Diels–Alder Trapping of *ortho*-Quinone Methides. A New Entry to Substituted Xanthene-1,4-diones

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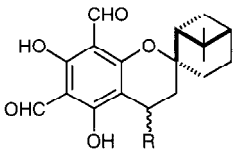
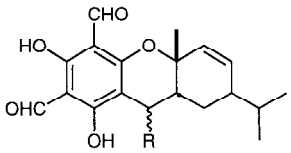
Abstract: Highly regioselective Diels–Alder reactions of a non-protected β-hydroxy quinone have been achieved after formation of chelated lithium alkoxides. In this report, we demonstrate on a model system, that the selectivity of reactions based on 1,3-dioxy-substituted quinones can be efficiently controlled by the addition of Lewis acid ($AlMe_3$), which chelates the substrate by the two oxygens.

Key words: *ortho*-quinomethanes, Diels–Alder reaction, lithium or aluminum complexation, chromanes

Recently, synthetic methods for the construction of chromane and spirochromane skeletons have been investigated as a route to robustadial and their important synthetic intermediates.[1–3] Interesting natural products of potential significance in treating malaria or as inhibitors of Epstein–Barr virus activation,[4,5] robustadials (e.g. robustadial A and B) and euglobals (e.g. euglobal $1a_1$ and $1a_2$), were isolated ten years ago from the leaves of *Eucalyptus robusta* by Nakanishi's group,[6] along with a variety of cycloadduct molecules whose structure suggested that their biosynthesis was the result of a biogenetic cycloaddition of corresponding terpenes and *ortho*-quinone methides (*ortho*-quinomethanes). The first total synthesis of robustadial dimethyl ethers, which was reported by Salomon and *al*.,[3,7] also proved their structure. It was followed by a few other studies describing partial or total syntheses.[8–12]



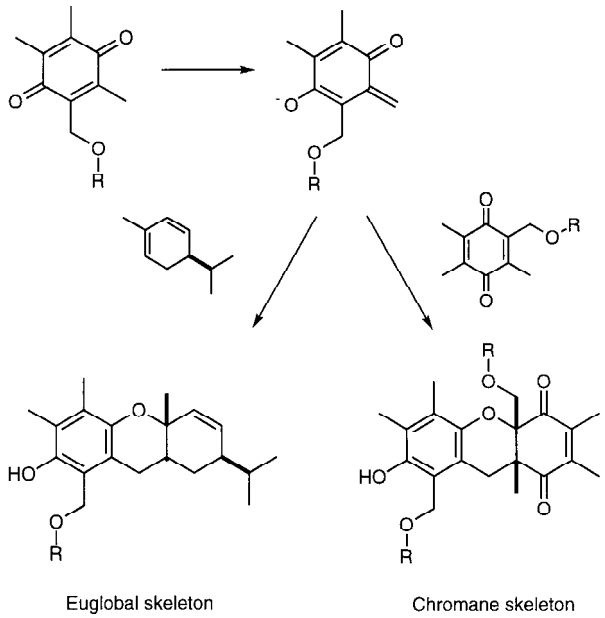
Robustadial A, B
A : R = 7β-CH_2CHMe_2
B : R = 7α-CH_2CHMe_2



Euglobal $1a_1$,$1a_2$
$1a_1$: R = 7β-CH_2CHMe_2
$1a_2$: R = 7α-CH_2CHMe_2

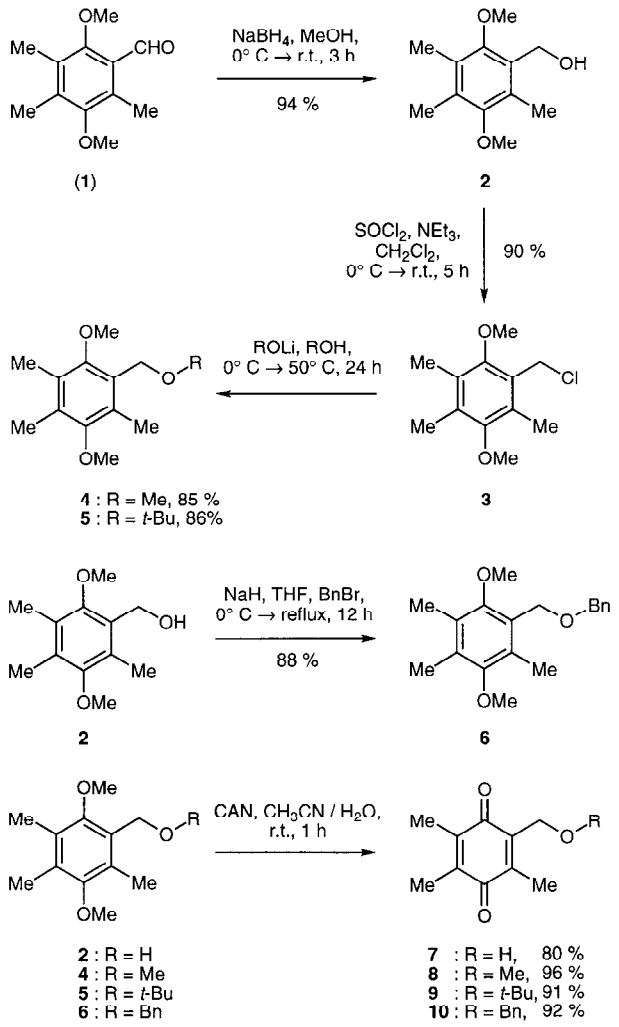
ortho-Quinone methide reactive dienes, readily available from quinoid compounds, have found numerous applications in organic synthesis.[13] For example, they are ideally suited for the generation of a variety of annulated ring systems via intramolecular hetero-Diels–Alder cycloadditions.[14,15] This potentially general method could conceivably be used to prepare a large number of chromanes as euglobal analogs.[16] In the present study, different substituted quinones were converted to the corresponding *o*-quinone methides by an anionic way,[17] before being successfully trapped in situ either by another quinone to give chromanes or by unactivated alkenes to form euglobal skeletons.[18]

The starting substituted quinones **7–9** were easily prepared on a multigram scale from 2,5-dimethoxy-3,4,6-trimethylbenzaldehyde **(1)**[19] in several steps (Scheme 1). Reduction of the aldehydic function of **1** with $NaBH_4$ in methanol furnished the corresponding alcohol **2**, which was converted either into the chloride **3** in over 85% yield by thionyl chloride in anhydrous dichloromethane, or into the benzyl ether derivative **6** in 88% yield by *O*-benzylation of **2** with benzyl bromide. Treatment of the chloride **3** with 1.1 equivalents of lithium methoxide (and respectively potassium *tert*-butoxide) gave the corresponding ether **4** (respectively **5**) in one step with good yields (>85%). Subsequent oxidation of **2**, **4**, **5** and **6** with cerium(IV) ammonium nitrate (CAN) restored the quinone function and afforded the quinones **7–10** in good to excellent yields (80–96%).

