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Addition of Cyclopentadiene and 2-Trimethylsilyloxyfuran to Quinones Bearing a Menthyl Ester Chiral Auxiliary

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Abstract: Addition of cyclopentadiene to 2-carbomethoxy-1,4-benzoquinone **9** afforded Diels-Alder adduct **10** using the Lewis acids $ZnCl_2$ and $ZnBr_2$ whereas the fragmenatation product **11** was the major product when using $SnCl_4$ and $TiCl_4$. Addition of cyclopentadiene to 1,4-benzoquinone **8** bearing a menthyl ester at C-2 afforded Diels-alder adduct **12** in moderate diastereomeric excess using $ZnCl_2$ and $ZnBr_2$ as Lewis acids. Use of $TiCl_4$ and $SnCl_4$ afforded the fragmentation product **13** also in moderate diastereomeric excess. Addition of 2-trimethylsilyloxyfuran to chiral naphthoquinone **4** and benzoquinone **8** afforded furofuran adducts **14** and **15** respectively as a 1:1 mixture of diastereomers.

INTRODUCTION

Asymmetric Diels-Alder reactions provide many opportunities for the stereoselective construction of various cyclic compounds in optically pure form.[1] Of the methods used to effect asymmetric Diels-Alder reactions the use of a chiral auxiliary attached to the dienophile[2] is the most common. The use of quinones as the dienophile component in Diels-Alder reactions provides access to a range of biologically active natural products.[3] In particular, Diels-Alder adducts from addition of cyclopentadiene to 1,4-benzoquinones and 1,4-naphthoquinones bearing an electron withdrawing group at C-2 can undergo fragmentation to afford a Michael acceptor which is then trapped by an incumbent hydroxyl group to form dihydrobenzofurans and dihydronaphthofurans.[4] Given that any asymmetric induction achieved in the initial Diels-Alder adduct is transferred to the fragmentation product an opportunity presents itself for preparing these compounds enantioselectively.

We have previously attempted an asymmetric variant[5] of this Diels-Alder / fragmentation[6] reaction using a range of chiral Lewis acid catalysts, however only moderate levels of enantiselectivity were observed. We therefore next turned our attention to the use of a chiral auxiliary on the quinone to control the stereochemical outcome of the reaction. The use of dienophiles bearing chiral auxiliaries based on menthol has provided high levels of stereocontrol,[7] thus we initially focussed on the use of a 1,4-benzoquinone and a 1,4-naphthoquinone containing a menthyl ester at C-2 as a means to control the facial selectivity in Diels-Alder reactions with cyclopentadiene. The use of chiral quinones as dienophiles in asymmetric Diels-Alder reactions has received little attention to date.[8]

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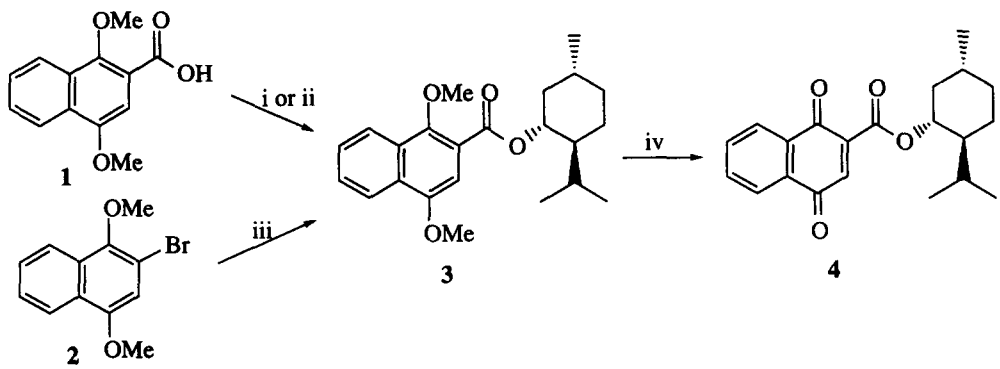
RESULTS AND DISCUSSION

Our initial attention turned to the synthesis of naphthoquinone **4** and benzoquinone **8** bearing menthyl esters at C-2 *via* oxidation of the corresponding dimethyl ethers **3** and **7**. Menthyl 1,4-dimethoxynaphthalene-2-carboxylate **3** was initially prepared (Scheme 1) from 1,4-dimethoxy-2-naphthoic acid **1** using dicyclohexylcarbodiimide, 4-dimethylaminopyridine and menthol in ether, however, the yield was only 32%. Use of a mixed anhydride generated using ethyl chloroformate and triethylamine in THF followed by addition of menthol and triethylamine only afforded a 24% yield of the desired product **3**.

An improved synthesis of menthyl ester **3** was finally realised using an orthometallation approach. Thus, 2-bromo-1,4-dimethoxynaphthalene **2** was treated with butyllithium in THF at -78°C to generate the naphthyl anion which was then added *via* cannula to (-)-menthyl chloroformate affording menthyl ester **3** in 49% yield after purification by flash chromatography. Menthyl ester **3** was often contaminated with unreacted (-)-menthyl chloroformate hence careful flash chromatography was required to obtain pure material.



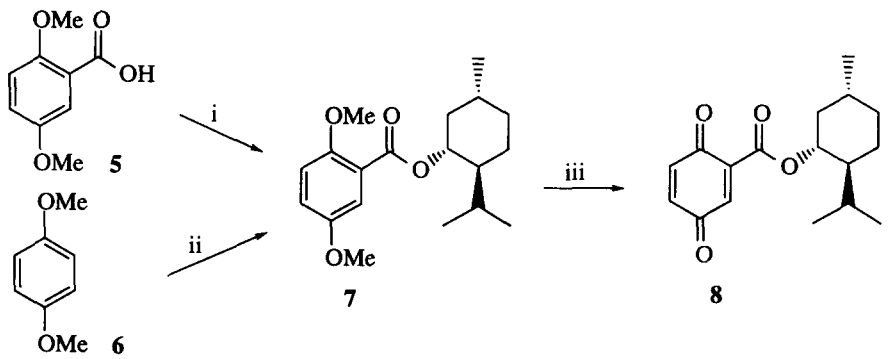
Reagents and Conditions: (i) DCC, DMAP (cat.), Et_2O, (-)-menthol, -78 °C to room temp., 32% ; (ii) EtCOCl, Et_3N, THF then (-)-menthol, Et_3N, 24%; (iii) BuLi, THF, -78 °C, 15 min. then (-)-menthyl chloroformate, 2 h., 49%; (iv) AgO, HNO_3, dioxane.

