{-1} in pentane, 0.47 mL, 0.48 mmol) was added dropwise to a stirred solution of **29** (90 mg, 0.22 mmol) and TMEDA (72 μL, 0.48 mmol) in THF (1.5 mL) at −78 °C under N_2 and after 1 h CO_2 was bubbled into the solution for 5 min. After 16 h, the mixture was worked up to yield a mixture (1.5 : 1) (^{1}H NMR) of 8-(t-butyldimethylsilyl)-9-[*N*-[2-(dimethylamino)ethyl]carboxamido]dibenzo[*b*,*e*][1,4]dioxin-1-carboxylic acid (**31**) and 7-(t-butyldimethylsilyl)-6-[*N*-[2]-(dimethylamino]carboxamido]dibenzo[*b*,*e*][1,4]dioxin-1-carboxylic acid (**42**), as a yellow oil (53.5 mg, 54%). PLC on neutral alumina (solvent A) gave a colourless oil. Anal. Found: M^+-C_4H_9 399.1373. $C_{24}H_{32}N_2O_5Si$ calc.: M^+-C_4H_9 399.1376. ν_{max}($CHCl_3$) 3425 (OH, NH), 1645 (CO_2H), 1635 (CONH), 1615, 1580, 1556 (aryl C=C), 1520 (amide II), 1455 (aryl C=C), 1275 (C−O), 1260, 810 cm^{-1} ($SiMe_2$). δ(H) (**31**): 0.14 (s, $Si(CH_3)_2$); 0.84 (s, $C(CH_3)_3$); 2.26 (s, $N(CH_3)_2$); 2.52 (br s, CH_2NMe_2); 3.45 (br s, $CONHCH_2$); 6.67 (br s, H(3,6)); 6.79 (d, $J_{3,4}$ = 7.9 Hz, H(4)); 7.09 (d, $J_{2,3}$ = 7.9 Hz, H(2)); 7.30 (br s H(7)); 8.56 (s, NH) ppm; CO_2H not observed; and (**42**): 0.29 (s, $Si(CH_3)_2$); 0.84 (s, $C(CH_3)_3$); 2.31 (s, $N(CH_3)_2$); 2.64 (br s, CH_2NMe_2); 3.55 (br s, $CONHCH_2$); 6.67 (br s, H(3,9)); 6.74, d, $J_{3,4}$ = 8.0 Hz, H(4)); 7.03 (d, $J_{2,3}$ = 8.0 Hz, H(2)); 7.22 (br s, H(8)); 7.76 (s, NH) ppm; CO_2H not observed. δ(C) (**31**): −3.5 ($Si(CH_3)_2$); 19.7 (CMe_3); 27.1 ($C(CH_3)_3$); 36.9 ($CONHCH_2$); 44.3 ($N(CH_3)_2$); 57.8 (CH_2NMe_2); 116.1 (C(6)): 117.0 (C(4)); 123.2 (C(1,3)); 126.0 (C(2)); 128.3 (C(9)); 131.3 (C(7)); 133.9 (C(8)); 139.4 (C(9a)); 140.3 (C(5a)); 141.8 (C(4a)); 142.9 (C(10a)); 167.7 (CONH); 170.9 (CO_2H); and (**42**): −2.8 ($Si(CH_3)_2$); 17.7 ($C(CH_3)_3$); 17.5 ($C(CH_3)_3$); 36.7 ($CONHCH_2$); 44.2 ($N(CH_3)_2$); 57.3 (CH_2NMe_2); 117.0 (C(9)); 117.3 (C(4)); 123.1 (C(3)); 125.4 (C(2)); 127.1 (C(1)); 130.3 (C(6)); 131.9 (C(8)); 132.2 (C(7)); 140.1 (C(5a); 140.2 (C(9a)); 142.0 (C(4a)); 142.6 (C(10a)); 167.4 (CONH); 170.9 (CO_2H) ppm. *m/z* M not observed, 441 (3, M − Me), 399 (26, M − C_4H_9), 370 (13, 399 − CHO), 72 (35, $CH_2CH_2NMe_2$), 58 (100, CH_2NMe_2).