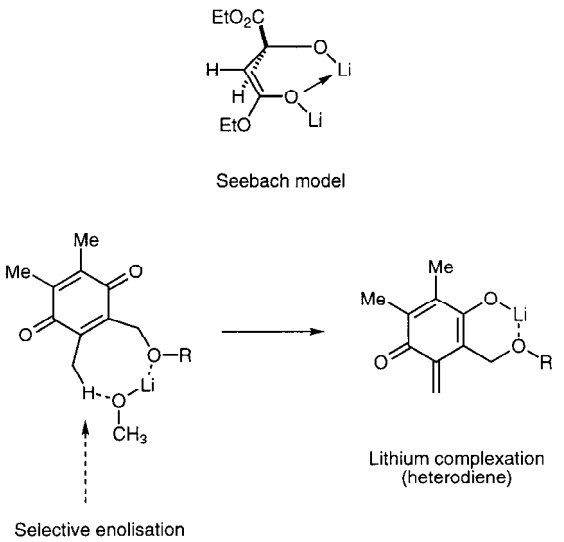


Among numerous reported methods for the formation of unstable *o*-quinone methides[20] we have chosen alkali treatment of the starting quinones.[17] This procedure has allowed us to generate selectively *o*-quinone methides with a total stereochemical control of the methyl-substituent in the C(3) position. Based on chelation control, the stereochemical outcome of the reaction is best explained by cyclic models which are very similar to the one proposed by Seebach for the alkylation of β-hydroxy ester enolates,[21] the cyclic system being maintained by lithium complexation.

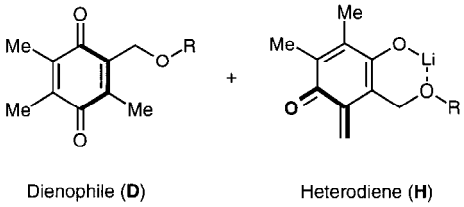
Diels–Alder trapping of *o*-quinone methide (as ambident heterodiene **H**) with one molecule of starting product (an asymmetrically substituted dienophile **D**) occurred with



Scheme 1

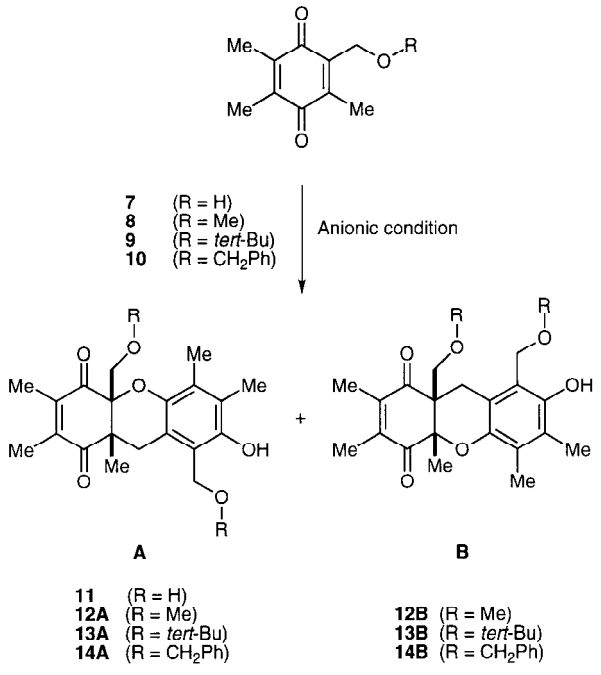


remarkable chemo- and regioselectivity, affording one or two of the twenty four possible Diels–Alder adducts.[22] Furthermore, the reaction was totally chemoselective, all the dienes are initially formed by abstraction of the proton borne by the methyl group at position C(3) and dienophiles react at their richer olefin [substituted at C(2) by a methoxy group]. This result is not surprising since control of the chemoselectivity in Diels–Alder reactions is generally excellent (Scheme 2). From a theoretical standpoint, cycloadditions can be studied in the frame of perturbation theory[23] by considering the relative position and the coefficients of the frontier orbital of the reagents. Inspection of the energies of the HOMO and the LUMO orbitals of the heterodiene **(H)** and the dienophile **(D)** leads to the conclusion that the dominant interaction takes place between the LUMO of the diene and the HOMO of the dienophile. Thus, we are dealing with an inverse Diels–Alder reaction.



Scheme 2

The *o*-quinone methides were generated from **7–10** using anionic conditions. Due to their instability, they were prepared in situ by addition of lithium methoxide to a solution of quinones **7–10** in MeOH at room temperature (Scheme 3). Results are summarized in the Table.



Scheme 3

We have observed that (i) the substituent R of the methoxy group at position C(2) influences the regiochemical outcome the ratio of regioisomers **A** and **B** and that (ii) the presence of lithium salt is the determining feature for the regioselectivity of the reaction (Table). Consequently, the

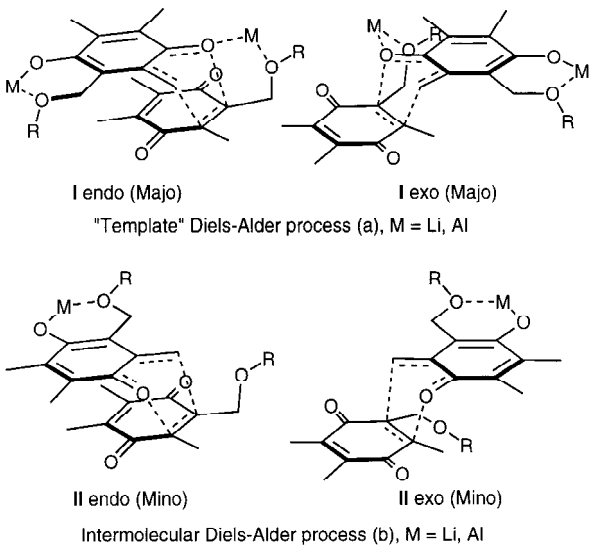
Table. Diels-Alder reactions of **7–10**

Entry	Pre-cursor	R	T °C	Additive	Yield (%)[c]	Product	Ratio **A/B**[d]
1	**7**	H	r.t.	–	70	**11**	32:1
2	**10**	CH_2Ph	r.t.	–	85	**14**	6.2:1
3	**8**	CH_3	r.t.	–	86	**12**	2.0:1
4	**8**	CH_3	–10	–	83	**12**	1.3:1
5	**8**	CH_3	reflux	–	76	**12**	5.2:1
6	**8**	CH_3	r.t.	crown ether[a]	83	**12**	1.1:1
7	**8**	CH_3	r.t.	$AlMe_3$[b]	72	**12**	15:1
8	**9**	*t*-Bu	r.t.	–	82	**13**	1:1

[a] 0.1 equiv of 12-crown-4 ether was used.
[b] 2 equiv of $AlCl_3$ were used.
[c] Yields are of isolated and purified products.
[d] The relative configuration was assigned by a combination of high field NMR analyses. Ratio of products **A** and **B** determined by GC with a temperature program.

regiochemical outcome of the reaction is best explained by a cyclic transition state fixed by lithium complexation (Scheme 4a).

