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Addition of Silyloxydienes to 2-Substituted 1,4-Benzoquinones and 1,4-Naphthoquinones

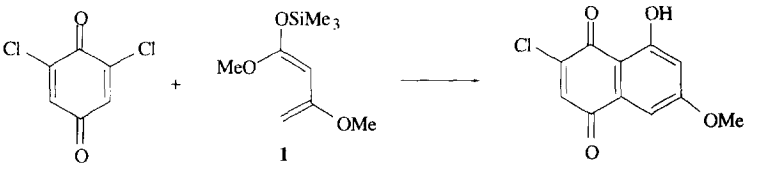
Margaret A. Brimble* **and Richard J. R. Elliott**

School of Chemistry, University of Sydney, NSW 2006, Australia

Abstract: Addition of 1-trimethylsilyloxybuta-1,3-diene **2** to the quinones **4,5,6,17,18,19,20** bearing formyl, acetyl, methoxycarbonyl or carboxamide substituents at C-2, afforded the Diels-Alder adducts **11,12,13,25,26,27,28** whereas addition of 2-trimethylsilyloxyfuran **3** afforded the fragmentation products **29,30,31,35,36,37,38**. Quinones **7,21** bearing a carboxyl group at C-2 afforded 1,4-naphthoquinone and 9,10-anthracenedione with **2** and no adducts were isolated from reaction with **3**. Benzoquinone-sulfide **8** afforded Diels-Alder adduct **14** and fragmentation product **32** with **2** and **3** respectively whereby reaction occurred on the less substituted double bond. No adducts were isolated upon treatment of naphthoquinone-sulfide **22** with either **2** or **3**. The Diels-Alder adducts of benzoquinone-sulfoxide **9** and naphthoquinone-sulfoxide **23** with **2** underwent facile aromatisation to 1,4-naphthoquinone and 9,10-anthracenedione with **2**. Addition of **3** to **9** afforded fragmentation product **33** whereas analogous reaction with **23** was unsuccessful. Addition of dienes **2,3** to benzoquinone-sulfone **10** afforded fragmentation products **16,34** respectively, whereas naphthoquinone-sulfone **24** afforded 9,10-anthracendione with **2** and no products with **3**. © 1997 Elsevier Science Ltd.

INTRODUCTION

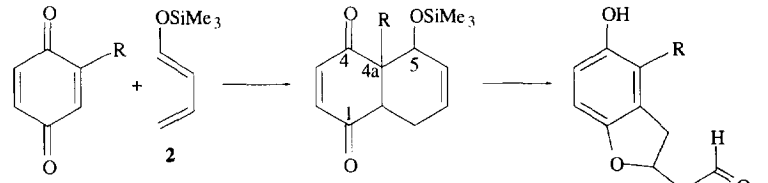
The Diels-Alder addition of silyloxydienes e.g **1** to benzoquinones and naphthoquinones has provided an efficient synthesis of oxygenated naphthoquinones and anthraquinones (Scheme 1[1]). This methodology has been elegantly used in the synthesis of natural products, examples of which include the synthesis of the ansamycin antibiotic, awamycin[2] and a derivative of an aphid pigment, quinone A.[3] In these cases the initial Diels-Alder adduct undergoes aromatization and the regiochemistry of the addition can be rationalized in terms of frontier orbital interactions. Introduction of a halogen onto the quinonoid dienophile is also effective in controlling the regiochemical outcome in that the nucleophilic end of an electron rich diene will add to the unsubstituted carbon of the quinone.[4,5,6]



Scheme 1

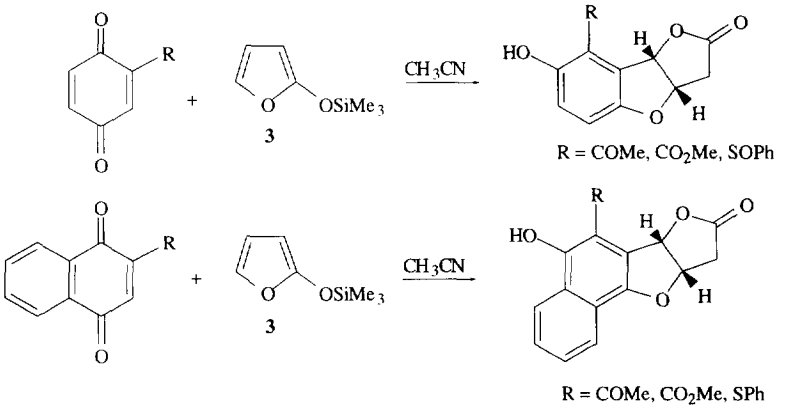
If the aromatisation step is prevented the oxygen functionality introduced in the initial Diels-Alder adducts can also be utilised. Moreover, in cases where 1,4-benzoquinones bearing electron withdrawing substituents at C-2 have been used, the Diels-Alder adducts can undergo selective fragmentation of the C-4a,5 bond affording a Michael acceptor which is then trapped by an incumbent hydroxyl group to afford dihydrobenzofurans (Scheme 2).[7,8,9] Despite the obvious synthetic potential of this transformation, only limited examples of its use in the synthesis of naturally occurring pyranonaphthoquinones,[10] Amaryllidaceae alkaloids,[11] and hexahydrodibenzofurans[12] have been reported.

Whilst a two step process namely the formation of Diels-Alder type adducts followed by fragmentation has been demonstrated in the reaction of 1-trimethylsilyloxybuta-1,3-diene **2** with activated 1,4-benzoquinones,[7,8,9] a direct Michael type addition has been proposed in the reactions of anthracenediquinone and naphthalenediquinone with 1,1-bis(*O,O*-substituted)dienes.[13] In reactions of strongly polarised dienes with quinonoid dienophiles conjugate addition has been observed to compete with and sometimes dominate conventional Diels-Alder cycloadditions.[14]



Scheme 2

We have previously reported the uncatalysed addition of the cyclic silylketene acetal, 2-trimethylsilyloxyfuran **3** to activated 1,4-benzoquinones and 1,4-naphthoquinones as a facile method to prepare *cis*-3a,8b-dihydrofuro[3,2-*b*]benzofuran-2(3*H*)-ones[15] and *cis*-6b,9a-dihydrofuro[3,2-*b*]naphtho[2,1-*d*]furan-8(9*H*)-ones (Scheme 3).[16] In this case we used acetonitrile as the solvent and interpreted the annulations to occur *via* a Michael addition of the silyloxydiene **3** to the quinone.



Scheme 3

In light of the results reported by Valderamma *et al.*[7,8,9] wherein dihydrobenzofurans were formed *via* a two step Diels-Alder fragmentation sequence, we cannot rule out the possibility that a similar mechanism operates for our annulation reactions. We therefore report herein a comparison of the addition of 1-trimethylsilyoxybuta-1,3-diene **2** and 2-trimethylsilyloxyfuran **3** to a more comprehensive range of 2-substituted 1,4-benzoquinones and 1,4-naphthoquinones in order to extend the scope of the annulation reactions and ascertain the stability of the initial Diels-Alder adducts when using various substituents. The use of 1,4-naphthoquinones as dienophiles with these dienes was of particular note in that previous work on the Diels-Alder / fragmentation reported by Valderamma *et al.*[7,8,9] focused on 1,4-benzoquinones.

RESULTS AND DISCUSSION

In order to directly compare Valderamma's work on the Diels-Alder additions of 1-trimethylsilyloxybuta-1,3-diene **2** to activated 1,4-benzoquinones in benzene[17] with our initial work on the addition of 2-trimethylsilyloxyfuran **3** to activated 1,4-benzoquinones and 1,4-naphthoquinones in acetonitrile, we revisited and extended our initial work using a solvent that would favour cycloaddition rather than Michael addition, namely, dichloromethane. The quinones were also more soluble in dichloromethane than benzene which was thought to lead to improved yields.

We initially repeated Valderamma's work on the addition of 1-trimethylsilyloxybuta-1,3-diene **2** to 2-substituted 1,4-benzoquinones in dichloromethane and extended the study to include 1,4-benzoquinones substituted at C-2 with a carboxyl **7**, phenylsulfanyl **8**, phenylsulfinyl **9** and phenylsulfonyl group **10**, respectively (Table 1). Reaction of benzoquinones **4,5,6** with diene **2** in dichloromethane provided the adducts **11,12,13** in lower yield than that reported by Valderamma *et al.*[17] using benzene. Benzoquinone **7** bearing a carboxyl group at C-2 only afforded 1,4-naphthoquinone presumably formed by facile aromatisation and decarboxylation of the unstable Diels-Alder adduct. In a similar manner reaction of diene **2** with 2-phenylsulfinyl-1,4-benzoquinone **9** also resulted in formation of 1,4-naphthoquinone presumably *via* elimination of phenylsulfinic acid from the unstable Diels-Alder adduct.