Scheme 1

Elemental analysis and high resolution mass spectroscopy established the molecular formula $C_{23}H_{30}O_4$ for the menthyl ester **3**, whilst the IR spectrum displayed the typical ester (C=O) stretch at 1713 cm^{-1}. The ^1H NMR spectrum exhibited features consistent with formation of menthyl ester **3**. Two singlets at δ 3.99 and δ4.01 each integrating for three protons supported the presence of two methoxy groups. The aromatic region exhibited a pattern characteristic of a 1,2,4-trisubstituted naphthalene ring system, whilst the aliphatic region gave characteristic peaks for a menthyl group. The material was optically active with an optical rotation $[\alpha]_D^{20}$ -55°. Oxidative demethylation of the dimethyl ether **3** was achieved using freshly prepared silver(II) oxide (8 mol equivalent) and nitric acid in dioxane. 1,4-Naphthoquinone **4** was then used directly without subsequent purification in Diels-Alder reactions.

Benzoquinone menthyl ester **8** was conveniently prepared (Scheme 2) by treating 2,5-dimethoxybenzoic acid **5** with thionyl chloride under reflux for three hours affording the acid chloride which was then treated directly with (-)-menthol affording the menthyl ester **7** in 68% yield. Oxidation of dimethyl ether **7** to

benzoquinone **8** was readily achieved using silver(II) oxide and nitric acid. This method proved to be superior to the orthometallation method used to prepare the corresonding naphthoquinone **4**.



Reagents and Conditions: (i) excess $SOCl_2$, reflux, 3h. then (-)-menthol, 24 h., 68% ; (ii) BuLi, THF, -78 °C, 20 min. then (-)-menthyl chloroformate, 2 h., 49%; (iii) AgO, HNO_3, dioxane.

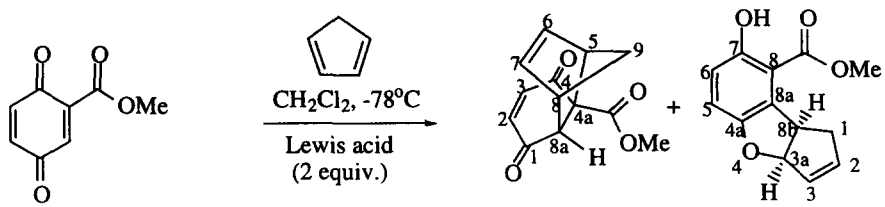
Scheme 2

Before studying the addition of chiral benzoquinone **8** to cyclopentadiene the Diels-Alder reaction of the achiral methyl ester benzoquinone **9** was investigated in order to establish the optimum catalyst and reaction conditions to afford the desired adducts in good yield. It was then envisaged that the optimum conditions for dienophile **9** could then be translated for use with the chiral menthyl ester dienophile **8**.

Benzoquinone **9** was treated with freshly distilled cyclopentadiene at -78 °C in dichloromethane in the presence of six different Lewis acids. The formation of two products, namely, Diels-Alder adduct **10** and/or fragmentation product **11** (Scheme 3), were observed depending on the nature of the catalyst used (Table 1). The use of milder Lewis acids such as zinc(II) chloride, zinc(II) bromide and titanium(IV) isopropoxide afforded the *endo* Diels-Alder adduct **10** for which the spectral characteristics were in agreement with the literature.[9] The stronger Lewis acids titanium(IV) chloride and tin(IV) chloride afforded the fragmentation product **11** whereas $TiCl_2(O^iPr)_2$ afforded a mixture of **10** and **11**.

The structure of the fragmentation product **11** was established as follows. Elemental analysis and high resolution mass spectrometry established the molecular formula to be $C_{13}H_{12}O_4$ and the IR spectrum exhibited an OH stretch. The ^1H NMR spectrum showed two multiplets at δ 4.33 and δ 5.70-5.73, *J* 8.7 Hz, suggesting the presence of two ortho coupled aromatic protons and a phenolic proton was observed at δ 10.40. Two olefinic protons resonated as multiplets at δ 5.83-5.86 and δ 5.97-5.99 whilst resonances at δ 4.33 and δ 5.72 were assigned to H-8b and H-3a and the singlet at δ 4.00 established the presence of the methyl ester.

The fragmentation product **11** is thought to arise *via* initial formation of the Diels-Alder adduct **10**. Coordination of the Lewis acid to the carbonyl group of the enedione allows bond cleavage between C-4a and C-5 to occur leading to formation of the dihydrobenzofuran **11**. Treatment of the Diels-alder adduct **10** with tin(IV) chloride in dichloromethane at -78 °C for 15 min. did in fact lead to formation of the fragmentation product **11** in near quantitative yield. Dihydrobenzofuran **11** was reasonably unstable to flash chromatography on silica gel and florisil. The crude yield for this reaction was satisfactory, however attempted purification by chromatography incurred large losses.



9 (±)-10 (±)-11

Lewis Acid Used	% Yield 10	% Yield 11
$ZnCl_2$	57	-
$ZnBr_2$	55	-
$Ti(O^iPr)_4$	65	
$TiCl_2(O^iPr)_2$	66	22
$TiCl_4$	-	83
$SnCl_4$	-	93

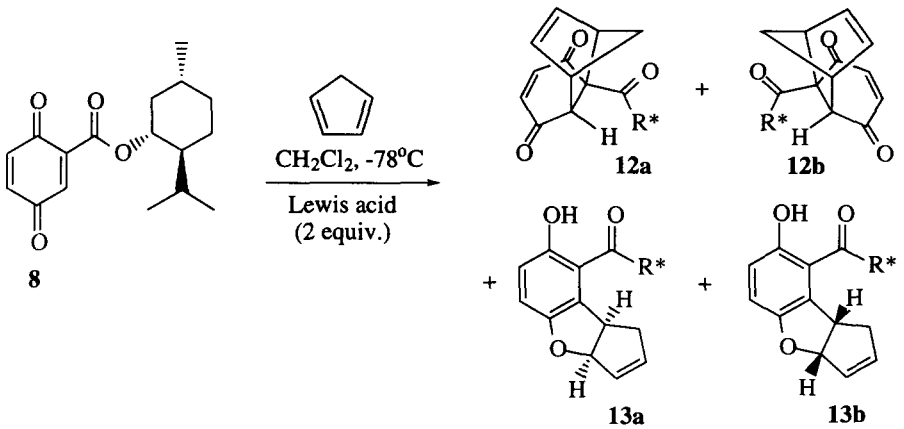
Scheme 3

Having studied the reaction of methyl ester benzoquinone **9** with cyclopentadiene, we were in a position to study the diastereoselectivity in the Diels-Alder addition of menthyl ester benzoquinone **8** to cyclopentadiene (Scheme 4). Use of the weaker Lewis acid catalysts zinc(II) chloride and zinc(II) bromide afforded Diels-Alder adduct **12** as a 3:1 and 2:1 inseparable mixture of diastereomers respectively. The formation of two *endo* adducts was established upon interpretation of the crude ^1H NMR spectrum which exhibited doublets for the bridgehead proton of the norbornene ring, H-8, at δ 1.85 (major isomer) and δ 1.86 (minor isomer) with the magnitude of the coupling to the vicinal *exo* proton at C-8a, J 3.90 Hz, confirming the formation of the kinetically favoured *endo* isomers. The ratio of the two *endo* adducts was established by integration of the double double doublets observed for each of the CHOR protons of the menthyl group for the two isomers.