However, in the absence of an additive, high regioselectivity was raised exclusively with hydroxy- (entry 1, **A**/**B** 32:1) and benzyloxy substituents (entry 2, **A**/**B** 6.2:1); methoxy and *tert*-butoxy substituents gave unsatisfactory results (entries 3, 8). In all cases, **A** was the major isomer. Consideration of the different models presented in Scheme 4 explains these results. When substituent R is a hydrogen atom (**7**) or a benzyl group (**10**), the reacting species adopt preferentially **I** *endo* and **I** *exo* conformations in the transition state. The regiochemistry of the reaction is governed by formation of the chelate complex (intramolecular reaction), which minimizes steric interactions and increases the kinetic. Reaction of free alcohol **7** showed the highest selectivity (entry 1), the quinone precursor being first quantitatively converted to a lithium alcoholate, which formed a cyclic system maintained by either lithium complexation or hydrogen bonding (Scheme 4a). The particular effect of the benzyl group may be attributed to an enhanced basicity of the oxygen atom caused by the phenyl moiety, that contributes to a better complexation system in the transition state and therefore increases the regioselectivity (entry 2).[24]



Scheme 4

When R is a methyl (**8**) or a *tert*-butyl (**9**) group (entries 3, 8), the complexation is not so effective: four transition states exist (**I** *endo* and *exo*, **II** *endo* and *exo*). In this case stereoelectronic interactions govern the regiochemistry of the reaction (intermolecular reaction). Hetero-Diels–Alder reactions are known to proceed generally via a concerted, but not synchronous, mechanism and their regioselectivity depends mainly on the relative ability of the dienophilic carbons to accommodate a positive charge (Scheme 4a,b).[25] Selectivity increased when compound **8** was first treated with 2 equivalents of Me_3Al (entry 7), but it decreased when 0.1 equivalents of crown ether were added to the reaction mixture (entry 6). Thus, the highest observed selectivity is presumably due to a complete chelation of the methoxy derivative **8** in its transition state while lower selectivities derive from a partially chelated transition state, which is expected since intramolecular Diels–Alder reactions occur faster than intermolecular ones (cf. Scheme 4a).

In the case of compound **8**, the best result was obtained in refluxing MeOH (ratio 5.2:1 for **12A**, entry 5), but selectivity decreased in MeOH at –10 °C (ratio 1.3:1 for **12A**, entry 4). The influence of temperature on the regioselectivity of Diels–Alder reactions is often attributed to the entropy of the system. In this case, on the one hand, the intermolecular mechanism (bimolecular process) was disfavored at high temperature and a good level of selectivity for the intramolecular mechanism (monomolecular process) was observed. On the other hand, the fact that none of the two mechanisms is dominating results in low selectivity.

In order to rationalize, the regioselectivity is governed by a delicate balance between three effects: (i) the intra- and intermolecular Diels–Alder (chelation model), (ii) the entropy of the system and (iii) the size of the substituent R.

The relative configurations of **11**; **12A**, **12B**; **13A**, **13B**; **14A**, **14B** were fully elucidated by a combination of high field NMR analyses after separation by flash chromatography. The absolute configuration of the major isomer **12A** was unambiguously confirmed by a single crystal X-ray structure analysis (Figure).[26]

In conclusion, we have demonstrated that simple quinone molecules can be converted under chelation control with high chemo- and regioselectivity in tricyclic compounds (chromanes) by Diels–Alder reactions. Interestingly, the regiochemical outcome of the reactions is not simply governed by the well established stereoelectronic effects. Complexation effects play also an important role in the preferential orientation of the transition state. Further study of the chelation by NMR techniques is actually underway in our laboratory as well as applications of this approach for the control of stereoselective Diels–Alder reactions.

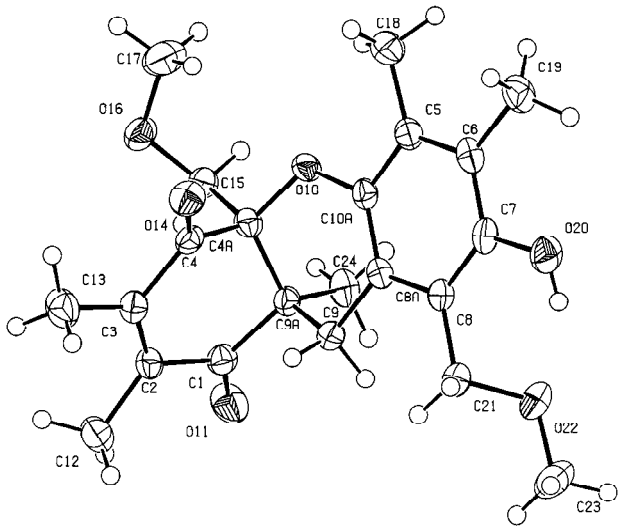


Figure. X-ray structure of **12A**.

THF and Et_2O were freshly distilled from Na/benzophenone under argon; CH_2Cl_2, DMF and benzene were distilled from CaH_2 under N_2 and toluene from Na under N_2. Solvents for chromatography were distilled. Flash column chromatography (FC) and filtration were performed with Baker silica gel (0.063–0.200 mm). TLC were run on Merck silica gel 60 F_{254} analytical plates; detection was carried out with either UV, iodine, spraying with a solution of phosphomolybdic acid (25 g), $Ce(NH_4)_2(NO_3)_6 \cdot 4H_2O$ (10 g), concd H_2SO_4 (60 mL) and water (940 mL), or with a solution of $KMnO_4$ (3 g), K_2CO_3 (20 g), water (300 mL) and 5% NaOH (5 mL), with subsequent heating. Mps were determined on a Reichert thermovar apparatus. IR spectra were recorded on a Mattson Unicam 5000 spectrophotometer, in cm^{-1}. NMR spectra were recorded on a Varian Gemini 200 (^1H 200 MHz and ^{13}C 50.3 MHz), or a Bruker Avance DRX-500 (^1H 500 MHz and ^{13}C 125.77 MHz); for ^1H δ are given in ppm relative to $CDCl_3$ (7.27 ppm), for ^{13}C δ are given in ppm relative to $CDCl_3$ (77.1 ppm), and coupling constants *J* are given in Hz. ^1H NMR splitting pattern abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. ^{13}C NMR multiplicities were determined by the APT and DEPT sequences, abbreviations are: q, CH_3; t, CH_2; d, CH; s, quaternary carbons. Assignments were confirmed by NOESY, COSY and HETCOR experiments. MS spectra were recorded on a Vacuum Generators Micromass VG 70/70E DS 11-250; EI (70 eV), CI (CH_4) are given in *m/z* (%). Elemental analyses were performed by Ciba Geigy Mikrolabor, Marly, Switzerland. Quantitative GC analyses were carried out on a Fisons HRGC MEGA 2 series gas chromatograph equipped with a Permabond SE 54 25 m × 0.32 mm capillary column.