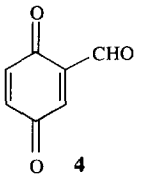
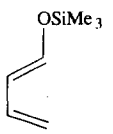
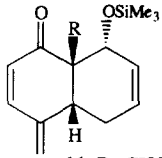
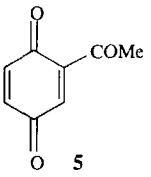
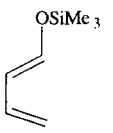
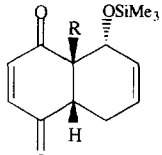
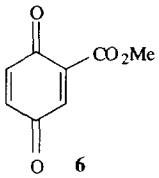
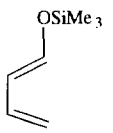
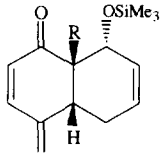
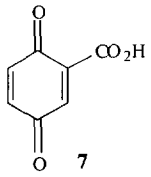
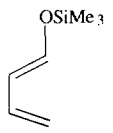
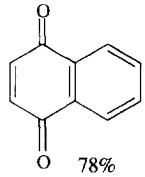
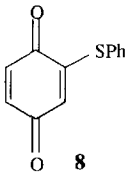
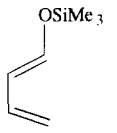
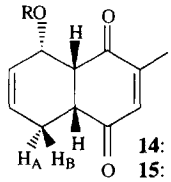
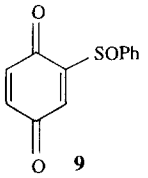
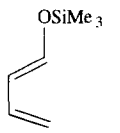
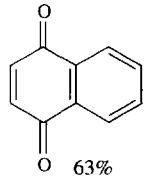
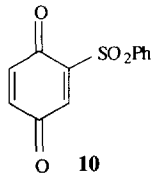
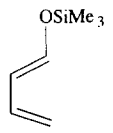
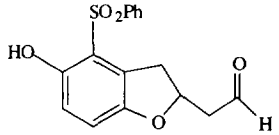
The reaction of 2-phenylsulfanyl-1,4-benzoquinone **8** with diene **2** was interesting in that regioselective addition occurred on the more electron deficient and less substituted double bond of the quinone system affording adduct **14** in 75% yield. The regiochemistry of the addition was supported by the observation of an n.O.e between the $SiMe_3$ group and the SPh group in the adduct **14**. The ability of the phenylsulphanyl group to direct the regiochemical outcome of the cycloaddition such that only one regioisomer of the Diels-alder adduct **14** was observed was initially surprising, however examples of the ability of a remote substituent to control the regiochemistry of Diels-Alder additions have been reported.[18]

Whereas the Diels-Alder adduct formed from benzoquinone-sulfoxide **9** and diene **2** underwent elimination and aromatisation to 1,4-naphthoquinone use of benzoquinone-sulfone **10** resulted in formation of the Diels-Alder fragmentation product **16** albeit in modest yield. None of the initial Diels-Alder product was isolated and the reaction was also hampered by the formation of 9,10-anthracenedione presumably *via* addition of diene **2** to both double bonds of the benzoquinone followed by aromatisation and elimination of phenylsulfonic acid. The formation of 9,10-anthracenedione was observed despite careful attention to the use of only one equivalent of the diene **2**.

The addition of diene **2** to 1,4-naphthoquinones **17-24** (Table 2) proceeded in a similar manner to the analogous reactions with 1,4-benzoquinones **4-10**. Thus, 1,4-naphthoquinones **17,18,19** all afforded Diels-Alder adducts **25,26,27** in good yield whereas 1,4-naphthoquinone **21**, bearing a carboxyl group at C-2 only afforded 9,10-anthracenedione. It is also of note that amide **20** afforded a Diels-Alder adduct **28** in moderate yield. 2-Phenylsulfanyl-1,4-naphthoquinone **22** failed to undergo reaction with diene **2** whereas the corresponding sulfoxide **23** and sulfone **24** afforded 9,10-anthracenedione.

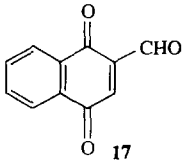
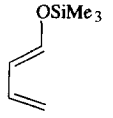
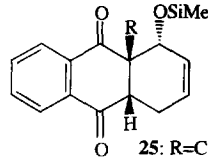
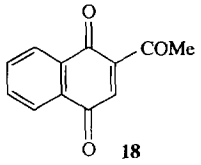
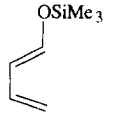
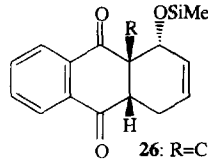
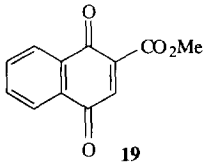
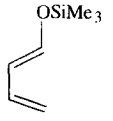
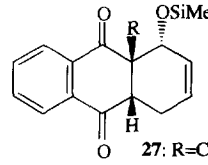
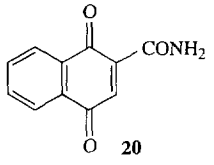
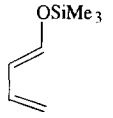
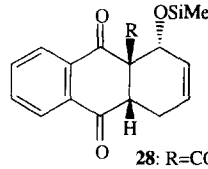
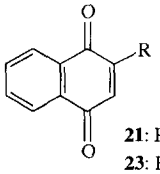
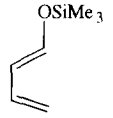
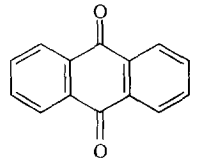
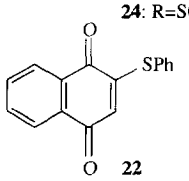
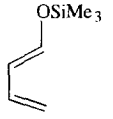
The results summarized in Tables 1, 2 suggest that Diels-Alder adducts of 2-substituted 1,4-benzoquinones and 1,4-naphthoquinones with diene **2** are isolable when the quinone bears an formyl, acetyl, methoxycarbonyl or carboxamide group at C-2, however, with a phenylsulfinyl or phenylsulfonyl group the Diels-Alder adducts decompose to fragmentation and/or elimination products.

Table 1 : Reaction of 1,4-Benzoquinones with 1-Trimethylsilyloxybuta-1,3-diene **2**#

1,4-Benzoquinone	*Diene*	*Products*
 **4**	 **2**	 **11**: R=CHO; 76%
 **5**	 **2**	 **12**: R=COMe; 69%
 **6**	 **2**	 **13**: R=CO_2Me; 74%
 **7**	 **2**	 78%
 **8**	 **2**	 **14**: R=$SiMe_3$; 75% **15**: R=H
 **9**	 **2**	 63%
 **10**	 **2**	 **16**; 36%

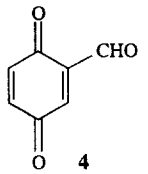
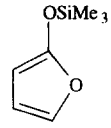
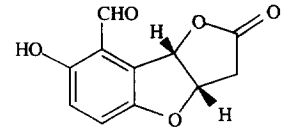
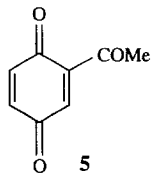
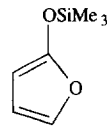
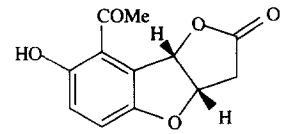
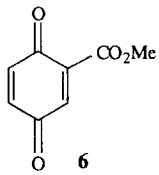
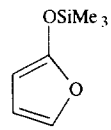
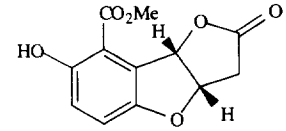
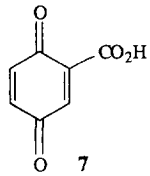
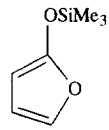
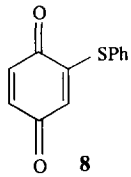
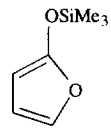
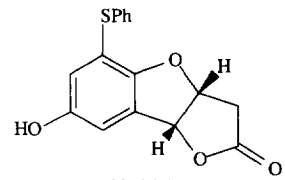
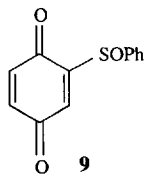
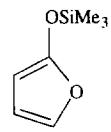
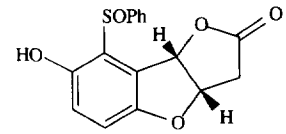
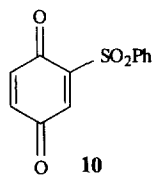
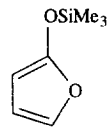
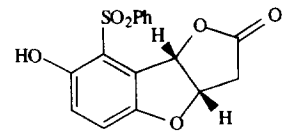
All reactions were carried out in CH_2Cl_2 at room temperature for 16 h. using 1 equiv. of diene and 1 equiv. of dienophile