The stronger Lewis acids, titanium(IV) chloride and tin(IV) chloride afforded the fragmentation product **13** as a 2:1 inseparable mixture of diastereomers in both cases. Once again the diastereomeric excess was also established by integration of CHO protons observed for menthyl group of each diastereomer. Fragmentation products **11** and **13** contain the ring system that is present in the benzoprostacyclins, important biological analogues of prostacyclin, (PGI_2),[10] however only moderate levels of asymmetric induction were achieved in the present work.

A key step in our synthesis of pyranonaphthoquinone antibiotics, e.g. kalafungin, frenolicin and the arizonins,[11] involves the addition of 2-trimethylsilyloxyfuran (TMS-furan) to an activated quinone. The furonaphthofuran adducts thus formed undergo facile oxidative rearrangement to the pyranonaphthoquinone ring system present in the naturally occurring antibiotics. To date our syntheses of these antibiotics has only been achieved in racemic form with no control over the absolute stereochemistry of the bridgehead protons. It was therefore proposed that attachment of a chiral auxiliary to C-2 of the naphthoquinone framework may lead to unequal formation of the diastereomeric TMS-furan adducts. Subsequent separation of the

diastereomeric adducts followed by removal of the chiral auxiliary then provides the furonaphthofuran adducts and hence the pyranonaphthoquinone ring system, in enantiomeric excess. With these ideas in mind the addition of TMS-furan to menthyl ester naphthoquinone **4** and benzoquinone **8** was undertaken.



Lewis Acid Used	% Yield 12	% Yield 13	d.r. 12#	d.r. 13#
$ZnCl_2$	80	-	3:1	
$ZnBr_2$	55	-	2:1	
$TiCl_4$	-	81	-	2:1
$SnCl_4$	-	82	-	2:1

Note that the absolute configuration of the dominant diastereomer is not known.

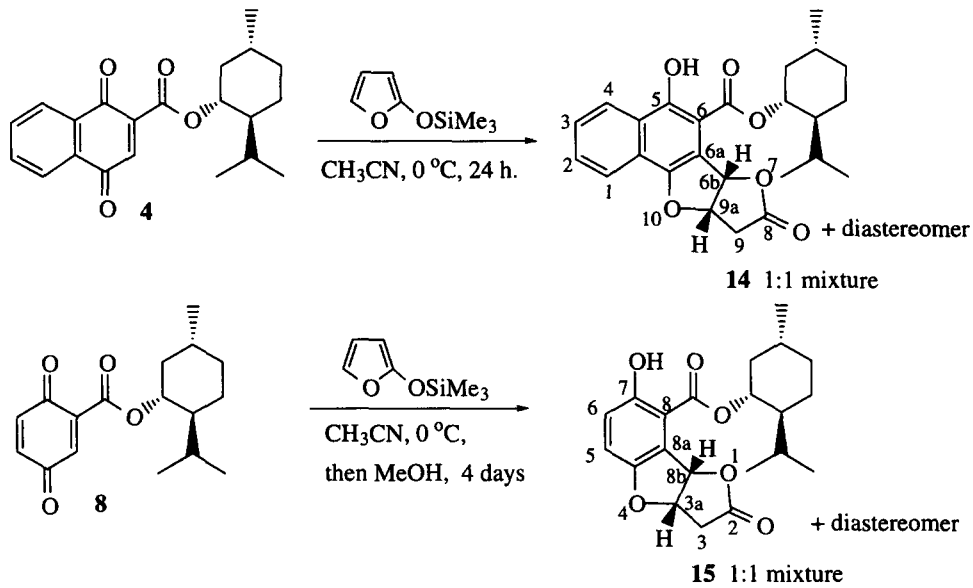
Scheme 4

Addition of TMS-furan to naphthoquinone **4** at 0 °C for 24 h. afforded furonaphthofuran **14** as a 1:1 inseparable mixture of diastereomers (Scheme 5). Evidence for the formation of two diastereomers was provided by the ^{1}H NMR spectrum which exhibited two doublets in a 1:1 ratio at δ 6.45 and δ 6.53 assigned to the bridgehead proton, H-6b, of the individual isomers. A 1:1 inseparable mixture of furobenzofurans **15** was obtained in 49% yield upon analogous reaction of benzoquinone **8** with TMS-furan, however, in this case methanol was added to the reaction mixture and a longer reaction time was required (4 days).

Adduct **15** was also a mixture of the two diastereomers. Evidence for this was provided by analysis of the ^{1}H NMR spectrum which exhibited two doublets at δ 0.78 and δ 0.82 assigned to the 5'-Me group of the two diastereomers in a ratio of 1:1. Duplicate signals in the ^{13}C NMR spectrum were observed providing additional confirmation that the two diastereomers were isolated as an inseparable mixture. The 1:1 diastereomeric ratio indicated no asymmetric induction had occurred in this furofuran annulation. A possible means to improve the diastereoselectivity of this addition could be to use a Lewis acid.

It has been well documented that Lewis acid coordination to menthyl acrylates increases the regio- and *endo*-selectivity in their [4+2] addition to 1,3-dienes.[12] More importantly, successful asymmetric Diels-Alder reactions have been carried out using menthyl acrylate dienophiles at low temperature in the presence of a

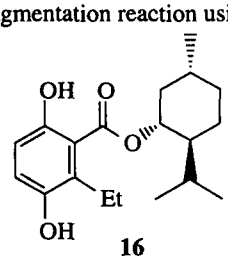
Lewis acid catalyst, in particular diethylaluminium chloride. Thus, it is envisaged that similar effects may be operative in the coordination of menthyl ester benzoquinone **8** to a Lewis acid which may well lead to a subsequent asymmetric addition of TMS-furan. With this in mind the addition of diethylaluminium chloride to quinone **8** was explored as a possible means of creating a diastereomeric excess in the formation of adduct **15**.