2,5-Dimethoxy-3,4,6-trimethylbenzaldehyde (1):
Anhyd TFA (200 mL) was added to a mixture of 1,4-dimethyl-2,3,5-trimethylbenzene (26 g, 144 mmol) and hexamethylenetetramine (20 g, 144 mmol). The solution was stirred at r.t. for 1 h and then heated at reflux for 24 h. After cooling, the solution was poured into iced water, neutralized with Na_2CO_3 (25 g) and extracted with CH_2Cl_2 (3 × 100 mL). The organic layer was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure to afford 15.5 g of a yellow-white solid. Recrystallization in H_2O/EtOH gave 22 g (73%) of compound **1**; mp 80 °C.
^1H NMR ($CDCl_3$, 200 MHz): δ = 10.49 (s, 1H, CHO); 3.78 (s, 3H, OCH_3); 3.65 (s, 3H, OCH_3); 2.49 (s, 3H, CH_3); 2.27 (s, 3H, CH_3); 2.21 (s, 3H, CH_3).
^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 192.8 (s, *C*HO); 159.1 (s, *C*-OCH_3); 153.6 (s, *C*-OCH_3); 138.4 (s, *C*-CH_3); 131.9 (s, *C*-CH_3); 129.1 (s, *C*-CH_3); 126.3 (s, *C*-CH_3); 63.3 (q, O*C*H_3); 60.3 (q, O*C*H_3); 13.7 (q, *C*H_3); 12.8 (q, *C*H_3); 12.1 (q, *C*H_3).
CI-MS (CH_4): *m/z* (%) = 209 (100, $[M + 1]^+$), 193 (5), 181 (10).

$C_{12}H_{16}O_3$	calcd	C	69.21	H	7.74	
(208.28)	found		69.24		7.78	

1-Hydroxymethyl-2,5-dimethoxy-3,4,6-trimethylbenzene (2):
To a stirred suspension of $NaBH_4$ (8 g, 200 mmol) in MeOH (100 mL) under N_2 at 0 °C, was introduced a solution of aldehyde **1** (20 g, 96 mmol) in MeOH (20 mL) with a syringe within ca. 10 min The mixture was stirred for a further 3 h at 0 °C and allowed to warm up to r.t. After evaporation of MeOH, the crude product was dissolved in CH_2Cl_2 (150 mL) and washed with water (3 × 100 mL). The organic layer was dried ($MgSO_4$) and evaporated in vacuo. The residue was purified by flash chromatography (CH_2Cl_2) to yield 19 g (94%) of alcohol **2**. Recrystallization from cyclohexane delivered **2** as a white solid; mp 119 °C.
^1H NMR ($CDCl_3$, 200 MHz): δ = 4.70 (s, 2H, CH_2OH); 3.72 (s, 3H, OCH_3); 3.64 (s, 3H, OCH_3); 2.31 (s, 3H, CH_3); 2.25 (s, 1H, OH); 2.19 (s, 3H, CH_3); 2.17 (s, 3H, CH_3).
^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 153.3 (s, *C*-OCH_3); 153.2 (s, *C*-OCH_3); 130.8 (s, *C*-CH_3); 130.0 (s, *C*-CH_3); 128.1 (s, *C*-CH_3); 61.5 (q, O*C*H_3); 60.0 (q, O*C*H_3); 57.7 (t, *C*H_2OH); 12.7 (q, *C*H_3); 12.5 (q, *C*H_3); 11.7 (q, *C*H_3).
CI-MS (CH_4): *m/z* (%) = 210 (24, M^+), 193 (100), 181 (20), 166 (2), 135 (1).

$C_{12}H_{18}O_3$	calcd	C	68.55	H	8.63	
(210.27)	found		68.29		8.58	

1-Chloromethyl-2,5-dimethoxy-3,4,6-trimethylbenzene (3):
To a solution of **2** (12 g, 57 mmol) and NEt_3 (8.9 mL, 63.4 mmol) in anhyd CH_2Cl_2 (40 mL) under N_2 in an ice bath, was introduced a solution of $SOCl_2$ (4.6 mL, 63 mmol) in CH_2Cl_2 (10 mL) with a syringe within ca. 30 min. The mixture was stirred for a further 3 h at 0 °C and allowed to warm up to r.t. After cooling, water (100 mL) was added and the aqueous layer was extracted with CH_2Cl_2 (3 × 100 mL), dried ($MgSO_4$) and evaporated in vacuo. The crude product was purified by flash chromatography (CH_2Cl_2). Recrystallization (cyclohexane) gave 11.8 g (90%) of **3** as a white solid; mp 63 °C.
^1H NMR ($CDCl_3$, 200 MHz): δ = 4.73 (s, 2H, CH_2Cl); 3.78 (s, 3H, OCH_3); 3.65 (s, 3H, OCH_3); 2.33 (s, 3H, CH_3); 2.20 (s, 3H, CH_3); 2.18 (s, 3H, CH_3).
^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 153.2 (s, *C*-OCH_3); 132.1 (s, *C*-CH_3); 128.8 (s, *C*-CH_3); 128.4 (s, *C*-CH_3); 127.4 (s, *C*-CH_3); 61.6 (q, O*C*H_3); 60.1 (q, O*C*H_3); 39.2 (t, *C*H_2Cl); 12.9 (q, *C*H_3); 12.6 (q, *C*H_3); 11.6 (q, *C*H_3).
CI-MS (CH_4): *m/z* (%) = 229 (26, M^+), 193 (100), 177 (1), 135 (1), 93 (1).

$C_{12}H_{17}ClO_2$	calcd	C	63.02	H	7.49	Cl	15.50
(228.72)	found		63.02		7.49		15.58

1,4-Dimethoxy-2-methoxymethyl-3,5,6-trimethylbenzene (4):
Lithium (0.1 g, 13 mmol) was dissolved in abs MeOH (20 mL) and the mixture was stirred at r.t. for 2 h. After cooling, a solution of **3** (3.0 g, 13 mmol) in anhyd MeOH (5 mL) was added. The resulting mixture was warmed to 50 °C for 24 h. The solvent was evaporated, water (50 mL) added and the aqueous layer extracted with CH_2Cl_2 (3 × 50 mL). The combined organic fractions were washed with sat. brine (100 mL), dried ($MgSO_4$) and concentrated in vacuo to give a yellow oil, which was purified by flash chromatography (CH_2Cl_2) yielding **4** (2.5 g, 85%) as a colorless liquid; bp 94 °C/11 × 10^{-4} Torr.
^1H NMR ($CDCl_3$, 200 MHz): δ = 4.40 (s, 2H, CH_2OCH_3); 3.63 (s, 3H, OCH_3); 3.57 (s, 3H, OCH_3); 2.22 (s, 3H, CH_3); 2.11 (s, 3H, CH_3); 2.10 (s, 3H, CH_3).
^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 153.7 (s, *C*-OCH_3); 153.1 (s, *C*-OCH_3); 131.1 (s, *C*-CH_3); 129.3 (s, *C*-CH_3); 128.0 (s, *C*-CH_3); 127.5 (s, *C*-CH_3); 66.9 (q, O*C*H_3); 61.9 (q, O*C*H_3); 60.1 (q, O*C*H_3); 58.2 (t, *C*H_2O); 12.9 (q, *C*H_3); 12.6 (q, *C*H_3); 11.8 (q, *C*H_3).