Table 2 : Reaction of 1,4-Naphthoquinones with 1-Trimethylsilyloxybuta-1,3-diene **2**#

1,4-Naphthoquinone	*Diene*	*Products*
 **17**	 **2**	 **25**: R=CHO; 74%
 **18**	 **2**	 **26**: R=COMe; 85%
 **19**	 **2**	 **27**: R=CO_2Me; 76%
 **20**	 **2**	 **28**: R=$CONH_2$; 81%
 **21**: R=CO_2H; 78% **23**: R=SOPh; 92% **24**: R=SO_2Ph; 80%	 **2**	
 **22**	 **2**	no reaction

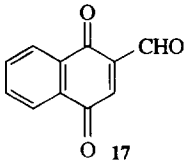
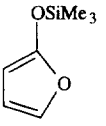
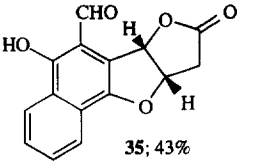
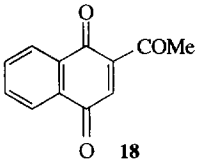
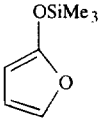
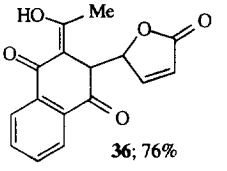
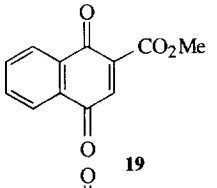
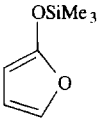
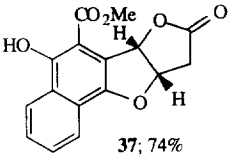
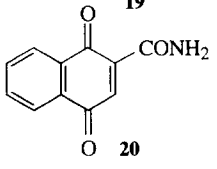
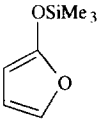
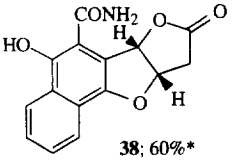
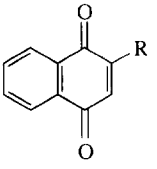
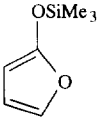
All reactions were carried out in CH_2Cl_2 at room temperature for 16 h. using 1 equiv. of diene and 1 equiv. of dienophile

Table 3 : Reaction of 1,4-Benzoquinones with 2-Trimethylsilyloxyfuran **3**[#]

1,4-Benzoquinone	*Diene*	*Products*
 **4**	 **3**	 **29**; 67%
 **5**	 **3**	 **30**; 72%
 **6**	 **3**	 **31**; 65%
 **7**	 **3**	no reaction
 **8**	 **3**	 **32**; 26%
 **9**	 **3**	 **33**; 66%
 **10**	 **3**	 **34**; 63%

All reactions were carried out in CH_2Cl_2 at room temperature for 16 h. using 1 equiv. of diene and 1 equiv. of dienophile

Table 4 : Reaction of 1,4-Naphthoquinones with 2-Trimethylsilyloxyfuran **3**#

1,4-Naphthoquinone	*Diene*	*Products*
 **17**	 **3**	 **35**; 43%
 **18**	 **3**	 **36**; 76%
 **19**	 **3**	 **37**; 74%
 **20**	 **3**	 **38**; 60%*
	 **3**	**21**: R=CO_2H **22**: R=SPh **23**: R=SOPh **24**: R=SO_2Ph } no reaction

Reactions with all quinones except **20** were carried out in CH_2Cl_2 at room temperature for 16 h. using 1 equiv. of diene and 1 equiv. of dienophile

* Reaction with quinone **20** was carried out in acetonitrile

Having examined the reactions of 1,4-benzoquinones **4-10** and 1,4-naphthoquinones **17-24** with acyclic diene **2** we then turned our attention to the reaction of the same quinones with the cyclic diene **3** (Tables 3,4). In our initial study[15,16] of the addition of diene **3** to benzoquinones **5,6** and naphthoquinone **19** in acetonitrile, the adducts **30,31** and **37** were isolated in poorer yield than in the present work using dichloromethane. In the case of 2-formyl-1,4-benzoquinone **4** and 2-formyl-1,4-naphthoquinone **17**, in our initial work no adducts were observed when the quinones were generated by oxidative demethylation of the appropriate 1,4-dimethoxyarene and the subsequent addition of diene **3** carried out in acetonitrile. It was therefore pleasing to note that when quinones **4** and **17** were formed by oxidation of 1,4-dihydroxy-2-formylbenzene and 1,4-dihydroxy-2-formylnaphthalene with activated manganese dioxide in dichloromethane and diene **3** added *in situ*, that the adducts **29** and **35** were afforded in 67% and 43% yield respectively.

One other observation in the naphthoquinone series was that addition of diene **3** to 2-acetyl-1,4-naphthoquinone **18** in dichloromethane afforded the butenolide **36** in 76% yield and none of the furonaphthofuran adduct was observed. This is in direct contrast to the reaction of diene **3** with **19** in acetonitrile in which the furonaphthofuran was the major product and **36** was isolated as a minor component.[16]

1,4-Benzoquinone **7** and 1,4-naphthoquinone **21**, bearing carboxyl groups at C-2, failed to afford annulation products in attempted reactions with diene **3** which mirrors the analogous reactions with acyclic diene **2**.

2-Phenylsulfanyl-1,4-benzoquinone **8** underwent reaction with diene **3** at the unsubstituted double bond of the benzoquinone affording annulation product **32** albeit in 26% yield. The regiochemistry of the annulation product **32** was established by the observed *meta* coupling between the two aromatic protons in the furobenzofuran ring. Whilst the addition of **3** to the unsubstituted side of the benzoquinone **8** was also observed in the addition of acyclic diene **2** to **8**, the regiochemistry of the addition to form the two adducts **14** and **32** is different. Whilst this difference in regiochemistry may well be attributed to different mechanisms operating in the reactions with the different dienes, one must be cautious drawing any conclusions given the moderate yield of material recovered from the reaction of diene **3** with 1,4-benzoquinone **8** despite substantial efforts to improve this.

2-Phenylsulfanyl-1,4-naphthoquinone **22** failed to undergo reaction with diene **3** in dichloromethane despite the fact that modest yields of the furonaphthofuran adduct were observed in our earlier work using acetonitrile as solvent.[19] One further illustration of this subtle solvent effect was observed in the reaction of amide **20** with diene **3** in that no reaction was observed in dichloromethane whereas adduct **38** was formed in 60% yield when using acetonitrile as solvent.

1,4-Benzoquinone-sulfoxide **9** and sulfone **10** underwent smooth reaction with diene **3** affording the adducts **33** and **34** in modest yield. This is in direct contrast to the analogous reactions of diene **3** with 1,4-naphthoquinone-sulfoxide **23** and sulfone **24** for which no isolable products were observed. In the latter cases only butenolide and the hydroquinone of the starting 1,4-naphthoquinone were recovered from the reaction, thus suggesting that redox processes were also a complication in these reactions. This latter observation demonstrates that successful reactions of silyloxydienes with 1,4-benzoquinones may not always be mirrored in analogous reactions with similarly substituted 1,4-naphthoquinones. Use of acetonitrile as solvent also failed to effect reaction of 1,4-naphthoquinones **23, 24** with diene **3**.[19]

In summary the addition of dienes **2,3** to a range of 2-substituted 1,4-benzoquinones and 1.4-naphthoquinones has been studied. It appears that the nature of the product depends on the nature of the quinone, diene and the solvent used. These observations may well be attributed to the fact that the mechanism of these additions may well lie at the borderline between a concerted and a stepwise process.[20]

EXPERIMENTAL

General Details

Melting points were determined using a Reichert Kofler block and are uncorrected. Infrared absorption spectra were recorded using Perkin Elmer 1600 Series FTIR spectrometer as Nujol Mulls or thin films between sodium chloride plates. ^{1}H NMR spectra were obtained using either a Bruker AM 400 or Bruker AC 200 spectrometer. ^{13}C NMR data were recorded using a Bruker AM 400 or Bruker AC 200 spectrometer. ^{13}C NMR spectra were

interpreted with the aid of DEPT 135 and DEPT 90 experiments. Low resolution mass spectra were recorded using a VG 70-SE spectrometer operating at an accelerating voltage of 70eV. High resolution mass spectra were recorded at a nominal resolution of 5000 or 10000 as appropriate. Elemental analyses were performed at the Microanalytical Laboratory, University of New South Wales, Sydney. Flash chromatography was performed using Merck Kieselgel 60 (230-400 Mesh) with the indicated solvents.