Scheme 5

A solution of quinone **8** was cooled to -30°C and diethylaluminium chloride (1 mol equivalent) was added followed by TMS-furan (1 mol equivalent) and the reaction mixture left to stir for 3 days. Flash chromatography afforded the dihydroquinone **16** in 39% yield as the sole product resulting from the direct conjugate addition of the ethyl group from the Lewis acid to the quinone **8**. No furonaphthofuran adduct **15** was observed. Use of other Lewis acids e.g. $BF_3.Et_2O$, $TiCl_4$, $TiCl_2(O^iPr)_2$, $SnCl_4$, $MgBr_2$, $Cu(OTf)_2$ and $ZnBr_2$ led to complex mixtures.

In summary, the addition of cyclopentadiene and TMS-furan to benzoquinone **8** bearing a chiral menthyl ester group at C-2 has been studied. Moderate diastereocontrol was observed in the Diels-Alder addition of cyclopentadiene and the ratio of Diels-Alder adduct **10** to fragmentation product **11** was dependant on the Lewis acid used. No stereocontrol was observed in the addition of TMS-furan to chiral benzoquinone **8** or naphthoquinone **4**. The work reported herein represents the first study of the development of an asymmetric variant of this Diels-Alder / fragmentation reaction using chiral quinones as dienophiles.



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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 70 eV. 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 Otago, New Zealand. Flash chromatography was performed using Merck Kieselgel 60 (230-400 Mesh) with the indicated solvents.

1,4-Dimethoxy-2-naphthoic acid **1**. A solution of 1,4-dimethoxynaphthalene[13] (4.7 g, 0.025 mmol) in cyclohexane (10 cm^3) was added under nitrogen to a mixture of *n*-butyllithium (2.1 M solution in hexane, 11.9 cm^3, 0.025 mmol) and tetramethylethylenediamine (2.9 g, 0.025 mmol) in cyclohexane (5 cm^3). The mixture was stirred at room temperature for 2 h., then poured onto a slurry of anhydrous ether and powdered solid carbon dioxide. Excess hydrochloric acid was then added and the solution extracted with ethyl acetate (3 x 60 cm^3). The organic layer was extracted with 10% sodium hydrogen carbonate solution (3 x 60 cm^3) and the aqueous layer was again acidified with hydrochloric acid and extracted with ethyl acetate (3 x 60 cm^3). The combined organic extracts were dried over $MgSO_4$ and the solvent was removed at reduced pressure to give the title compound as a colourless solid (3.3 g, 56%); mp 165-167 °C (lit.[14] mp 167-168 °C).

(1'R, 2'S, 5'R)-(-)-Menthyl 1,4-dimethoxy-2-naphthoate **3**. *(i) from 1,4-dimethoxy-2-naphthoic acid* **1**. Naphthoic acid **1** (201 mg, 0.87 mmol) and (1'*R*, 2'*S*, 5'*R*)-(-)-menthol (146 mg, 0.93) were dissolved in diethyl ether (5 cm^3) and cooled to -78 °C under nitrogen. A solution of dicyclohexylcarbodiimide (178 mg, 0.86 mmol) and 4-dimethylaminopyridine (7 mg, 0.06 mmol) in diethyl ether (5 cm^3) was added and the mixture stirred for 16 h. whilst warming to room temperature. The mixture was filtered and washed with dilute hydrochloric acid (5 cm^3). Drying ($MgSO_4$) and removal of solvent at reduced pressure afforded a yellow residue which was purified by flash chromatography using hexane-ethyl acetate (35:1) as eluent to give the *title compound* **3** (101 mg, 32%) as a colourless oil, $[\alpha]_D^{20}$ -55° (c, 0.774, $CHCl_3$); (Found: C, 74.5; H, 8.0. $C_{23}H_{30}O_4$ requires C, 74.6; H, 8.2%); ν_{max} (nujol)/cm^{-1} 1713 (C=O); δ_H (200 MHz; $CDCl_3$) 0.85 (1H, d, *J* 6.6, 5'-Me), 0.88-0.97 [6H, m, Me(^{i}Pr)], 1.01-2.29 (9H, m, 3 x CH_2, 2'-H, 5'-H, C*H*Me$_2$), 3.99 (3H, s, 4-OMe), 4.01 (3H, s, 1-OMe), 5.04 (1H, ddd, $J_{1'ax,6'ax}$ 12.9, $J_{1'ax,2'ax}$ 12.9 and $J_{1'ax,6'eq}$ 4.4, 1'ax-H), 7.14 (1H, s, 3-H), 7.56-7.60 (2H, m, 6-H and 7-H) and 8.19-8.26 (2H, m, 5-H and 8-H); δ_C (50 MHz; $CDCl_3$) 16.3 [q, Me(^{i}Pr)], 20.9 [q, Me(^{i}Pr)], 22.1 (q, 5'-Me), 26.2 (d, CHMe$_2$), 31.4 (d, C-5'), 34.3 (t, C-4'), 40.9 (t, C-6'), 47.2 (d, C-2'), 55.7 (q, 4-OCH_3), 63.3 (q, 1-OCH_3), 75.1 (d, C-1'), 103.6 (d, C-3), 119.8 (s, C-2), 122.3, 123.4 (d, C-5, C-8), 127.0, 127.5 (d, C-6, C-7), 128.5, 129.2 (s, C-4a, C-8a), 151.3, 151.4 (s, C-1, C-4) and 166.2 (s, C=O); *m/z* 370 (*M*$^+$, 43%), 232 (*M*-$C_{10}H_{18}$, 100) and (*M* -$C_{11}H_{21}$, 35). *(ii) from 2-bromo-1,4-dimethoxynaphthalene* **3**. To a solution of 2-bromo-1,4-dimethoxynaphthalene **2**[15] (253 mg, 0.95 mmol) in THF (10 cm^3) cooled to -78°C, was added *n*-butyllithium (0.66 cm^3 of a 1.43 mol dm^{-3} solution) dropwise under nitrogen. The mixture was stirred for 15 min then transferred *via* cannula under

positive nitrogen pressure to a cooled solution (-78°C) of (1*R*, 2*S*, 5*R*)-(-)-menthyl chloroformate (0.204 cm^3, 0.95 mmol) in THF (8 cm^3). The mixture was stirred at -78°C for 2 h., quenched with saturated aqueous ammonium chloride (10 cm^3) then extracted with dichloromethane (30 cm^3). The organic phase was dried ($MgSO_4$) and the solvent removed under reduced pressure to give a yellow oil. Flash chromatography using hexane-ethyl acetate (34:1) as eluent provided the *title compound* **3** (175 mg, 49%) as a colourless oil for which the NMR data and optical rotation were in agreement with that reported above.