Bromination of dibenzo[b,e][1,4]dioxin (2)

A solution of *N*-bromosuccinimide (0.19 g, 1.09 mmol) in DMF [42] (5.5 mL) was added dropwise to a stirred solution of **2** (0.20 g, 1.09 mmol) in DMF (5.5 mL). The solution was allowed to stand for 1 h and re-treated with NBS (0.12 g, 0.65 mmol) in DMF (3 mL). After 72 h workup and chromatography gave an inseparable mixture (1.9 : 1.0 : 0.19 : 0.13) (^{13}C NMR) of **32**, 2,8-dibromodibenzo[*b*,*e*][1,4]dioxin (**33**), and 2,7-dibromodibenzo[*b*,*e*][1,4]dioxin (**43**) as a white solid (0.20 g). δ(H) (**32**): 6.62 (d, $J_{3,4}$ = 8.1 Hz, H(4)); 6.78 (m, H(7,8)); 6.83 (m, H(6,9)); 6.90 (s, H(1)); 6.91 (dd, $J_{1,3}$ = 2.3, $J_{3,4}$ = 8.0 Hz, H(3)) ppm. δ(C) (**32**): 115.2 (C(2)); 116.37 (C(6)*); 116.40 (C(9)*); 117.5 (C(4)); 119.5 (C(1)); 124.0 (C(7)#); 124.1 (C(8)#); 126.5 (C(3)); 141.4 (C(4a)); 141.5 (C(5a)**); 141.7 (C(9a)**); 142.8 (C(10a)) ppm.

(**33**): 117.6 (C(4,6)); 119.6 (C(1,9)); 126.9 (C(3,7)) ppm; quaternary carbons not observed. (**43**): 117.6 (C(4,9)); 119.5 (C(1,6)); 126.8 (C(3)) ppm; quaternary carbons not observed. *m/z* (**32**): 264, 262 (50, M), 155 (22, M − Br–CO); 127 (21, 155 − CO); and (**33**) and (**43**): 344, 342, 340 (10, 20, 10, M).

*Metal-halogen exchange and quenching of 2-bromodibenzo[*b,e*][1,4]dioxin (32)*

(a) *With chlorotrimethylsilane.* Butyllithium (2.0 mol L^{-1} in hexanes, 0.19 mL, 0.38 mmol) was added dropwise to a stirred mixture of **32**, **2**, and the dibromodibenzodioxins **33** and **43** (2.3 : 1.0 : 0.37 : 0.30) (0.11 g, *ca.* 0.24 mmol **32**) in THF (1.5 mL) at −78 °C under N_2. After 7 min, chlorotrimethylsilane (0.40 mL, 3.13 mmol) was added. After a further 60 min the mixture was worked up and the crude product was heated at 70–80 °C/0.1 mmHg (Kugelrohr) to distil out the more volatile dibenzodioxin contaminants and leave a residue of 2-trimethylsilyldibenzo [*b,e*][1,4]dioxin (**34**) (53 mg, 87%) as a white waxy solid, m.p. 55–59 °C. ν_{max}(KBr) 1580, 1490, 1458 (aryl C=C), 1280 (C–O), 1240, 830 ($SiMe_3$), 815 (aromatic), 745 ($SiMe_3$), 740 cm^{-1} (aromatic). δ(H) 0.22 (s, $Si(CH_3)_3$); 6.82 (d, $J_{3,4}$ = 7.9 Hz, H(4)); 6.85 (m, H(6–9)); 6.96 (d, $J_{1,3}$ = 1.4 Hz, $J_{3,4}$ = 7.8 Hz, H(3)) ppm. δ(C) −1.2 ($Si(CH_3)_3$); 116.0 (C(4)), 116.4 (C(6,9)); 120.9 (C(1)); 123.6 (C(8)*); 123.8 (C(7)*); 128.9 (C(3)); 136.1 (C(2)); 141.7 (C(10a)); 142.2 (C(4a)); 142.4 (C(9a)#); 142.7 (C(5a)#) ppm. *m/z* 256 (60%, M), 241 (100, M − Me).