Preparation of Starting Materials

2-formyl-1,4-dihydroxynaphthalene

To a solution of 2-formyl-1,4-dimethoxynaphthalene[21] (1.05 g, 4.8 mmol) in dichloromethane (80 mL) at -60 °C was added boron tribromide (2.74 g, 29 mmol). The reaction mixture was stirred under nitrogen for 2.5 h. whilst warming to room temperature, then cooled to -10 °C and water (20 mL) added. The mixture was left to stand for 15 min., then extracted with dichloromethane (4 x 50 mL), washed with water, dried over sodium sulfate, and the solvent removed under reduced pressure. The resultant crude product was purified by flash chromatography using hexane : ethyl acetate (2:1) as eluent, yielding 2-formyl-1,4-dihydroxynaphthalene (0.88 g, 98%) as a tan solid, m.p. 187-189 °C (lit.[22] m.p. 188-190 °C); (Found: M^+ 188.0464. $C_{11}H_8O_3$ requires M^+ 188.0473) υ_{max} (Nujol) (cm^{-1}) 2989-3688 (OH), 1628 (C=O, *o*-hydroxyaryl aldehyde); δ_H (200 MHz; d^6-acetone) 7.04 (1H, s, 3-H), 7.58-7.78 (2H, m, 6-H and 7-H), 8.24 (1H, d, J_{ortho} 7.8 Hz, 5-H or 8-H), 8.36 (1H, d, J_{ortho} 7.4 Hz, 8-H or 5-H), 8.90 (1H, bs, 4-OH), 9.96 (1H, s, CHO), 12.29 (1H, bs, 1-OH); δ_C (200 MHz; d^6-acetone) 106.8 (CH, C-3), 123.1 (CH, C-5), 123.1 (CH, C-8), 124.5 (quat., C-4a), 127.2 (quat., C-8a), 130.4 (CH, C-6), 130.4 (CH, C-7), 146.5 (quat., C-2), 153.7 (quat., C-1 or C-4), 156.0 (quat., C-4 or C-1), 197.8 (CHO); *m/z* (%) 188 (M^+, 100). The product was then used in Diels-Alder additions where quinone **17** was generated *in situ* with manganese(IV) dioxide (*vide infra*).

2-acetyl-1,4-dihydroxynaphthalene

To a solution of 2-acetyl-1,4-dimethoxynaphthalene[23] (0.17 g, 0.73 mmol) in dichloromethane (50 mL) at -78°C was added boron tribromide (1.10 g, 4.4 mmol) with stirring. The reaction mixture was allowed to warm to room temperature and after 4 h. quenched by the addition of ice (30 mL) followed by vigorous stirring. The aqueous layer was extracted with dichloromethane (3 x 30 mL) and the combined organic extracts dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the crude product recrystallised from ethanol to yield 2-acetyl-1,4-dihydroxynaphthalene (0.144 g, 98%) as yellow crystals, m.p. 202-204°C (lit.[24] 201-203°C). The product was then used in Diels-Alder additions where quinone **18** was generated *in situ* with activated manganese dioxide (*vide infra*).

1,4-dimethoxynaphthalene-2-carboxamide

To a solution of 2-cyano-1,4-dimethoxynaphthalene[25] (0.279 g, 1.31 mmol) in *tert*-butanol (10 mL) was added potassium hydroxide (0.197 g, 3.51 mmol). The reaction mixture was heated under reflux for 3 h., diluted with water (20 mL) and neutralised with hydrochloric acid (10 M). The mixture was then extracted with ethyl acetate (3 x 20 mL) and the combined organic layers washed with water (3 x 10 mL). After drying over anhydrous magnesium sulfate, the solvent was removed under reduced pressure to yield *1,4-dimethoxynaphthalene-2-carboxamide* (0.258 g, 85%) as an off-white solid, m.p. 153-154°C (Found: C, 67.4;

H, 5.9; N, 6.0. $C_{13}H_{13}O_3N$ requires C, 67.5; H, 5.7; N, 6.1%); υ_{max} (Nujol) (cm^{-1}) 3448 (NH), 3389 (NH) and 1651 (C=O); δ_H (200 MHz; $CDCl_3$) 3.99 (3H, s, 4-OMe), 4.05 (3H, s, 1-OMe), 6.07 (2H, bs, $CONH_2$), 7.44 (1H, s, 3-H), 7.57-7.62 (2H, m, 6-H and 7-H), 8.10-8.14 (1H, m, 5-H or 8-H), 8.27-8.30 (1H, m, 8-H or 5-H); *m/z* (%) 231 (M^+, 100), 216 (M-CH_3, 53), 200 (M-NH_2-CH_3, 20), 188 (M-CONH, 39).

1,4-Dioxo-1,4-dihydronaphthalene-2-carboxamide **20**

To a solution of 1,4-dimethoxynaphthalene-2-carboxamide (30 mg, 0.13 mmol) in acetonitrile (2 mL) was added a solution of ceric ammonium nitrate (0.142 g, 0.26 mmol) in water (1 mL). After stirring at room temperature for 5 min. the reaction mixture was extracted with dichloromethane (3 x 10 mL) and washed with water (10 mL). The organic layer was then dried over anhydrous magnesium sulfate and filtered through a layer of florisil. The solvent was removed under reduced pressure to afford *1,4-naphthoquinone* **20** (22 mg, 84%) as a yellow solid, m.p. 176-178°C (dec.) (Found: C, 65.7; H, 3.8; N, 7.0. $C_{11}H_7O_3N$ requires C, 65.7; H, 3.5; N. 7.0%); υ_{max} (Nujol) (cm^{-1}) 3390 (NH), 1658 (C=O); δ_H (200 MHz; $CDCl_3$) 3.35 (2H, s, $CONH_2$), 7.24 (1H, s, 3-H), 7.87-8.07 (4H, m, 5-H, 6-H, 7-H and 8-H); δ_C (50 MHz, $CDCl_3$) 125.7 (CH, C-5 or C-8), 126.4 (CH, C-8 or C-5), 131.5 (quat., C-4a or C-8a), 131.7 (quat., C-8a or C-4a), 134.5 (CH, C-6 or C-7), 134.6 (CH, C-7 or C-6), 137.0 (CH, C-3), 141.6 (quat., C-2), 163.7 (quat., $CONH_2$), 183.5 (quat., C-1 or C-4), 184.9 (quat., C-4 or C-1); *m/z* (%) 201 (M^+, 100), 185 (M-NH_2, 6), 158 (M-CONH, 93). The quinone was then reacted with the appropriate diene in an analogous procedure to quinones **22-24**.

Diels-Alder Cycloadditions

General Procedure for the Synthesis of Diels-Alder Adducts **11,12,13,25,26,27,29,30,31,36,37,38**

To manganese dioxide (Aldrich, activated) (10 equivalents), anhydrous magnesium sulfate (2-4 g) and the appropriate diene (1 equivalent) in dichloromethane (50 mL) was added the required dihydroxybenzene or dihydroxynaphthalene (1 equivalent) in dichloromethane (50-100 mL) at room temperature with stirring. After 16 h. the manganese dioxide was filtered off and the solvent removed under reduced pressure to afford the crude product. Purification could be carried out via flash chromatography using hexane-ethyl acetate as eluent, however, some of the products decomposed upon contact with silica gel resulting in reduced yields. Trituration with an appropriate solvent or column chromatography over neutral alumina was therefore used to minimise decomposition.