(1'R, 2'S, 5'R)-(-)-Menthyl 2,5-dimethoxybenzoate **7**. *(i) from 1,4-dimethoxy-2-benzoic acid* **5**.
2,5-Dimethoxybenzoic acid (500 mg, 2.74 mmol) was heated under reflux with thionyl chloride (650 mg, 5.48 mmol) for 3 h. The reaction mixture was allowed to cool to room temperature and (1'*R*, 2'*S*, 5'*R*)-(-)-menthol (427 mg, 2.74 mmol) was added. The reaction mixture was stirred for 24 h., quenched with water (5 cm^3) and extracted into ethyl acetate (10 cm^3). After washing with 10% sodium bicarbonate (5 cm^3), water (2 x 5 cm^3) and drying (MgSO4), the solvent was removed at reduced pressure to give the a pale brown oil that was purified by flash chromatography using hexane-ethyl acetate (4:1) as eluent affording the *title compound* **7** (597 mg, 68%) as a colourless oil, $[\alpha]_D^{20}$ -74° (c, 0.10, CH_2Cl_2); (Found: C, 70.9; H, 8.8. $C_{19}H_{28}O_4$ requires C, 71.2; H, 8.8%); ν_{max} (nujol)/cm^{-1} 1723s (C=O); δ_H (400 MHz; $CDCl_3$) 0.78 (3H, d, *J* 7.0, 5'-Me), 0.88 [3H, d, *J* 5.6, Me(^{i}Pr)], 0.91 [3H, d, *J* 5.9, Me(^{i}Pr)], 1.04-2.19 (9H, m, 3 x CH_2, 2'-H, 5'-H, C*H*Me_2), 3.74 (3H, s, 5-OMe), 3.79 (3H, s, 2-OMe), 4.88 (1H, ddd, $J_{1'ax,6'ax}$ 10.9, $J_{1'ax,2'ax}$ 10.9, $J_{1'ax,6'eq}$ 4.4, 1'ax-H), 6.87 (1H, s, 6-H), 6.94 (1H, d, $J_{3,4}$ 3.2, 3-H or 4-H) and 7.27 (1H, d, $J_{4,3}$ 3.2, 4-H or 3-H); δ_C (100 MHz; $CDCl_3$) 16.2 [q, Me(^{i}Pr)], 21.0 [q, Me(^{i}Pr)], 22.1 (q, 5'-Me), 23.3 (t, C-3'), 26.1 (d, C*H*Me_2), 31.4 (d, C-5'), 34.3 (t, C-4'), 40.9 (t, C-6'), 47.2 (d, C-2'), 55.8 (q, 5-OCH_3), 56.7 (q, 2-OCH_3), 74.9 (d, C-1'), 113.9 (d, C-6), 116.1, 118.5 (d, C-3, C-4), 121.8 (s, C-1), 153.0, 153.3 (s, C-2, C-5) and 165.7 (s, C=O); *m/z* 320 (M^+, 20%) and 182 (M-$C_{10}H_{18}$, 100).
(ii) from 1,4-dimethoxynaphthalene **6**. To a solution of 1,4-dimethoxybenzene **6** (1 g, 7.24 mmol) in THF (20 cm^3) was added *n*-butyllithium (5.06 cm^3 of a 1.43 mol dm^{-3} solution) at room temperature under nitrogen. After stirring at room temperature for 1 h., the mixture was cooled to -78°C for 20 min. then transferred *via* cannula to a cooled soluton (-78°C) of (1*R*, 2*S*, 5*R*)-(-)-menthyl chloroformate (1.55 cm^3, 7.24 mmol) in THF (15 cm^3). The mixture was stirred for 2 h. at -78°C then quenched with saturated aqueous ammonium chloride (20 cm^3) and water (20 cm^3). After extraction into dichloromethane (50 cm^3) and drying ($MgSO_4$) the solvent was removed at reduced pressure to give an orange oil. Flash chromatography using hexane-ethyl acetate (34:1) as eluent gave the *title compound* **7** (1.14 g, 49%) as a colourless oil for which the NMR data and optical rotation were in agreement with that reported above.

(1'R, 2'S, 5'R)-(-)-Menthyl 1,4-dioxocyclohexa-2,5-diene-2-carboxylate **8**. Menthyl ester **7** (99 mg, 0.309 mmol) and freshly prepared AgO[16] (153 mg, 1.24 mmol) were mixed in dioxane (5 cm^3). HNO_3 (6 mol dm^{-3}, 0.3 cm^3) was added and the mixture stirred in air for 5 min., after which time further AgO (158 mg, 1.27 mmol) and HNO_3 (6 mol dm^{-3}, 0.3 cm^3) were added. After stirring for 5 min, water (10 cm^{-3}) was added and the reaction mixture extracted with chloroform (25 cm^3). The organic extract was washed with water (2 x 10 cm^3), dried ($MgSO_4$) and the solvent removed under reduced pressure affording the *title compound* **8** (80 mg, 89%) as an orange oil which was used without further purification in the next step, $[\alpha]_D^{20}$ -74° (c, 0.24, CH_2Cl_2); ν_{max}(nujol)/cm^{-1} 1736 (ester) and 1660s (C=O); δ_H (200 MHz; $CDCl_3$) 0.76 (3H, d, *J* 6.1, 5'-Me),

0.93-0.98 [6H, m, Me(^{i}Pr)], 1.05-2.15 (9H, m, 3 x CH_2, 2'-H, 5'-H, C*H*Me$_2$), 4.87 (1H, ddd, $J_{1'ax,6'ax}$ 10.8, $J_{1'ax,2'ax}$ 10.8 and $J_{1'ax,6'eq}$ 4.4, 1'ax-H), 6.79 (2H, s, 5-H and 6-H) and 6.98 (1H, s, 3-H); δ_C (50 MHz; $CDCl_3$) 16.2 [q, Me(^{i}Pr)], 20.8 [q, Me(^{i}Pr)], 21.9 (q, 5'-Me), 23.1 (t, C-3'), 25.9 (d, C*H*Me$_2$), 31.4 (d, C-5'), 34.3 (t, C-4'), 40.5 (t, C-6'), 46.9 (d, C-2'), 76.6 (d, C-1'), 135.1 (d, C-3), 135.9, 136.6 (s, C-5, C-6), 138.2 (s, C-2), 162.1 (s, C=O), 182.7 (s, C-4) and 186.4 (s, C-1); *m/z* 292 (*M*$^+$+2, 3%), 154 (*M*-$C_{10}H_{18}$, 54), 95 (100).