(b) *With-t-butylchlorodimethylsilane.* Repetition of (a) using a mixture (1.90 : 1.00 : 0.19 : 0.13) of 2-bromodibenzodioxin (**32**), **2**, **33**, and **43** and t-butylchlorodimethylsilane gave mainly **2** which was sublimed out, leaving a yellow oil (14 mg) which was a mixture (2 : 1) (^{13}C NMR) of 2-butyl-8-(t-butyldimethylsiloxy)dibenzo[*b,e*][1,4]dioxin (**35**) and 2-butyl-7-(t-butyldimethylsiloxy)dibenzo [*b,e*][1,4]dioxin (**44**), b.p. (Kugelrohr) 85–90 °C/0.08 mmHg. Anal. Found: C, 71.0; H, 7.6. $C_{22}H_{30}O_3Si$ calc.: C, 71.3; H, 8.2%. ν_{max}($CHCl_3$) 1585, 1492 (aryl C=C), 1285 (C–O), 1250, 830 cm^{-1} ($SiMe_2$). δ(H) (**35**); 0.16 (s, $Si(CH_3)_2$); 0.93 (m, CH_2CH_3); 0.95 (s, $C(CH_3)_3$); 1.23 (br s, $CH_2CH_2CH_2$); 6.35 (d, $J_{6,7}$ = 7.8 Hz, H(7)); 6.36 (s, H(9)); 6.79 ($J_{6,7}$ = 7.9 Hz, H(6)); 6.84 (m, H(1,3,4)) ppm. δ(C) (**35**): −4.5 ($Si(CH_3)_2$); 13.9 (CH_2CH_2); 18.2 ($C(CH_3)_3$); 18.9 ($CH_2CH_2CH_3$); 25.6 ($C(CH_3)_3$); 29.7 ($CH_2CH_2CH_3$); 41.0 (CH_2CH_2); 108.4 (C(9)); 114.7 (C(7)); 116.3 (C(1,4)); 116.3 (C(6)); 123.8 (C(3)); 136.54 (C(5a)); 140.9 (C(2)); 142.1 (C(4a)); 142.2 (C(10a)); 142.3 (C(9a)); 151.6 (C(8)) ppm. *m/z* 370 (1, M), 314 (50, M − C_4H_8), 257 (100, 314 − C_4H_9).

*Acyl-desilylation of 2-trimethylsilyldibenzo[*b,e*][1,4]dioxin (34)*

A mixture of **34** (26 mg, 0.10 mol) and resublimed $AlCl_3$ (27 mg, 0.20 mmol) was cooled to 0 °C, and acetyl chloride (7 μL, 0.10 mmol) was added. After heating under reflux for 1 h the mixture was cooled and worked up. PLC (CH_2Cl_2/hexanes, 1 : 1) gave (i) **2** (10 mg, 56%), and (ii) 2-acetyldibenzo[*b,e*][1,4]dioxin [38] (8 mg, 36%) as white crystals, m.p. 129–132 °C. ν_{max}(KBr) 1670 (C=O), 1590, 1497, 1427 (aryl C=C), 1300 (C–O), 752 cm^{-1} (aromatic). δ(H) 2.53 (s, CH_3); 6.90 (m, H(4)), H(6–9)); 7.45 (d, $J_{1,3}$ = 2.0 Hz, H(1)); 7.53 (dd, $J_{1,3}$ = 2.0, $J_{3,4}$ = 8.4 Hz, H(3)) ppm. δ(C) 26.4 (CH_3); 116.3 (C(1)*); 116.45 (C(4)*); 116.51 (C(9)#); 116.53 (C(6)#); 124.1 (C(3)); 124.6 (C(8)**); 124.9 (C(7)**); 133.3 (C(2)); 141.4 (C(10a)); 141.7 (C(9a)##); 142.1 (C(5a)##); 146.2 (C(4a)); 196.0 (CO) ppm. *m/z* 226 (76, M), 211 (100, M − Me), 183 (46, 211 − CO), 155 (4, 183 − CO), 127 (16, 155 − CO).