General Procedure for the Synthesis of Diels-Alder Adducts using Quinones **8,9,10,22,23,24** *as the Dienophile.*

Sulfur substituted quinones **8,9,10,22,23,24** are stable and therefore they do not need to be generated *in situ* with manganese dioxide. To the appropriate diene (1 equivalent) in dry dichloromethane (10 mL) at 0°C under nitrogen was added the required quinone (1 equivalent) in dry dichloromethane (20-30 mL) with stirring. After 10 h. the solvent was removed under reduced pressure. The crude residue was then purified by either recrystallisation , trituration or flash chromatography with the appropriate solvent.

(4aR, 5R*, 8aS*)-4a-formyl-5-trimethylsilyloxy-1,4,4a,5,8,8a-hexahydronaphthalene-1,4-dione* **11**

The title compound was prepared from manganese dioxide (2.5 g, 30.0 mmol), 2,5-dihydroxybenzaldehyde (Aldrich) (0.404 g, 2.92 mmol) and 1-trimethylsilyloxy-1,3-butadiene **2** (0.52 mL, 2.96 mmol) in dichloromethane (300 mL). The solvent was removed under reduced pressure and the crude product purified

by flash chromatography using hexane : ethyl acetate (1:1) as eluent to afford adduct **11** (0.299 g, 76%) as a tan solid, m.p. 79-81 °C (lit.[17] m.p. 80-82 °C). The proton n.m.r data were in agreement with the literature.[17]

(4aR, 5R*, 8aS*)-4a-acetyl-5-trimethylsilyloxy-1,4,4a,5,8,8a-hexahydronaphthalene-1,4-dione* **12**
The title compound was prepared from a mixture of manganese dioxide (3.69 g, 42.4 mmol), 2,5-dihydroxyacetophenone (Aldrich) (0.108 g, 0.071 mmol) and 1-trimethylsilyloxy-1,3-butadiene **2** (0.14 mL, 0.80 mmol) in dichloromethane (250 mL). The solvent was removed under reduced pressure and the crude product purified by flash chromatography using hexane : ethyl acetate (4:1) as eluent to afford *adduct* **12** (142 mg, 69%) as an orange oil. The proton n.m.r data were in agreement with the literature.[17]

methyl (4aR, 5R*, 8aS*)-1,4-dioxo-5-trimethylsilyloxy-1,4,4a,5,8,8a-hexahydronaphthalene-4a-carboxylate* **13**
The title compound was prepared from a mixture of manganese dioxide (2.73 g, 31 mmol), methyl gentisate (Aldrich) (0.513, 3.05 mmol) and 1-trimethylsilyloxy-1,3-butadiene **2** (0.54 mL, 3.08 mmol) in dichloromethane (50 mL). The solvent was removed under reduced pressure and the crude product purified by flash chromatography using hexane : ethyl acetate (4:1) as eluent to afford *adduct* **13** (0.706 g, 74%) as an orange oil. The proton n.m.r data were in agreement with the literature.[17]

(4aR, 5R*)-1,4-dioxo-3-phenylsulfanyl-5-trimethylsilyloxy-1,4,4a,5,8,8a-hexahydronaphthalene* **14**
The title compound was prepared from 2-phenylsulfanyl-1,4-benzoquinone[15] (0.080 g, 0.37 mmol) and 1-trimethylsilyloxy-1,3-butadiene **2** (0.075 mL, 0.43 mmol) in dichloromethane (10 mL). The solvent was removed under reduced pressure and the crude product triturated with ether to afford *adduct* **14** (99 mg, 75%) as an orange solid, m.p. 135-137 °C; (Found: M^+, 358.1085. $C_{19}H_{22}O_3SiS$ requires M^+, 358.1059); υ_{max} (Nujol) (cm^{-1}) 1679 (C=O, quinone), 1250 (Si-Me), 691 (C-S); δ_H (400 MHz; $CDCl_3$) 0.054 ($SiMe_3$), 2.01-2.07 (1H, m, 8-H_B), 2.99-3.05 (1H, m, 8-H_A), 3.11-3.15 (1H, m, 8a-H), 3.26 (1H, dd, $J_{4a,8a}$ 6.0 Hz, $J_{4a,5}$ 4.0 Hz, 4a-H), 4.40-4.42 (1H, m, 5-H), 5.77-5.82 (2H, m, 6-H and 7-H), 6.00 (1H, s, 2-H), 7.45-7.50 (5H, m, SPh); δ_C (100 MHz; $CDCl_3$) -0.137 ($SiMe_3$), 21.4 (CH_2, C-8), 41.6 (CH, C-8a), 52.6 (CH, C-4a), 65.1 (CH, C-5), 126.8 (quat., C-3), 127.0 (CH, C-6), 128.6 (CH, C-7), 130.2 (CH, C-2'), 130.3 (CH, C-2), 132.4 (CH, C-4'), 135.7 (CH, C-3'), 157.5 (quat., C-1'), 194.3 (quat., C-1 or C-4), 197.2 (C-4 or C-1); *m/z* (%) 358 (M^+, 35), 285 (M-$SiMe_3$). The trimethylsilyl group of adduct **14** hydrolysed in solution (hexane/ether) over several days to form *(4aR*, 5R*)-1,4-dioxo-5-hydroxy-3-phenylsulfanyl-1,4,4a,5,8,8a-hexahydronaphthalene* **15** (63 mg, 80%) as colourless crystals, m.p. 139 °C (dec.); υ_{max} (NaCl plates) (cm^{-1}) 3201-3586 (OH), 1669 (C=O, quinone); δ_H (200 MHz; $CDCl_3$) 1.60 (1H, bs, OH), 2.10-2.35 (1H, m, 8-H_B), 2.48-2.27 (1H, m, 8-H_A), 3.10-3.20 (1H, m, 8a-H), 3.46 (1H, dd, $J_{4a,8a}$ 5.0 Hz, $J_{4a,5}$ 5.0 Hz, 4a-H), 4.89-4.48 (1H, m, 5-H); *m/z* (%) 286 (M^+, 55), 268 (M-H_2O, 56).

5-hydroxy-2-(2-oxoethyl)-4-phenylsulfonyl-2,3-dihydrobenzofuran **16**
The title compound was obtained from 2-phenylsulfonyl-1,4-dihydroxybenzene[26] (0.100 g, 0.40 mmol), manganese dioxide (0.40 g, 4.4 mmol) and 1-(trimethylsilyloxy)-1,3-butadiene **2** (0.160 mL, 0.88 mmol) in dichloromethane (200 mL). The solvent was removed under reduced pressure and the crude product purified by flash chromatography using hexane : ethyl acetate (4 : 1) as eluent to yield *benzofuran* **16** (0.046 g, 36%) as an orange oil, (Found M^+, 318.0558. $C_{16}H_{14}O_5S$ requires M^+, 318.0562); υ_{max} (Nujol) (cm^{-1}) 3500-3248 (OH),

1640 (CHO), 1380 (SO_2); δ_H (200 MHz, $CDCl_3$) 2.73 (1H, ddd, J_{gem} 17.5, $J_{1'A,2}$ 5.8 and $J_{1'A,2'}$ 0.9 Hz, 1'-H_A), 2.92 (1H, ddd, J_{gem} 17.5, $J_{1'B,2}$ 7.0 and $J_{1'B,2'}$ 1.7, 1'-H_B), 2.99 (1H, dd, J_{gem} 17.4, $J_{3A,2}$ 7.6 Hz, 3-H_A), 3.45 (J_{gem} 17.4, $J_{3B,2}$ 8.8 Hz, 3-H_B), 5.09-5.39 (1H, m, 2-H), 6.70-7.02 (2H, m, 6-H and 7-H), 7.45-7.69 (4H, m, 2'-H, 3'-H, 5'-H, 6'-H), 7.89-7.99 (1H, m, 4'-H), 9.15 (1H, bs, OH), 9.82 (1H, br.s, CHO); *m/z* (%) 318 (M^+, 70), 274 ($M-C_2H_3O$).