2-(Carbomethoxy)-1,4-benzoquinone **9**. 2-(Carbomethoxy)-1,4-benzoquinone **9** was prepared as an orange oil from methyl 1,4-dihydroxybenzoate *via* oxidation with manganese dioxide in benzene according to the literature.[17]

endo-4a-Methoxycarbonyl-4a,5,8,8a-tetrahydro-5,8-methano-1,4-naphthoquinone **10.** To a stirred solution of benzoquinone **9** (500 mg, 3.62 mmol) and freshly distilled cyclopentadiene (311 mg, 4.71 mmol) in dichloromethane (25 cm^3) was added two mole equivalents of Lewis acid (Table). The reaction mixture was stirred for 1 h. at –78°C under nitrogen, quenched with water (15 cm^3) and extracted with dichloromethane (50 cm^3). The organic layer was washed with water (2 x 15cm^3) and dried over $MgSO_4$. The solvent was removed under reduced pressure to give a yellow oil. Further purification by flash chromatography using hexane-ethyl acetate (4:1) as eluent afforded the *title compound* **10** for which the ^{1}H NMR data was in agreement with that reported by Narazaki and Naemura.[9]

Lewis Acid Used	Yield
$ZnCl_2$ (978 mg, 7.24 mmol)	479 mg, 57%
$ZnBr_2$ (1.63 g, 7.24 mmol)	462 mg, 55%
$Ti(O^iPr)_4$ (2.05 g, 7.24 mmol	546 mg, 65%
$TiCl_2(O^iPr)_2$ (1.72 g, 7.24 mmol	554 mg, 66%

(3aR, 8bR*)-Methyl 7-Hydroxy-1H-cyclopenta[b]benzofuran-8-carboxylate* **11**. To a solution of quinone **9** (500 mg, 3.62 mmol) and freshly distilled cyclopentadiene (311 mg, 4.71 mmol) in dichloromethane (25 cm^3), was added one mole equivalent of Lewis acid (Table). The solution was stirred at –78 °C under nitrogen for 10 min., quenched with water (15 cm^3), and extracted into dichloromethane (50 cm^3). The organic layer was washed with water (2 x 15 cm^3) and dried over $MgSO_4$. The solvent was removed under reduced pressure to give a colourless solid. Recrystallisation from benzene afforded the *title compound* **11** (Found: C, 66.8; H, 5.6, $C_{13}H_{12}O_4$ requires C, 66.9; H 5.6%); ν_{max} (nujol/cm^{-1} 3377 (OH); 1712 (C=O); δ_H (400MHz; $CDCl_3$) 2.36-2.34 (1H, m, 1β-1H), 2.89-2.97 (1H, m, 1α-H), 4.00 (3H, s, Ome), 4.33 (1H, td, $J_{1\beta,8b}$ 8.71, $J_{1\alpha,8b}$ 3.03, 8b-H), 5.70-5.73 (1H, m, 3a-H), 5.83-5.86 (1H, m, 2H), 5.97-5.99 (1H, m, 3-H), 6.70 (1H, d, *J* 8.8, 6-H), 6.83 (1H, d, *J* 8.8, 5-H), 10.4 (1H, s, OH); δ_C (100MHz; $CDCl_3$) 42.1 (t, C-1), 46.2 (d, C-8b), 52.2 (q, OMe), 92.1 (d, C-3a), 109.1 (s, C-8a), 131.2 (s, C-8), 117.2 (d, C-6), 117.6 (d, C-5), 129.3 (d, C-2), 136.2 (d, C-3), 151.5 (s, C-4a), 156.4 (s, C-7), 168.1 (s, C=O); *m/z* 232 (M$^+$, 40), 201 (M$^+$-OMe. 100).

Lewis Acid Used	Yield
$SnCl_4$ (943 mg, 3.62 mmol)	781 mg, 93%
$TiCl_4$ (686 mg, 3.62 mmol)	697 mg, 83%
$TiCl_2(O^iPr)_2$ (857 mg, 3.62 mmol)	185 mg, 22%

endo-4a-(1'R, 2'S, 5"S)-(-)-Menthoxycarbonyl-4a,5,8,8a-tetrahydro-5,8-methano-1,4-naphthoquinone **12**. To a stirred solution of benzoquinone **8** (500 mg, 1.72 mmol) and freshly distilled cyclopentadiene (311 mg, 4.71 mmol) in dichloromethane (25 cm^3) was added two mole equivalents of Lewis acid (Table). The reaction mixture was stirred for 3 h. at –78°C under nitrogen, quenched with water (15 cm^3) and extracted with dichloromethane (50 cm^3). The organic layer was washed with water (2 x 15cm^3) and dried over $MgSO_4$. The solvent was removed under reduced pressure to give a yellow oil. Further purification by flash chromatography using hexane-ethyl acetate (4:1) as eluent afforded the *title compound* **12** as a colourless oil; $[\alpha]_D^{20}$ -72° (c, 0.01, CH_2Cl_2); (Found: C, 74.2; H, 7.9. $C_{22}H_{28}O_4$ requires C, 74.1; H, 7.9%); ν_{max}(nujol)/cm^{-1} 1743 (C=O); δ_H (400 MHz; $CDCl_3$) 0.78 (3H, d, *J* 7.0, 5'-Me), 0.88 [3H, d, *J* 7.0, Me(^{i}Pr)], 0.91 [3H, d, *J* 7.0, Me(^{i}Pr)], 1.04-2.19 (9H, m, 3 x CH_2, 2'-H, 5'-H, C*H*Me_2), 1.85-2.01 (2H, m, 9-H), 3.29 (1H, d, *J* 3.9, 8a-H), 3.70-3.75 (1H, m, 5-H), 4.70 (1H, ddd, $J_{1'ax,6'ax}$ 10.9, $J_{1'ax,2'ax}$ 10.9 and $J_{1'ax,6'eq}$ 4.4, 1'ax-H), 6.01-6.06 (2H, m, 6-H, 7-H), 6.55 (2H, s, 2-H, 3-H); δ_C (100 MHz; $CDCl_3$) 16.2 [q, Me(^{i}Pr)], 20.8 [q, Me(^{i}Pr)], 21.8 (q, 5'-Me), 23.2 (t, C-3'), 26.1 (d, C*H*Me_2), 31.4 (d, C-5'), 34.0 (t, C-4'), 40.4 (t, C-6'), 46.8 (d, C-2'), 48.0 (t, C-9), 48.1 (d, C-8), 51.6 (d, C-5), 54.3 (s, C-4a), 76.3 (d, C-1'), 76.4 (d, C-8a), 136.3, 136.9 (d, C-6, C-7), 141.1, 141.3 (d, C-2, C-3), 169.9 (s, C=O), 194.8 (s, C-1), 197.8 (s, C-4); *m/z* 356 (*M*$^+$, 30%), 290 (*M*-C_5H_6, 100) and 218 (25).