EI-MS: *m/z* (%) = 224 (100, M^+), 193 (54), 181 (10), 162 (2), 131 (2).

$C_{13}H_{20}O_3$	calcd	C	69.64	H	8.93
(224.30)	found		69.65		8.93

1-(*tert*-Butoxymethyl)-2,5-dimethoxy-3,4,6-trimethylbenzene (5):
A mixture of **3** (200 mg, 0.87 mmol) and *t*-BuOK (130 mg, 1.16 mmol) in anhyd THF (5 mL) was refluxed for 24 h, i.e., until complete conversion of **3** had occurred. The solvent was evaporated, water (50 mL) was added and the mixture extracted with EtOAc (3 × 50 mL). The combined organic fractions were washed with sat. brine (100 mL), dried ($MgSO_4$) and concentrated in vacuo to give a colorless oil. The residue was purified by flash chromatography (Et_2O/hexane 1:1) yielding **5** (200 mg, 86%) as a colorless liquid.
^{1}H NMR ($CDCl_3$, 200 MHz): δ = 4.46 (s, 2H, CH_2O); 3.74 (s, 3H, OCH_3); 3.65 (s, 3H, OCH_3); 2.30 (s, 3H, CH_3); 2.17 (s, 3H, CH_3); 1.33 (s, 9H, CH_3).
^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 153.6 (s, *C*-OCH$_3$); 153.1 (s, *C*-OCH$_3$); 130.6 (s, *C*-CH$_3$); 129.3 (s, *C*-CH$_3$); 128.2 (s, *C*-CH$_3$); 127.5 (s, *C*-CH$_3$); 73.1 (s, *C*-O); 61.8 (q, O*C*H$_3$); 59.9 (q, O*C*H$_3$); 56.3 (t, *C*H$_2$O); 27.6 (q, C-*C*H$_3$); 12.7 (q, *C*H$_3$); 12.4 (q, *C*H$_3$); 11.6 (q, *C*H$_3$).
EI-MS: *m/z* (%) = 266 (100, M^+), 209 (39), 193 (14), 179 (8), 164 (3), 149 (2).

$C_{16}H_{26}O_3$	calcd	C	72.14	H	9.84
(266.38)	found		72.08		9.92

1-Benzyloxymethyl-2,5-dimethoxy-3,4,6-trimethylbenzene (6):
A solution of **2** (500 mg, 2.38 mmol) in THF (5 mL) was added dropwise to a stirred suspension of NaH (55% in paraffin, 114 mg, 4.8 mmol) in THF (5 mL) at 0 °C. The mixture was stirred for 30 min at r.t. and benzyl bromide (0.31 mL, 2.62 mmol) was added. After 12 h under reflux, the solvent was evaporated and the residue was dissolved in CH_2Cl_2 (60 mL). The organic layer was washed with water (3 × 20 mL) and dried ($MgSO_4$). Evaporation of the solvent gave the crude product which was purified by flash chromatography (Et_2O/hexane 1:1) yielding **6** (628 mg, 88%) as a colorless liquid.
^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.36–7.29 (m, 5 arom H); 4.58 (AB, J_{AB} = 4.9 Hz, 2H, OCH_2); 4.46 (s, 2H, OCH_2); 3.66 (s, 3H, OCH_3); 3.63 (s, 3H, OCH_3): 2.28 (s, 3H, CH_3); 2.18 (s, 3H, CH_3); 2.17 (s, 3H, CH_3).
^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 153.7 (s, *C*-OCH$_3$); 153.1 (s, *C*-OCH$_3$); 131.0 (s, *C*-CH$_3$); 129.4 (s, *C*-CH$_3$); 128.9 (d, *C*H); 128.7 (d, *C*H); 128.2 (d, *C*H); 128.0 (d, *C*H); 127.9 (s, *C*-CH$_3$); 127.7 (s, *C*-CH$_3$); 127.4 (s); 72.7 (t, *C*H$_2$O); 64.6 (t, *C*H$_2$O); 61.8 (q, O*C*H$_3$); 59.9 (q, O*C*H$_3$); 12.8 (q, *C*H$_3$); 12.5 (q, *C*H$_3$); 11.8 (q, *C*H$_3$).
EI-MS: *m/z* (%) = 300 (100, M^+), 214 (32), 198 (45), 191 (11), 176 (7), 161 (5).

$C_{19}H_{24}O_3$	calcd	C	75.97	H	8.05
(300.40)	found		76.04		8.11

2-Hydroxymethyl-3,5,6-trimethyl-1,4-benzoquinone (7):
To a solution of **2** (1.50 g, 7.13 mmol) dissolved in CH_3CN (10 mL) was slowly added a solution of CAN (10.0 g, 18.3 mmol) in water (10 mL). The resulting mixture was stirred for 1 h at r.t. and diluted with water (50 mL). The organic layer was extracted with CH_2Cl_2 (3 × 50 mL), dried ($MgSO_4$) and concentrated in vacuo to give an orange solid, which was purified by flash chromatography (CH_2Cl_2) yielding **7** (1.08 g, 80%) as an orange solid; mp 81–82 °C (cyclohexane).
^{1}H NMR ($CDCl_3$, 200 MHz): δ = 4.55 (s, 2H, CH_2O); 4.21 (s, 1H, O*H*); 2.09 (s, 3H, CH_3); 2.03 (s, 6H, CH_3).
^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 184.6 (s, CO); 182.8 (s, CO); 147.6 (s); 140.9 (s); 140.2 (s); 140.1 (s); 56.1 (t, *C*H$_2$O); 12.6 (q, *C*H$_3$); 12.3 (q, *C*H$_3$); 11.8 (q, *C*H$_3$).
CI-MS (CH_4): *m/z* (%) = 181 (100, $[M + 1]^+$), 180 (54, M^+), 162 (86), 152 (12), 149 (33), 121 (8), 93 (11), 91 (3).