Reaction of lithiated N-*[2-(dimethylamino)ethyl]dibenzo[*b,e*][1,4]dioxin-2-carboxamide (11) with DMF*

Butyllithium (1.47 mol^{-1} in hexanes, 0.15 mL, 0.20 mmol) was added dropwise to a stirred solution of **11** (30 mg, 0.10 mmol) in THF (2.5 mL) at −78 °C under N_2, and after 25 min DMF (30 μL, 0.39 mmol) was added. After 1 h the mixture was allowed to warm to room temperature and worked up. PLC (solvent A) gave 2-[2-(dimethylamino)ethyl]-3-hydroxy-1*H*-[[1,4]dibenzodioxino][2,3-*e*]isoindol-1-one (**73**) (18 mg, 54%) which crystallized from CH_2Cl_2/hexanes as white crystals, m.p. 170–171 °C. Anal. Found: C, 66.0; H, 5.3; N, 8.5; $M^{+\cdot}$ 326.1262. $C_{18}H_{18}N_2O_4$ calc.: C, 66.3; H, 5.6; N, 8.6%; $M^{+\cdot}$ 326.1267). ν_{max}(KBr) 3450 (OH), 1600 (CO), 1484 (aryl C=C), 1295, 1285 (C–O), 745 cm^{-1} (aromatic). δ(H) 2.45 (s, $N(CH_3)_2$); 2.57 (br d, $J = 13.3$ Hz, $(CH_aH_b)NMe_2$)); 2.81 (7 lines, $J_{obs} = 2.7$, 10.8, 13.4 Hz, $(CH_aH_b)NMe_2$); 3.28 (ddd, $J = 2.3$, 10.9, 15.1 Hz, $N(CH_aH_b)$); 4.27 (ddd, $J = 2.9$, 3.8, 15.2 Hz, $N(CH_aH_b)$); 5.85 (s, CHOH); 6.92 (m overlapping with d, $J_{10,11} = 8.1$ Hz, H(10, 5–8)); 7.32 (d, $J_{10,11} = 8.0$ Hz, H(11)) ppm; OH not observed. δ(C) 39.8 ($N(CH_aH_b)$); 44.5 ($N(CH_3)_2$); 58.6 ($(CH_aH_b)NMe_2$); 80.8 (CHOH); 116.6 (C(5)*); 116.9 (C(8)*); 117.8 (C(10)); 119.1 (C(11)); 124.3 (C(6)#); 124.4 (C(7)#); 127.5 (C(3a)); 130.7 (C(11a)); 138.0 (C(3b)); 141.4 (C(4a)**); 141.5 (C(8a)**); 145.6 (C(9a)); 166.6 (CON) ppm. *m/z* 326 (2, M), 329 (1, $M - NHCH_2CH_2NMe_2$), 211 (1, 239 − CO), 183 (1, 211 − CO), 155 (1, 183 − CO), 127 (2, 155 − CO), 71 (10, $CH_2{=}CHNMe_2$), 58 (100, CH_2NMe_2); and **11** (2 mg, 5%).