Lewis Acid Used	Yield
$ZnCl_2$ (469 mg, 3.44 mmol)	490 mg, 80%
$ZnBr_2$ (775 mg, 3.44 mmol)	337 mg, 55%

(1'R, 2'S, 5"S, 3aR, 8bR*)-(-)-Menthyl 7-Hydroxy-1H-cyclopenta[b]benzofuran-8-carboxylate* **13**. To a solution of quinone **8** (500 mg, 1.72 mmol) and freshly distilled cyclopentadiene (311 mg, 4.71 mmol) in dichloromethane (25 cm^3) at –78 °C, was added one mole equivalent of Lewis acid (Table). The solution was stirred at –78 °C under nitrogen for 10 min., quenched with water (15 cm^3), and extracted into dichloromethane (50 cm^3). The organic layer was washed with water (2 x 15 cm^3) and dried over $MgSO_4$. The solvent was removed under reduced pressure to give a colourless solid. Recrystallisation from benzene afforded the *title compound* **13** as a colourless oil, $[\alpha]_D^{20}$ -50° (c, 0.02, CH_2Cl_2); (Found: C, 74.2; H, 7.9. $C_{22}H_{28}O_4$ requires C, 74.1; H, 7.9%); ν_{max}(nujol)/cm^{-1} 3369 (OH), 1743 (C=O); δ_H (400 MHz; $CDCl_3$) 0.79 (3H, d, *J* 6.9, 5'-Me), 0.85 [3H, d, *J* 7.1, Me(^{i}Pr)], 0.93 [3H, d, *J* 7.1, Me(^{i}Pr)], 1.09-2.19 (9H, m, 3 x CH_2, 2'-H, 5'-H, C*H*Me_2), 2.47-2.56 (1H, m, 1β-H), 2.97-3.05 (1H, m, 1α-H), 4.34-4.41 (1H, m, 8b-H), 5.04 (1H, ddd, $J_{1'ax,6'ax}$ 10.9, $J_{1'ax,2'ax}$ 10.9 and $J_{1'ax,6'eq}$ 4.4, 1'ax-H), 5.79 (1H, dd, $J_{3a,8b}$ 9.1, $J_{3a,3}$ 9.1, 3a-H), 5.91-5.96 (1H, m, 2-H), 6.07-6.08 (1H, m, 3-H), 6.78 (1H, d, *J* 8.7, 6-H), 6.90 (1H, d, *J* 8.8, 5-H), 10.8 (1H, s, OH); δ_C (100 MHz; $CDCl_3$) 16.0 [q, Me(^{i}Pr)], 21.9 [q, Me(^{i}Pr)], 21.9 (q, 5'-Me), 23.3 (t, C-3'), 26.3 (d, C*H*Me_2), 31.5 (d, C-5'), 34.1 (t, C-4'), 40.6 (t, C-6'), 42.8 (t, C-1), 46.2 (d, C-8b), 47.3 (d, C-2'), 75.2 (d, C-1'), 92.0 (d, C-3a), 109.0, 130.9 (s, C-8, C-8a), 117.2 (d, C-6), 117.6 (d, C-5), 129.3 (d, C-2), 136.4 (d, C-3), 156.7 (s, C-7, C-4a), 169.7 (s, C=O); *m/z* 356 (*M*$^+$, 5%), 218 (*M*$^+$-$C_{10}H_{18}$, 95) and 201 (*M*$^+$-$C_{10}H_{18}O$, 95)

Lewis Acid Used	Yield
$SnCl_4$ (448 mg, 1.72 mmol)	501 mg, 82%
$TiCl_4$ (327 mg, 1.72 mmol)	495 mg, 81%

(1'R, 2'S, 5'R, 6bR, 9aR*)-(-)-Menthyl 6b,8,9a,9-Tetrahydro-5-hydroxy-8-oxofuro[3,2-b]naphtho[2,1-d]furan-6-carboxylate* **14**. Menthyl ester **3** (167 mg, 0.45 mmol) and AgO (223 mg, 1.80 mmol) were mixed in dioxane (4 cm^3). HNO_3 (6 mol dm^{-3}, 0.40 cm^3) was added and the reaction mixture stirred for 5 min., after which time further AgO (220 mg, 1.78 mmol) and HNO_3 (6 mol dm^{-3}, 0.40 cm^3) were added. After stirring for 10 min., the reaction was quenched with water (10 cm^3) and extracted into chloroform (25 cm^3). The organic phase was washed with water (2 x 20 cm^3), dried ($NaSO_4$) and the solvent removed under reduced pressure to give the crude quinone **4** as an orange oil. The oil was redissolved in acetonitrile (5 cm^3) and 2-trimethylsilyloxyfuran (70.4 mg, 0.45 mmol) was added under nitrogen at 0°C. After stirring for 24 h. the solvent was removed under reduced pressure to give a red oil. Flash chromatography using hexane-ethyl acetate (9:1) as eluent afforded the *title compound* **14** (107 mg, 56%) as an off white solid and as a 1:1 mixture of diastereomers, m.p. 71-73°C; $[\alpha]_D^{20}$ -28° (c, 0.458, $CHCl_3$); (Found: M^+, 424.1886. $C_{25}H_{28}O_6$ requires M^+, 424.1886); ν_{max} (nujol)/cm^{-1} 1781 (C=O, lactone) and 1721 (C=O, ester); δ_H (200 MHz; $CDCl_3$) 0.79-0.97 (9H, m, 3 x Me), 1.12-2.16 (9H, m, 3 x CH_2, 2'-H, 5'-H, C*H*Me_2), 3.13-3.16 (2H, m, 9-H), 5.05-5.22 (1H, m, 1'-H), 5.45-5.55 (1H, m, 9a-H), 6.45 (1H, d, $J_{6b,9a}$ 6.2, 6b-H), 6.53* (1H, d, $J_{6b,9a}$ 6.2, 6b-H), 7.62-7.70 (2H, m, 2-H and 3-H), 7.93 (1H, m, 1-H or 4-H) and 8.43 (1H, m, 4-H or 1-H); δ_C (50 MHZ; $CDCl_3$) 16.3 [q, $CH_3(^iPr)$], 21.0 [q, $CH_3(^iPr)$], 21.9 (q, 5'-CH_3), 23.2 (t, C-3'), 26.7 (d, C*H*Me_2), 31.6 (t, C-5'), 34.1 (t, C-4'), 35.9 (t, C-9), 40.3 (t, C-6'), 47.2 (d, C-2'), 75.8 (d, C-1'), 81.0 (d, C-9a), 86.6 (d, 6b), 102.0 (s, C-6), 112.1 (s, C-6a), 122.0, 124.7 (d, C-1, C-4), 123.9, 127.0 (s, C-4a, C-10b), 127.7, 129.7 (d, C-2, C-3), 149.5 (s, C-10a), 157.3 (s, C-5), 170.0 (s, *C*O_2Men) and 175.1 (s, C-8); *m/z* 424 (M^+, 7), 286 (M-$C_{10}H_{18}$, 37) and 268 (M-$C_{10}H_{20}O$, 100).