$C_{10}H_{12}O_3$	calcd	C	66.66	H	6.66
(180.20)	found		66.70		6.68

2-Methoxymethyl-3,5,6-trimethyl-1,4-benzoquinone (8):
To a solution of **4** (2.50 g, 11.15 mmol) dissolved in CH_3CN (20 mL) was slowly added a solution of CAN (15.28 g, 27.86 mmol) in water (20 mL). The resulting mixture was stirred for 1 h at r.t. and diluted with water (100 mL). The organic layer was extracted with CH_2Cl_2 (3 × 100 mL), dried ($MgSO_4$) and concentrated in vacuo to give an orange oil, which was purified by flash chromatography (hexane/Et_2O 1:1) yielding **8** (2.08 g, 96%) as an orange solid; mp 49–50 °C (cyclohexane).
^{1}H NMR ($CDCl_3$, 200 MHz): δ = 4.28 (s, 2H, CH_2O); 3.31 (s, 3H, OCH_3); 2.05 (s, 3H, CH_3); 1.96 (s, 6H, CH_3).
^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 187.7 (s, CO); 186.4 (s, CO); 144.2 (s); 140.7 (s); 140.5 (s); 138.2 (s); 64.7 (q, O*C*H$_3$); 58.7 (t, *C*H$_2$O); 12.3 (q, *C*H$_3$); 12.3 (q, *C*H$_3$); 12.2 (q, *C*H$_3$).
CI-MS (CH_4): *m/z* (%) = 195 (100, $[M + 1]^+$), 194 (13, M^+), 179 (4), 163 (52), 135 (15), 107 (1), 91 (1), 67 (1).

$C_{11}H_{14}O_3$	calcd	C	68.02	H	7.26
(194.23)	found		68.09		7.23

2-(*tert*-Butoxymethyl)-3,5,6-trimethyl-1,4-benzoquinone (9):
A solution of CAN (1.29 g, 2.35 mmol) in water (10 mL) was slowly added to a solution of **5** (0.25 g, 0.94 mmol) dissolved in CH_3CN (20 mL). The mixture was stirred for 1 h at r.t. and diluted with water (50 mL). The organic layer was extracted with CH_2Cl_2 (3 × 50 mL), dried ($MgSO_4$) and concentrated in vacuo to give a yellow oil. Purification by flash chromatography (hexane/Et_2O 1:1) gave **9** (0.20 g, 91%) as a yellow liquid.
^{1}H NMR ($CDCl_3$, 200 MHz): δ = 4.32 (s, 2H, CH_2O); 2.12 (s, 3H, CH_3); 2.01 (s, 6H, CH_3); 1.27 (s, 9H, CH_3).
^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 187.8 (s, CO); 186.3 (s, CO); 144.1 (s); 140.5 (s); 139.4 (s); 73.9 (s, *C*-CH$_3$); 54.7 (t, *C*H$_2$O); 27.4 (q, C-*C*H$_3$); 12.3 (q, *C*H$_3$); 12.1 (q, *C*H$_3$).
CI-MS (CH_4): *m/z* (%) = 237 (100, $[M + 1]^+$), 236 (8, M^+), 179 (23), 163 (45), 135 (19), 107 (1), 91 (1), 67 (1).

$C_{14}H_{20}O_3$	calcd	C	71.16	H	8.53
(236.31)	found		70.99		8.50

2-Benzyloxymethyl-3,5,6-trimethyl-1,4-benzoquinone (10):
A solution of CAN (2.28 g, 4.16 mmol) in water (20 mL) was slowly added to a solution of **6** (0.50 g, 1.66 mmol) dissolved in CH_3CN (20 mL). The mixture was stirred for 1 h at r.t. and diluted with water (50 mL). The organic layer was extracted with CH_2Cl_2 (3 × 100 mL), dried ($MgSO_4$) and concentrated in vacuo to give a yellow oil. Purification by flash chromatography (hexane/Et_2O 9:1) gave **10** (0.41 g, 92%) as a yellow liquid.
^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.33 (s, 5 arom H); 4.56 (s, 2H, CH_2O); 4.44 (s, 2H, CH_2O); 2.09 (s, 3H, CH_3); 2.02 (s, 6H, CH_3).
^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 187.7 (s, CO); 186.4 (s, CO); 144.3 (s); 140.7 (s); 140.5 (s); 138.5 (s); 137.9 (s); 128.4 (d, *C*H); 127.9 (d, *C*H); 127.8 (d, *C*H); 73.3 (t, *C*H$_2$O); 62.6 (t, *C*H$_2$O); 12.3 (q, *C*H$_3$).
CI-MS (CH_4): *m/z* (%) = 270 (100, M^+), 179 (45), 163 (23), 135 (9), 107 (5), 92 (2), 77 (1).

$C_{17}H_{18}O_3$	calcd	C	75.53	H	6.71
(270.33)	found		75.31		6.79

Diels–Alder Reactions; General Procedure:
To a solution of quinone (2.57 mmol) in MeOH (20 mL) at r.t. was slowly added a mixture of MeOLi (2.57 mmol) in MeOH (5 mL) over a period of 12 h with a syringe pump. The mixture was stirred for 24 h at r.t., the solvent evaporated and the residue dissolved in EtOAc (50 mL). The organic layer was washed with water (3 × 50 mL) and dried ($MgSO_4$). Evaporation of the solvent gave the crude product which was purified by FC (Flash Chromatography).

According to the General Procedure (Table, Entry 1):
From **7** (500 mg, 2.77 mmol), MeOLi (106 mg, 2.77 mmol) at r.t. FC (hexane/Et_2O 1:1) gave **11** (350 mg, 70%).

(4aS,9aS*)-7-Hydroxy-4a,8-bis(hydroxymethyl)-2,3,5,6,9a-pentamethyl-4,4a,9,9a-tetrahydro-1*H*-xanthene-1,4-dione* **(11)**: orange solid; recrystallized (Et_2O); mp 191 °C.
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.31 (s, 1H, OH); 4.65 (s, 2H, OH); 4.46 (AB, J_{AB} = 12.4 Hz, 2H, C(8)-CH_2O); 3.81 (AB, J_{AB} = 11.1 Hz, 2H, C(4)-CH_2O); 2.52 (AB, J_{AB} = 17.1 Hz, 2H, C(9)H_2); 2.22 (s, 3H, C(5)-CH_3); 2.19 (s, 3H, C(6)-CH_3); 2.01 (q, J = 1.1 Hz, 3H, CH_3); 1.97 (q, J = 1.1 Hz, 3H, CH_3); 1.24 (s, 3H, C(9a)-CH_3).
^{13}C NMR ($CDCl_3$, 125.77 MHz): δ = 200.5 (s, CO); 195.5 (s, CO); 149.0 (s); 148.2 (s); 146.8 (s); 143.1 (s); 123.4 (s); 123.3 (s); 117.1 (s); 112.7 (s); 88.5 (s, C(4a)); 57.5 (t, C(4a)-*C*H$_2$O); 56.9 (t, C(8)-*C*H$_2$O); 48.9 (s, C(9a)); 32.1 (t, C(9)); 17.6 (q, C(9a)-*C*H$_3$); 12.8 (q, *C*H$_3$); 12.6 (q, *C*H$_3$); 12.1 (q, *C*H$_3$); 11.8 (q, *C*H$_3$).
CI-MS (CH_4): *m/z* (%) = 360 (56, M^+), 342 (100), 324 (77), 312 (14), 284 (32), 256 (23), 226 (8), 196 (9), 166 (16), 136 (3), 104 (21), 84 (2).