*Reaction of lithiated 2-[2-(dimethylamino)ethyl]-3-hydroxy-1*H*-[[1,4]benzodioxino][2,3-*e*]isoindol-1-one (73) with DMF*

Butyllithium (1.83 mol L^{-1} in hexanes, 0.12 mL, 0.22 mmol) was added dropwise to a stirred suspension of **73** (33 mg, 0.10 mmol) in THF (1.5 mL) at −78 °C under N_2. After 30 min DMF (50 μL, 0.65 mmol) was added. After a further 20 min the mixture was worked up. PLC (solvent A) yielded *N*-[2-(dimethylamino)ethyl]-1-(hydroxypentyl)dibenzo[*b,e*][1,4]dioxin-2-carboxamide (**36**) (7 mg, 18%) as a colourless oil. Anal. Found: $M^{+\cdot}$-H_2O 366.1916. $C_{22}H_{28}N_2O_4$ calc.: $M^{+\cdot}$-H_2O 366.1943). ν_{max}($CHCl_3$) 3650 (OH), 3325 (NH), 1680 (CO), 1508 (amide II), 1485 (aryl C=C), 1285 cm^{-1} (C–O). δ(H) 0.81 (t, $J = 7.3$ Hz, CH_2CH_3); 1.25 (m, $CH_2CH_2CH_3$); 1.95 (m, $CH(OH)CH_2$); 2.51 (s, $N(CH_3)_2$); 2.83 (m, CH_2NMe_2); 3.25 (m, $CONHCH_2$); 4.65 (m, CHOH); 6.88 (d, $J_{3,4} = 8.1$ Hz, H(4)); 6.93 (m, H(6–9), NH); 6.98 (d, $J_{3,4} = 8.0$ Hz, H(3)) ppm. δ(C) 13.9 (CH_2CH_3); 22.6 ($CH_2CH_2CH_3$); 24.3 ($CH_2CH_2CH_2$); 30.3 ($CH(OH)CH_2$); 37.0 ($CONHCH_2$); 44.8 ($N(CH_3)_2$); 56.4 (CH_2NMe_2); 59.0 (CHOH); 116.3 (C(9)*); 116.8 (C(6)*); 117.3 (C(4)); 119.4 (C(1), C(3)); 124.2 (C(8)*); 124.4 (C(7)#); 139.6 (C(2)); 141.5 (C(10a)); 141.6 (C(9a)**); 141.7 (C(5a)**); 141.8 (C(4a)); 166.4 (CONH) ppm. *m/z* M not observed, 366 (10, $M - H_2O$), 296 (6, $366 - C_5H_{10}$ or $366 - CH{=}CHNMe_2$), 252 (6, $296 - NMe_2$ or $296 - C_3H_8$), 71 (26, $CH_2{=}CHNMe_2$), 58 (100, CH_2NMe_2); and **73** (7 mg, 21%).

Reaction of lithiated N-*[3-(dimethylamino)propyl]dibenzo[*b,e*][1,4]dioxin-2-carboxamide (14) with DMF*

Butyllithium (1.7 mol L^{-1} in hexanes, 0.15 mL, 0.26 mmol) was added dropwise to a stirred solution of **14** (37 mg, 0.12 mmol) in THF (3 mL) at −78 °C under N_2. DMF (12 μL, 0.15 mmol) was added after 3.5 h, and after a further 30 min workup