(1R, 4aS*, 9aR*)-9a-formyl-1-trimethylsilyloxy-1,4,4a,9,9a,10-hexahydroanthracene-9,10-dione* **25**

The title compound was prepared from 2-formyl-1,4-dihydroxynaphthalene (74 mg, 0.39 mmol), manganese dioxide (0.32 g, 3.70 mmol) and 1-trimethylsilyloxy-1,3-butadiene **3** (0.14 mL, 0.80 mmol) in dichloromethane (50 mL). The solvent was removed under reduced pressure and the crude product purified by flash chromatography using hexane : ethyl acetate (9:1) as eluent to afford *adduct* **25** (95 mg, 74%) as pale orange crystals, m.p. 72-74 °C; (Found; M^+, 328.1164. $C_{18}H_{20}O_4Si$ requires M^+, 328.1131) υ_{max} (Nujol) (cm^{-1}) 1731 (CHO), 1678 (C=O, quinone), 1252 (Si-CH_3) and 1077 (CO-Si); δ_H (200 MHz; $CDCl_3$) -0.318 (3H, s, $OSiMe_3$), 2.12 (1H, dd, J_{gem} 19.3 and $J_{4B,4a}$ 7.4 Hz, 4-H_B), 3.24 (1H, dd, J_{gem} 19.3 and $J_{4A,3}$ 3.4 Hz, 4-H_A), 3.74 (1H, d, $J_{4a,4B}$ 7.4 Hz, 4a-H), 4.80 (1H, d, $J_{1,2}$ 4.8 Hz, 1-H), 5.83-5.90 (2H, m, 2-H and 3-H), 7.66-7.72 (2H, m, 6-H and 7-H), 7.98-8.03 (2H, m, 5-H and 8-H), 9.82 (1H, s, CHO); δ_C (50 MHz; $CDCl_3$) -0.734 ($OSiMe_3$), 20.3 (CH_2, C-4), 42.3 (CH, C-4a), 66.8 (CH, C-1), 125.3 (CH, C-5 or C-8), 125.7 (CH, C-8 or C-5), 126.1 (CH, C-3), 131.0 (CH, C-2), 133.1 (CH, C-6 or C-7), 133.4 (quat., C-4b or C-8a), 134.3 (CH, C-7 or C-6), 134.8 (quat., C-8a or C-4b), 137.0 (quat., C-9a), 194.9 (quat., C-10 or C-9), 197.0 (quat., C-9 or C-10), 197.1 (CHO); *m/z* (%) 328 (M+, 40), 299 (M-CHO, 30), 73 ($M-C_{15}H_{11}O_4$, 85).

(1R, 4aS*, 9aR*)-9a-acetyl-1-trimethylsilyloxy-1,4,4a,9,9a,10-hexahydroanthracene-9,10-dione* **26**

The title compound was prepared from 2-acetyl-1,4-dihydroxynaphthalene (108 mg, 0.535 mmol), manganese dioxide (460 mg, 5.29 mmol) and 1-trimethylsilyloxy-1,3-butadiene **2** (81 mg, 0.57 mmol) in dichloromethane (200 mL). The crude product was recrystallized from hexane to yield *adduct* **26** (155 mg, 85%) as colourless crystals, m.p. 147-149°C; [Found: $(M-COMe)^+$, 299.1103. $C_{17}H_{19}O_3Si$ requires $(M-COMe)^+$, 299.1103]; υ_{max} (Nujol) (cm^{-1}) 1703 (C=O, acetyl), 1677 (C=O, quinone), 1250 (Si-CH_3), 1081 (CO-Si); δ_H (400MHz, $CDCl_3$) -0.325 (3H, s, $SiMe_3$), 2.00 (1H, dd, J_{gem} 18.6 and $J_{4B,4a}$ 7.0 Hz, 4-H_B), 2.40 (3H, s, CO<u>Me</u>), 3.21 (1H, d, J_{gem} 18.6 Hz, 4-H_A), 3.87 (1H, d, $J_{4B,4a}$ 7.0 Hz, 4a-H), 4.80 (1H, s, 1-H), 5.86 (2H, br.s, 2-H and 3-H), 7.68-7.74 (2-H, m, 6-H and 7-H), 8.00-8.04 (2-H, m, 5-H and 8-H); δ_C (100 MHz, $CDCl_3$) -0.757 ($SiMe_3$), 20.8 (CH_2, C-4), 28.2 (CH_3, Ac), 44.3 (CH, C-4a), 67.5 (CH, C-1), 69.6 (quat., C-8b), 125.5 (CH, C-3), 126.3 (CH, C-6 or C-7), 126.7 (CH, C-7 or C-6), 129.3 (CH, C-2), 133.0 (CH, C-5 or C-8), 134.0 (CH, C-8 or C-5), 135.0 (quat., C-4b or C-8a), 137.4 (quat., C-8a or C-4b), 195.0 (quat., C-9 or C-10), 196.6 (quat., C-10 or C-9), 202.9 (COMe); *m/z* (%) 342 (M+, 6), 299 (M-COMe, 30), 210 ($M-C_5H_{12}O_2Si$, 100), 73 ($M-C_{16}H_{13}O_4$, 100), 43 ($M-C_{17}H_{19}O_4$, 65).

methyl (1R, 4aS*, 9aR*)-9,10-dioxo-1-trimethylsilyloxy-1,4,4a,9,9a,10-hexahydroanthracene-9a-carboxylate* **27**

The title compound was prepared from methyl 1,4-dihydroxynaphthalene-2-carboxylate (100 mg, 0.46 mmol), manganese dioxide (0.406g, 4.67 mmol) and 1-trimethylsilyloxy-1,3-butadiene **2** (65 mg, 0.460 mmol) in dichloromethane (50 mL). The product was purified by flash chromatography using hexane : ethyl acetate

(4:1) as eluent to afford *adduct* **27** (114 mg, 76%) as orange crystals, m.p. 138-140°C; (Found: C, 63.4; H, 6.45; M^+, 358.1278. $C_{19}H_{22}O_5Si$ requires C, 63.7; H, 6.19%; M^+, 358.1236); υ_{max} (Nujol) (cm^{-1}) 1744 (CO_2Me), 1686 (C=O, quinone), 1252 (Si-CH_3) and 1060 (CO-Si); δ_H (400MHz, $CDCl_3$) -0.370 (3H, s, $SiMe_3$), 2.04 (1H, dd, J_{gem} 19.2 and $J_{4B,4a}$ 6.8 Hz, 4-H_B), 3.18 (1H, dd, J_{gem} 19.2 and $J_{4a,3}$ 3.72 Hz, 4-H_A), 3.79 (3H, s, $CO_2\underline{Me}$), 3.84 (1H, d, $J_{4a,4B}$ 6.8 Hz, 4a-H), 4.77 (1H, d, $J_{1,2}$ 4.2 Hz, 1-H), 5.81 (2H, s, 2-H and 3-H), 7.65-7.70 (2H, m, 6-H and 7-H) and 7.97-8.07 (2H, m, 5-H and 8-H); δ_C (100 MHz, $CDCl_3$) -0.077 ($SiMe_3$), 21.1 (CH_2, C-4), 45.3 (CH_3, $CO_2\underline{Me}$), 52.8 (CH, C-4a), 65.0 (quat., C-9a), 67.0 (CH, C-1), 125.5 (CH, C-3), 126.5 (CH, C-2), 127.1 (CH, C-5 or C-8), 127.8 (CH, C-8 or C-5), 133.0 (CH, C-6 or C-7), 134.0 (CH, C-7 or C-6), 135.0 (quat., C-4b or C-8a), 137.4 (quat., C-8a or C-4b), 169.2 (quat., $\underline{C}O_2Me$), 194.4 (quat., C-9 or C-10), 194.8 (C-10 or C-9); *m/z* (%) 358 (M^+, 30), 299 (M-CO_2Me, 15), 73 (M-$C_{15}H_{13}O_5$, 100).