$C_{20}H_{24}O_6$	calcd	C	66.65	H	6.71
(360.41)	found		66.91		6.87

According to the General Procedure (Table, Entry 3):
From **8** (500 mg, 2.57 mmol), MeOLi (98 mg, 2.57 mmol) at r.t. FC (hexane/Et_2O 1:1) gave **12A** (285 mg, 57%) along with **12B** (145 mg, 29%).

According to the General Procedure (Table, Entry 4):
From **8** (500 mg, 2.57 mmol), MeOLi (98 mg, 2.57 mmol) at –10 °C. FC (hexane/Et_2O 1:1) gave **12A** (235 mg, 47%) along with **12B** (180 mg, 36%).

According to the General Procedure (Table, Entry 5):
From **8** (500 mg, 2.57 mmol), MeOLi (98 mg, 2.57 mmol) at reflux of the solvent. FC (hexane/Et_2O 1:1) gave **12A** (320 mg, 64%) along with **12B** (60 mg, 12%).

According to the General Procedure (Table, Entry 6):
From **8** (500 mg, 2.57 mmol), 1,4,7,19-tetraoxacyclododecane (12-crown-4) (45 mg, 0.25 mmol) and MeOLi (98 mg, 2.57 mmol) at r.t. FC (hexane/Et_2O 1:1) gave **12A** (217 mg, 43%) along with **12B** (198 mg, 40%).

According to the General Procedure (Table, Entry 7):
From **8** (500 mg, 2.57 mmol), $AlMe_3$ (371 mg, 5.14 mmol) and MeOLi (98 mg, 2.57 mmol) at r.t. FC (hexane/Et_2O 1:1) gave **12A** (340 mg, 68%) along with **12B** (20 mg, 4%).

(4aS,9aS*)-7-Hydroxy-4a,8-bis(methoxymethyl)-2,3,5,6,9a-pentamethyl-4,4a,9,9a-tetrahydro-1*H*-xanthene-1,4-dione* **(12A)**: orange solid; recrystallized (Et_2O); mp 167 °C.
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.38 (s, 1H, OH); 4.44 (AB, J_{AB} = 12.3 Hz, 2H, C(8)-CH_2O); 3.70 (AB, J_{AB} = 10.6 Hz, 2H, C(4)-CH_2O); 3.37 (s, 3H, C(8)-CH$_2$OCH_3); 3.34 (s, 3H, C(4)-CH$_2$OCH_3); 2.57 (AB, J_{AB} = 16.6 Hz, 2H, C(9)H_2); 2.25 (s, 3H, C(5)-CH_3); 2.15 (s, 3H, C(6)-CH_3); 2.03 (q, J = 1.1 Hz, 3H, CH_3); 1.99 (q, J = 1.1 Hz, 3H, CH_3); 1.28 (s, 3H, C(9a)-CH_3).
^{13}C NMR ($CDCl_3$, 125.77 MHz): δ = 199.3 (s, CO); 196.2 (s, CO); 148.5 (s); 143.2 (s); 142.9 (s); 142.8 (s); 125.5 (s); 124.0 (s); 115.8 (s); 111.8 (s); 85.4 (s, C(4a)); 76.1 (t, C(4a)-*C*H$_2$O); 69.3 (t, C(8)-*C*H$_2$O); 59.9 (q, C(4a)CH$_2$O-*C*H$_3$); 58.2 (q, C(9)CH$_2$O-*C*H$_3$); 48.8 (s, C(9a)); 33.9 (t, C(9)); 15.8 (q, C(9a)-*C*H$_3$); 13.1 (q, *C*H$_3$); 12.9 (q, *C*H$_3$); 12.1 (q, *C*H$_3$); 11.7 (q, *C*H$_3$).
CI-MS (CH_4): *m/z* (%) = 388 (38, M^+), 357 (100), 296 (4), 223 (3), 195 (19), 165 (5), 135 (1), 84 (5), 61 (2).

$C_{22}H_{28}O_6$	calcd	C	68.02	H	7.26
(388.46)	found		67.87		7.11

Crystallographic data for compound **12A**. $C_{22}H_{28}O_6$, triclinic, space group *P*, *a* = 8.3573(6), *b* = 11.0918(6), *c* = 11.2923(7) Å, α = 96.095(5)°, β = 104.247(5)°, γ = 91.868(6)°, *V* = 1006.96(11) Å^3, *Z* = 2, d_{calc} = 1.281 Mg/m^3. 3746 independent reflections were measured and 2917 were considered observed [$I>2\sigma(I)$], final *R1* = 0.0537, *wR2* = 0.1279 (all data), goodness of fit 1.085, residual density max/min 0.283/–0.258 e Å^{-3}. Absorption coefficient μ = 0.055 mm^{-1}; no correction for absorption was applied. Suitable crystals of **12A** were grown from Et_2O as orange blocks. Intensity data were collected at 223(2) K on a Stoe AED2 4-circle diffractometer using MoKα graphite monochromated radiation, using $2\theta/\omega$ scans in the range 4–51° in 2θ. The structure was solved by direct methods using the programme SHELXS-97.[27] The refinement and all further calculations were carried out using SHELXL-97.[28] All of the H-atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. The bond lengths and angles are normal within experimental error. In the molecule there is a relatively strong hydrogen bond linking hydroxy O_{20} to oxygen atom O_{22}, the molecular structure and crystallographic numbering scheme of **12A** is illustrated in the PLATON drawing.[29] In the crystal the molecules are linked to form "dimers" by an intermolecular hydrogen bond involving hydroxy O_{20} and carbonyl O_{14}, the crystal packing diagram was drawn using PLUTON.[29]