(1'R, 2'S, 5'R, 3aR, 8bR*)-Menthyl 2,3,3a,8b-tetrahydro-7-hydroxy-2-oxo-furo[3,2-b]benzofuran-8-carboxylate* **15.** To a solution of benzoquinone **8** (80 mg, 0.28 mmol) in acetonitrile (7 cm^3) was added 2-trimethylsilyloxyfuran (43 mg, 0.28 mmol) under nitrogen at 0°C. After stirring at 0°C for 40 min., methanol (1 cm^3) was added and the reaction mixture left stirring for 4 days. The solvent was removed under reduced pressure to give a brown oil. Flash chromatography using hexane-ethyl acetate (8:2) as eluent gave the *title compound* **15** (51 mg, 49%) as a colourless oil and as a 1:1 mixture of the diastereomers; $[\alpha]_D^{20}$ -36° (c, 0.42, CH_2Cl_2); (Found: C, 67.6; H, 6.9. $C_{21}H_{26}O_6$ requires C, 67.4; H, 7.0%); ν_{max} (nujol)/cm^{-1} 1784s (ester) and 1671s (C=O); δ_H (200 MHz; $CDCl_3$); 0.78 (3H, d, *J* 6.8, 5'-Me), 0.82 (3H, d, *J* 6.8, 5'-Me*), 0.92-0.97 [12H, m, Me(^iPr) and Me(^iPr)], 1.02-2.13 (18H, m, 3 x CH_2, 3 x CH_2*, 2'-H, 2'-H*, 5'-H, 5'-H*, C*H*Me_2 and C*H*Me_2*), 3.00-3.05 (4H, m, 3-H and 3-H*), 5.01-5.19 (2H, m, 1'-H and 1'-H*), 5.28-5.38 (2H, m, 3-Ha and 3-Ha*), 6.28 (1H, d, $J_{8b,3a}$ 6.0, 8b-H), 6.29 (1H, d, $J_{8b,3a}$ 6.0, 8b*-H), 7.01 (4H, s, 5-H, 5*-H, 6-H and 6*-H) and 10.84 (2H, s, OH and OH*); δ_C (100 MHz; $CDCl_3$) 15.7, 16.2 [q, $CH_3(^iPr)$], 20.8, 20.9 [q, $CH_3(^iPr)$], 21.9, 22.0* (q, 5'-CH_3), 22.7, 23.3* (t, C-3'), 25.4, 26.6* (d, C*H*Me_2), 33.5 (t, C-5'), 33.9, 34.0* (t, C-4'), 35.5, 35.6* (t, C-3), 40.2, 41.4* (t, C-6), 47.1, 47.2* (d, C-2'), 76.1, 76.5* (d, C-1'), 81.0, 81.1* (d, C-3a), 84.6, 84.8* (d, C-8b), 109.7, 109.8* (s, C-8), 118.1 (d, C-5), 121.3, 121.5* (s, C-8a), 121.9, 122.0* (d, C-6), 154.0, 154.1* (s, C-4a), 157.4, 157.4* (s, C-7), 168.7, 168.8* (s, *C*O_2Men) and 174.2, 174.6* (s, C-2); *m/z* 374 (M^+, 7%), 236 (M-$C_{10}H_{18}$, 100) and 218 (M-$C_{10}H_{20}O$, 82).

(1'R, 2'S)-(-)-Menthyl 3,6-dihydroxy-2-ethylbenzoate **16.** To a solution of the quinone **8** (52 mg, 0.18 mmol) in acetonitrile (7 cm^3) was added diethylaluminium chloride (0.18 cm^3 of a 1 mol dm^{-3} solution in hexane,

0.18 mmol) under nitrogen at -30°C. After stirring for 15 min., 2-trimethylsilyloxyfuran (28 mg, 0.18 mmol) was added then after 40 min., methanol (1 cm^3) was added and the reaction mixture left stirring for 3 days. After quenching with saturated ammonium chloride (10 cm^3) and extraction with dichloromethane (25 cm^3), the organic extract was dried ($MgSO_4$) and the solvent removed under reduced pressure to yield a brown oil. Flash chromatography using hexane-ethyl acetate (8:2) as eluent afforded the *title compound* **16** (26 mg, 39%) as a yellow oil; $[\alpha]_D^{20}$ -66° (c, 0.3, CH_2Cl_2); (Found: M^+, 320.1986. $C_{19}H_{28}O_4$ requires 320.1988); δ_H (200 MHz; $CDCl_3$) 0.80 (3H, d, *J*=6.9, 5'-Me), 0.90-0.97 [6H, m, Me(^{i}Pr)], 1.24 (3H, t, *J* 7.4, CH_2CH_3), 1.11-2.18 (9H, m, 3 x CH_2, 2'-H, 5'-H and $CHCH_3$), 5.10 (1H, ddd, $J_{1'ax,6'ax}$ 10.9, $J_{1'ax,2'ax}$ 10.9 and $J_{1'ax,6'eq}$ 4.4, 1'ax-H), 6.74 (1H, d, $J_{4,5}$ 8.8, 4-H or 5-H), 6.91 (1H, d, $J_{5,4}$ 8.85, 5-H or 6-H) and 10.57 (2H, s, 3-OH and 6-OH); δ_C (100 MHz; $CDCl_3$) 14.4 [q, $CH_3(^iPr)$], 15.9 [q, $CH_3(^iPr)$], 20.7 (q, 5'-CH_3), 20.9 (t, $\underline{C}H_2CH_3$), 21.5 (q, $CH_2\underline{C}H_3$), 23.0 (t, C-3'), 26.2 (d, $\underline{C}HMe_2$), 29.7 (t, C-5'), 34.1 (t, C-4'), 40.8 (t, C-6'), 47.2 (d, C-2'), 76.0 (d, C-1'), 115.6 (d, C-5), 122.3 (d, C-4), 123.7 (s, C-2), 131.4 (s, C-1), 146.3 (s, C-3), 156.0 (s, C-6) and (s, $\underline{C}O_2$Men); *m/z* 320 (M^+, 9%), 182 (M-$C_{10}H_{18}$, 54) and 164 (M-$C_{10}H_{20}O$, 100).

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