(1R, 9aR*, 4aS*)-9,10-dioxo-1-trimethylsilyloxy-1,4,4a,9,9a,10-hexahydroanthracene-9a-carboxamide* **28**
The title compound was prepared from quinone **20** (28 mg, 0.14 mmol) and 1-trimethylsilyloxy-1,3-butadiene **3** (0.028 mL, 0.16 mmol) in dichloromethane (25 mL). The solvent was removed and the crude product recrystallized from chloroform to yield *adduct* **28** (39 mg, 81%) as a colourless solid, m.p. 120-122°C (dec.); [Found: $(M-CH_3)^+$, 328.0978. $C_{18}H_{21}NO_4Si$ requires $(M-CH_3)^+$, 328.0975]; υ_{max} (NaCl plates) (cm^{-1}) 3190-3622 (NH_2), 1680 (C=O, quinone) 1660 (amide), 1251 (Si-CH_3) and 1070 (CO-Si); δ_H (400MHz, $CDCl_3$) 2.41-2.49 (1H, m, 4-H_B), 3.21-3.28 (1H, m, 4-H_A), 4.52 (1H, d, $J_{4a,4B}$ 7.2 Hz, 4a-H), 4.52 (1H, d, $J_{1,2}$ 5.2 Hz, 1-H), 5.78-5.83 (1H, m, 2-H), 5.93-5.97 (1H, m, 3-H), 6.40 (1H, bs, $CONH_2$), 7.64-7.73 (2H, m, 6-H and 7-H), 7.98-8.04 (2H, m, 5-H and 8-H); δ_C (100 MHz, $CDCl_3$) -0.636 ($SiMe_3$), 21.6 (CH_2, C-4), 44.6 (CH, C-4a), 64.8 (quat., C-9a), 70.1 (CH, C-1), 125.0 (CH, C-3), 125.7 (CH, C-2), 126.7 (CH, C-5 or C-8), 131.3 (CH, C-8 or C-5), 133.0 (CH, C-6 or C-7), 134.2 (CH, C-7 or C-6), 134.8 (quat., C-4b or C-8a), 137.1 (quat., C8a or C-4b), 170.4 (quat., $\underline{C}ONH_2$), 195.2 (quat., C-9 or C-10), 196.0 (C-10 or C-9); *m/z* (%) 343 (M^+, 6), 328 (M-CH_3, 4), 210 (100), 142 942), 73 (82).

(3aS,8bS*)-dihydro-8-formyl -7-hydroxyfuro[3,2-b]benzo[2,1-d]furan-2(3H)-one* **29**
The title compound was prepared from a mixture of manganese dioxide (3.32 g, 38 mmol), 2,5-dihydroxybenzaldehyde (Aldrich) (0.54 g, 3.9 mmol) and 2-trimethylsilyloxyfuran **3** (0.60 mL, 3.5 mmol) in dichloromethane (200 mL). The resultant crude product was purified by flash chromatography using hexane : ethyl acetate (2:1 then 1:1) as eluent to afford *cis-8-formyl-3a,8b-dihydro-7-hydroxyfuro[3,2-b]benzo[2,1-d]furan-2(3H)-one* **29** (0.57 g, 67%) as bright yellow crystals, m.p. 146-147 °C; (Found: C, 59.7; H, 3.97; M^+, 220.0381. $C_{11}H_8O_5$ requires: C, 59.9; H, 3.66; M+, 220.0372); υ_{max} (Nujol) (cm^{-1}) 3000-3750 (OH), 1754 (C=O, γ-lactone) and 1660 (C=O, *o*-hydroxyaryl aldehyde); δ_H (200 MHz; d^6-acetone) 2.95 (1H, dd, J_{gem} 19.0 and $J_{3A,3a}$ 1.1 Hz, 3_A-H), 3.32 (1H, dd, J_{gem} 19.0 and $J_{3B,3a}$7.1 Hz, 3_B-H), 5.62-5.69 (1H, m, 3a-H), 6.64 (1H, d, $J_{3a,8b}$ 6.1 Hz, 8b-H), 7.06 (1H, d, $J_{5,6}$ 8.9 Hz, 5-H), 7.23 (1H, d, $J_{6,5}$ 8.9 Hz, 6-H), 10.35 (1H, s, CHO), 10.50 (1H, bs, OH); δ_C (50 MHz; d^6-acetone) 35.0 (CH_2, C-3), 82.5 (CH, C-3a), 82.5 (CH, C-8b), 118.4 (CH, C-6), 121.1 (CH, C-5), 118.9 (quat., C-8), 121.6 (quat., C-8a), 154.0 (quat., C-4a), 156.0 (quat., C-7), 175.3 (C=O, C-2), 189.7 (CHO); *m/z* (%) 220 (M^+, 100), 176 (M-CO_2, 60), 162 (M-$C_2H_2O_2$, 50).

(3aS,8bS*)-dihydro-7-hydroxyfuro[3,2-b]benzo[2,1-d]furan-2(3H)-one* **30**
The title compound was obtained from manganese dioxide (2.4 g, 27.6 mmol), 2,5-dihydroxyacetophenone (Aldrich) (0.495 g, 3.25 mmol) and 2-trimethylsilyloxyfuran **3** (0.60 mL, 3.5 mmol) in dichloromethane (200

mL). The solvent was removed under reduced pressure and the resultant residue purified by flash chromatography using hexane : ethyl acetate (1:1) as eluent to affford *cis*-8-acetyl-3a,8b-dihydro-7-hydroxyfuro[3,2-*b*]benzo[2,1-*d*]furan-2(3*H*)-one **30** (0.546 g, 72%) as a yellow solid, m.p. 163-165 °C (lit.[26] m.p. 164-165 °C). The proton n.m.r. data were in agreement with the literature.[15]

methyl (3aS,8bS*)-dihydro-7-hydroxy-3-oxofuro[3,2-b]benzo[2,1-d]furan-8-carboxylate* **31**

The title compound was obtained from manganese dioxide (2.23 g, 25.6 mmol), methyl gentisate (Aldrich) (0.430 g, 2.56 mmol) and 2-trimethylsilyloxyfuran **3** (0.44 mL,2.56 mmol) in dichloromethane (50 mL). The solvent was removed under reduced pressure to yield dihydrobenzofuran **31** (0.416 g, 65%) as white crystals, m.p. 170-172 °C (lit.[26] 171.5-172.0 °C). The proton n.m.r. data were in agreement with the literature.[15]

(3aS,8bS*)-dihydro-5-phenylsulfanyl-7-hydroxyfuro[3,2-b]benzo[2,1-d]furan-2(3H)-one* **32**

The title compound was obtained from 2-phenylsulfanyl-1,4-benzoquinone[15] (126 mg, 0.583 mmol) and 2-trimethylsilyloxyfuran **3** (0.20 mL, 1.17 mmol) in dichloromethane (25 mL). The crude product was purified by flash chromatography using hexane : ethyl acetate (4:1) to yield *dihydrobenzofuran* **32** (46 mg, 26%) as an orange oil (Found: M^+, 300.0458. $C_{16}H_{12}O_4S$ requires M^+, 300.0456); υ_{max} (thin film) (cm^{-1}) 3000-3639 (OH), 1778 (γ-lactone); δ_H (200 MHz; d^6-acetone) 2.95-2.98 (2H, m, 3-H_A and 3-H_B), 5.35-5.37 (1H, m, 3a-H), 5.92 (1H, d, $J_{8b,3a}$ 6.1 Hz, 8b-H), 6.65 (1H, d, $J_{6,8}$ 2.5 Hz, 6-H), 6.85 (1H, d, $J_{8,6}$ 2.5 Hz, 8-H), 7.23-7.31 (5H, m, SPh); δ_C (50 MHz; d^6-acetone) 37.5 (CH_2, C-3), 85.5 (CH, C-3a or C-8b), 85.8 (CH, C-8b or C-3a), 120.5 (CH, C-6), 124.8 (CH, C-8), 125.4 (quat., C-5), 131.0 (CH, C-2'), 131.6 (CH, C-4'), 131.7 (quat., C-8a), 136.4 (CH, C-3'), 144.6 (quat., C-1'), 153.2 (quat., C-4a), 158.0 (quat., C-7), 176.9 (quat., C-2); *m/z* (%) 300 (M^+, 100), 255 (M-CO_2H, 60).