and PLC (CH_2Cl_2/EtOH/Et_3N, 100:7:1) gave 2-[3-(dimethylamino)propyl]-3-hydroxy-1*H*-[[1,4]benzodioxino][2,3-*e*]isoindol-1-one (**74**) (20 mg, 49%) which crystallized from CH_2Cl_2/hexanes as white crystals, m.p. 157–158 °C. Anal. Found: C, 66.9; H, 5.8; N, 8.3. $C_{19}H_{20}N_2O_4$ calc.: C, 67.1; H, 5.9; N, 8.2%. ν_{max}($CHCl_3$) 3375 (OH), 1692 (CO), 1488 (aryl C=C), 1295, 1288 (C–O), 760 cm^{-1} (aromatic). δ(H) 1.72 (m, $N(CH_aH_b)(CH_aH_b)$); 2.13 (s, $N(CH_3)_2$); 2.25 (m, $N(CH_aH_b)(CH_aH_b)$); 2.48 (apparent t, J = 6.2, 5.6 Hz, $(CH_aH_b)NMe_2$); 3.26 (7 lines, J_{obs} = 3.8, 10.2, 14.2 Hz, $N(CH_aH_b)$); 3.92 (apparent dt, J = 4.9, 14.2 Hz, (CH_aH_b)); 5.81 (s, CHOH); 6.87 (m overlapping d, $J_{10,11}$ = 8.0 Hz, H(10,5–8)); 7.27 (d, $J_{10,11}$ = 8.0 Hz, H(11)) ppm; OH not observed. δ(H) 24.3 ($N(CH_aH_b)(CH_aH_b)$); 40.6 ($N(CH_aH_b)$); 44.0 ($N(CH_3)_2$); 57.1 ($(CH_aH_b)NMe_2$); 81.8 (CHOH); 116.5 (C(5)*); 117.0 (C(8)*); 117.6 (C(10)); 118.6 (C(11)); 124.27 (C(6)#); 124.31 (C(7)#); 127.9 (C(3a)); 131.9 (C(11a)); 138.0 (C(3b)); 141.5 (C(4a)**); 141.6 (C(8a)**); 145.4 (C(9a)); 166.8 (CON) ppm. m/z 340 (52, M), 240 (9, M – $HN{=}CHCH_2CH_2NMe_2$), 239 (15, M – $NH(CH_2)_3NMe_2$), 211 (8, 239 – CO), 183 (5, 211 – CO), 127 (7, 183 – CO), 86 (20, $(CH_2)_3NMe_2$), 72 (23, $CH_2CH_2NMe_2$), 58 (100, CH_2NMe_2).

N,N-*bis[2-(Dimethylamino)ethyl]dibenzo[*b,e*][1,4]dioxin-1,9-dicarboxamide (38)*

A mixture of the amide-ester **23** (10 mg, 0.05 mmol) and *N,N*-dimethyl-1,2-ethanediamine (100 μL, 0.91 mmol) was heated in a vial at *ca.* 110 °C for 5 h. Removal of excess amine and chromatography on alumina (CH_2Cl_2/EtOH, 10:1) gave *N,N*-bis[2-(dimethylamino)ethyl]dibenzo[*b,e*][1,4]dioxin-1,9-dicarboxamide (**38**) (7 mg, 44%) which crystallized from Me_2CO/hexanes as white crystals, m.p. 183–185 °C. Anal. Found: $M^{+\cdot}$ 412.2108. $C_{22}H_{28}N_4O_4$ calc.: $M^{+\cdot}$ 412.2111). ν_{max}(KBr) 3375 (NH), 1642 (CO), 1530 (amide II), 1450 (aryl C=C), 1280 cm^{-1} (C–O). δ(H) 2.30 (s, 2x$N(CH_3)_2$); 2.59 (apparent t, J = 6.5 Hz, 2xCH_2NMe_2); 3.59 (apparent q, 6.3, 5.6, 6.3 Hz, 2xCONHCH_2); 6.98 (m, H(3,4,6,7)); 7.45 (dd, J = 2.4, 7.0 Hz, H(2,8)); 7.74 (s, 2xNH) ppm. δ(C) 37.7 (2xNHCH_2); 45.4 (2x$N(CH_3)_2$); 58.0 (2xCH_2NMe_2); 119.0 (C(4,6)); 122.9 (C(1,9)); 123.9 (C(2,8)); 124.6 (C(3,7)); 140.2 (C(9a,10a)); 142.3 (C(4a,5a)); 164.4 (2xCONH) ppm. m/z 412 (< 1, M), 410 (< 1, M – H_2), 408 (< 1, 410 – H_2), 271 (5, M – $CH_2{=}CHNMe_2$–$CH{=}CHNMe_2$), 239 (3, M – $NHCH_2CH_2NMe_2$–$HN{=}CHCH_2NMe_2$), 71 (23, $CH_2{=}CHNMe_2$), 58 (100, CH_2NMe_2), 44 (NMe_2).

The bisamide **38** was also prepared (23%) by treatment of the diester **18** with *N,N*-dimethyl-1,2-ethanediamine as above.

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