(3aS,8bS*)-dihydro-7-hydroxy-8-phenylsulfinylfuro[3,2-b]benzo[2,1-d]furan-2(3H)-one* **33**

The title compound was obtained from 2-phenylsulfinyl-1,4-benzoquinone[15] (93 mg, 0.40 mmol) and 2-trimethylsilyloxyfuran **3** (119 mg, 0.80 mmol) in dichloromethane (25 mL). The crude product was purified by flash chromatography using hexane : ethyl acetate (1:1) as eluent to yield dihydrobenzofuran **33** (84 mg, 66%) as a colourless solid, m.p. 153-156 °C (lit.[15] 154.5-155.5 °C). The proton n.m.r. data were in agreement with the literature.[15]

(3aS,8bS*)-dihydro-7-hydroxy-8-phenylsulfonylfuro[3,2-b]benzo[2,1-d]furan-2(3H)-one* **34**

The title compound was obtained from 2-phenylsulfonyl-1,4-dihydroxybenzene[26] (0.356 g, 1.42 mmol), manganese dioxide (1.60 g, 18 mmol) and diene **3** (0.372 g, 2.33 mmol) in dichloromethane (25 mL). The crude product was recrystallised from acetone to afford *dihydrobenzofuran* **34** (0.297 g, 63%) as colourless crystals, m.p. 136-138 °C (dec.) (Found: M^+, 332.0359. $C_{16}H_{12}O_6S$ requires M^+, 332.0354) υ_{max} (Nujol) (cm^{-1}) 3515-3138 (OH), 1779 (C=O, γ-lactone), 1370 (SO_2); δ_H (400 MHz, d^6-acetone) 2.88 (1H, d, J_{gem} 18.8 Hz, 3_A-H), 3.27 (1H, dd, J_{gem} 18.8 and $J_{3B,3a}$ 6.6 Hz, 3_B-H), 5.53-5.57 (1H, m, 3a-H), 6.71 (1H, d, $J_{8b,3a}$ 5.6 Hz, 8b-H), 7.01 (1H, d, $J_{5,6}$ 8.8 Hz, 5-H), 7.09 (1H, d, $J_{6,5}$ 8.8 Hz, 6-H), 7.58-7.62 (2H, m, 2'-H and 6'-H), 7.67-7.69 (2H, m, 3'-H and 5'-H), 8.11-8.14 (1H, m, 4'-H), 9.16 (1H, bs, OH); δ_C (100 MHz, d^6-acetone) 35.6 (CH_2, C-3), 83.6 (CH, C-3a or C-8b), 83.9 (CH, C-8b or C-3a), 118.6 (CH, C-6), 122.8 (CH, C-5), 123.5 (quat., C-8a),

128.9 (C-H, C-2'), 129.7 (quat., C-8), 129.7 (CH, C-4'), 134.5 (CH, C-3'), 142.7 (quat., C-1'), 151.3 (quat., C-4a), 156.0 (quat., C-7), 175.0 (quat., C-2); m/z (%) 332 (M+, 100), 287 (M-CO_2H, 70), 146 (M-$C_7H_6O_4S$, 45).

(3aS,8bS*)-dihydro-6-formyl-5-hydroxyfuro[3,2-b]naphtho[2,1-d]furan-8(9H)-one* **35**

The title compound was prepared from 2-formyl-1,4-dihydroxynaphthalene (109 mg, 0.58 mmol), manganese dioxide (5 g, 57 mmol) and 2-trimethylsilyloxyfuran **3** (0.6 mL, 0.59 mmol) in dichloromethane (120 mL). The solvent was removed under reduced pressure and the resultant residue purified by flash chromatography using hexane : ethyl acetate (1:1) to afford *dihydronaphthofuran* **35** (67 mg, 43%) as a tan solid, m.p. 96-98 °C; (Found: M^+, 270.0545. $C_{15}H_{10}O_5$ requires M^+, 270.0528) υ_{max} (Nujol) (cm^{-1}) 3150-3800 (OH), 1778 (C=O, γ-lactone) and 1689 (C=O, *o*-hydroxyaryl aldehyde); δ_H (400 MHz; $CDCl_3$) 3.11 (1H, dd, J_{gem} 19.2 and $J_{9A,9a}$ 2.0 Hz, 9-H_A), 3.20 (1H, dd, J_{gem} 19.2 and $J_{9B,9a}$ 7.6 Hz, 9-H_B), 5.61-5.69 (1H, m, 9a-H), 6.50 (1H, d, $J_{6b,9a}$ 6.8 Hz, 6b-H), 7.64-7.77 (2H, m, 2-H and 3-H), 7.94 (1H, d, $J_{1,2}$ 8.2 Hz, 1-H), 8.46 (1H, d, $J_{3,4}$ 9.0 Hz, 4-H), 10.16 (1H, s, CHO), 12.72 (1H, bs, OH); δ_C (100 MHz; $CDCl_3$) 35.5 (CH_2, C-9), 81.6 (CH, C-9a), 83.3 (CH, C-6b), 109.7 (quat., C-6a or C-6), 112.1 (quat., C-6 or C-6a), 122.3 (CH, C-1 or C-4), 125.1 (quat., C-10b or C-4a), 125.4 (CH, C-4 or C-1), 127.0 (quat., C-4a or C-10b), 128.0 (CH, C-2 or C-3), 131.0 (CH, C-3 or C-2), 150.0 (quat., C-10a), 158.6 (quat., C-5), 174.6 (quat., C-8), 192.9 (CHO); *m/z* (%) 270 (M^+, 100), 226 (M-CO_2, 50), 43 (M-$C_{13}H_7O_4$, 55)

5-[1,2,3,4-tetrahydro-3-(1-hydroxyethylidene)-1,4-dioxo-2-naphthyl]furan-2(5H)-one **36**

The title compound was prepared from 2-acetyl-1,4-dihydroxynaphthalene (0.109 g, 0.54 mmol), manganese dioxide (0.53 g, 5.9 mmol) and 2-(trimethylsilyloxy)furan **3** (0.093 g, 0.58 mmol) in dichloromethane (50 mL). The solvent was removed under reduced pressure and the crude residue purified by flash chromatography using hexane : ethyl acetate (1 : 1) as eluent to yield butenolide **36** (0.117 g, 76%) as a yellow solid, m.p. 191-193 °C (dec.) (lit.[16] m.p. 192-192.5 °C). The ^1H n.m.r. data were in agreement with the literaure.[16]

methyl (6bS,9aS*)-dihydro-5-hydroxy-8-oxo-6b,8,9,9a-tetrahydrofuro[3,2-b]naphtho[2,1-d]furan-6-carboxylate* **37**

The title compound was prepared from methyl 1,4-dioxo-1,4-dihydronaphthalene-2-carboxylate[27] (432 mg, 2 mmol), manganese dioxide (1.36 g, 16 mmol) and 2-trimethylsilyloxyfuran **3** (312 mg, 2 mmol) in dichloromethane (120 mL). The solvent was removed under reduced pressure and the resultant residue purified by flash chromatography using hexane : ethyl acetate (1:1) to afford *dihydronaphthofuran* **37** (444 mg, 74%) as a pale yellow solid, m.p. 246-247 °C (lit.[27] m.p. 247-247.5 °C)

(6bS,9aS*)-dihydro-5-hydroxy-8-oxofuro[3,2-b]naphtho2,1-d]furan-6-carboxamide* **38**

The title compound was prepared from quinone **20** (20 mg, 0.10 mmol) and 2-trimethylsilyloxyfuran **3** (0.034 mL, 0.20 mmol) in acetonitrile (5 mL). The solvent was removed at reduced pressure and the crude residue purified by flash chromatography using hexane : ethyl acetate (1:1) as eluent to give *dihydronaphthofuran* **38** (17 mg, 60%) as a colourless solid, m.p. 247-249°C (dec.) (Found: C, 62.8; H, 4.2; N, 5.0. $C_{15}H_{11}O_5N$ requires C, 63.2; H, 3.9; N, 4.9%); υ_{max} (Nujol) (cm^{-1}) 3519 (NH), 3311 (NH), 1762 (C=O, γ-lactone), 1665 (C=O, amide); δ_H [200 MHz; $(CD_3)_2SO$] 3.02 (1H, d, J_{gem} 18.3 Hz, 9-H_A), 3.37 (1H, dd, J_{gem} 18.3 and $J_{9,9a}$ 6.2 Hz, 9-H_B), 5.80-5.84 (1H, m, 9a-H), 6.68 (1H, d, $J_{6b,9a}$ 6.2 Hz, 6b-H), 7.63-7.74 (2H, m , 2-H and 3-H), 7.89-7.92 (1H,

m, 1-H or 4-H), 8.27-8.31 (1H, m, 4-H or 1-H); δ_C [50 MHz; $(CD_3)_2SO$] 35.3 (CH_2, C-9), 81.7 (CH, C-9a), 84.8 (CH, C-6b), 106.1 (quat., C-6), 112.3 (quat., C-6a), 121.9 (CH, C-1 or C-4), 124.1 (CH, C-4 or C-1), 122.5 (quat., C-4a or C-10b), 126.8 (quat., C-10b or C-4a), 127.8 (CH, C-2 or C-3), 129.3 (CH, C-3 or C-2), 149.8 (quat., C-10a), 157.0 (quat., C-5), 171.5 (quat., $CONH_2$), 174.8 (quat., C-8); *m/z* (%) 285 (M^+, 35), 268 (M-NH_3, 100), 223 (M-NH_3CO_2H, 73).

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