(4aS,9aS*)-7-Hydroxy-8,9a-bis(methoxymethyl)-2,3,4a,5,6-pentamethyl-4,4a,9,9a-tetrahydro-1*H*-xanthene-1,4-dione* **(12B)**: orange liquid.
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54 (s, 1H, OH); 4.66 (AB, J_{AB} = 12.6 Hz, 2H, C(8)-CH_2O); 3.45 (s, 3H, C(8)CH$_2$O-CH_3); 3.44 (AB, J_{AB} = 9.3 Hz, 2H, C(9a)-CH_2O); 3.36 (d, J = 16.3 Hz, 1H, C(9)H_2); 3.19 (s, 3H, C(9a)CH$_2$OCH_3); 2.35 (d, J = 16.5 Hz, 1H, C(9)H_2); 2.10 (s, 3H, C(6)-CH_3); 2.07 (q, J = 1.1 Hz, 3H, CH_3); 1.98 (s, 3H, C(5)-CH_3); 1.93 (q, J = 1.1 Hz, 3H, CH_3); 1.41 (s, 3H, C(4a)-CH_3).
^{13}C NMR ($CDCl_3$, 125.77 MHz): δ = 196.9 (s, CO); 193.7 (s, CO); 147.6 (s); 142.8 (s); 141.6 (s); 124.9 (s); 122.8 (s); 114.8 (s); 112.2 (s); 78.7 (s, C(4a)); 75.3 (t, C(9a)-*C*H$_2$O); 68.5 (t, C(8)-*C*H$_2$O); 58.5 (q, C(9a)CH$_2$O-*C*H$_3$); 57.1 (q, C(8)CH$_2$O-*C*H$_3$); 53.8 (s, C(9a)); 24.3 (t, C(9)); 15.1 (q, C(4a)-*C*H$_3$); 12.4 (q,*C*H$_3$); 12.1 (q, *C*H$_3$); 11.0 (q, C(5)-*C*H$_3$); 10.7 (q, C(6)-*C*H$_3$).
CI-MS (CH_4): *m/z* (%) = 388 (54, M^+), 357 (100), 296 (5), 223 (3), 195 (23), 165 (3), 135 (2), 84 (4), 61 (1).

$C_{22}H_{28}O_6$	calcd	C	68.02	H	7.26
(388.46)	found		68.14		7.32

According to the General Procedure (Table, Entry 8):
From **9** (500 mg, 2.12 mmol), MeOLi (81 mg, 2.12 mmol) at r.t. FC (hexane/Et_2O 8:2) gave **13A** (205 mg, 41%) along with **13B** (205 mg, 41%).

(4aS,9aS*)-4a,8-Bis(tert-butoxymethyl)-7-hydroxy-2,3,5,6,9a-pentamethyl-4,4a,9,9a-tetrahydro-1*H*-xanthene-1,4-dione* **(13A)**: orange liquid.
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.42 (s, 1H, OH); 4.35 (AB, J_{AB} = 11.9 Hz, 2H, C(8)-CH_2O); 3.59 (AB, J_{AB} = 8.9 Hz, 2H, C(4)-CH_2O); 2.51 (AB, J_{AB} = 16.4 Hz, 2H, C(9)H_2); 2.23 (s, 3H, C(5)-CH_3); 2.14 (s, 3H, C(6)-CH_3); 2.07 (q, J = 1.2 Hz, 3H, CH_3); 2.04 (q, J = 1.2 Hz, 3H, CH_3); 1.33 (s, 3H, C(9a)-CH_3); 1.28 (s, 9H, CH_3); 1.05 (s, 9H, CH_3).
^{13}C NMR ($CDCl_3$, 125.77 MHz): δ = 199.6 (s, CO); 197.9 (s, CO); 148.7 (s); 144.6 (s); 143.9 (s); 142.4 (s); 125.2 (s); 124.0 (s); 116.4 (s); 112.3 (s); 84.2 (s, C(4a)); 75.4 (s); 74.0 (s); 66.8 (t, C(4a)-*C*H$_2$O); 60.4 (t, C(8)-*C*H$_2$O); 54.3 (s, C(9a)); 34.0 (t, C(9)); 27.4 (q, *C*H$_3$); 26.9 (q, *C*H$_3$); 15.8 (q, *C*H$_3$); 13.3 (q, *C*H$_3$); 12.8 (q, *C*H$_3$); 11.7 (q, *C*H$_3$).
CI-MS (CH_4): *m/z* (%) = 473 (100, M^+), 416 (45), 359 (18), 343 (8), 327 (4), 299 (6), 271 (3).

$C_{28}H_{40}O_6$	calcd	C	71.16	H	8.53
(472.62)	found		71.32		8.67

(4aS,9aS*)-8,9a-Bis(tert-butoxymethyl)-7-hydroxy-2,3,4a,5,6-pentamethyl-4,4a,9,9a-tetrahydro-1*H*-xanthene-1,4-dione* **(13B)**: orange liquid.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.51 (s, 1H, OH); 4.69 (AB, J_{AB} = 12.0 Hz, 2H, C(8)-CH_2O); 3.38 (AB, J_{AB} = 8.6 Hz, 2H, C(9a)-CH_2O); 3.38 (d, J = 16.0 Hz, 1H, C(9)H_2); 2.17 (d, J = 16.0 Hz, 1H, C(9)H_2); 2.08 (s, 3H, C(6)-CH_3); 1.95 (s, 3H, C(5)-CH_3); 1.94 (q, J = 1.1 Hz, 3H, CH_3); 1.91 (q, J = 1.1 Hz, 3H, CH_3); 1.40 (s, 3H, C(4a)-CH_3); 1.36 (s, 9H, CH_3); 1.00 (s, 9H, CH_3).

^{13}C NMR ($CDCl_3$, 125.77 MHz): δ = 198.8 (s, CO); 193.9 (s, CO); 148.6 (s); 144.5 (s); 142.4 (s); 142.0 (s); 124.9 (s); 123.7 (s); 116.1 (s); 111.3 (s); 79.1 (s, C(4a)); 75.3 (s); 73.6 (s); 64.8 (t, C(9a)-*C*H$_2$O); 60.1 (t, C(8)-*C*H$_2$O); 48.0 (s, C(9a)); 27.3 (q, *C*H$_3$); 26.7 (q, *C*H$_3$); 24.6 (t, C(9)); 14.9 (q, *C*H$_3$); 13.2 (q,*C*H$_3$); 11.9 (q, *C*H$_3$); 11.6 (q, *C*H$_3$).

CI-MS (CH_4): *m/z* (%) = 473 (100, M^+), 416 (43), 359 (17), 343 (7), 327 (4), 299 (3), 271 (1).

$C_{28}H_{40}O_6$	calcd	C	71.16	H	8.53
(472.62)	found		71.41		8.71

According to the General Procedure (Table, Entry 2):

From **10** (500 mg, 1.85 mmol), MeOLi (71 mg, 1.85 mmol) at r.t. FC (hexane/Et_2O 1:1) gave **14A** (366 mg, 73%) along with **14B** (60 mg, 12%).

(4aS,9aS*)-4a,8-Bis(benzyloxymethyl)-7-hydroxy-2,3,5,6,9a-pentamethyl-4,4a,9,9a-tetrahydro-1*H*-xanthene-1,4-dione* **(14A)**: yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.42 (s, 1H, OH); 7.34–7.18 (m, 10H, 10 arom H); 4.52 (AB, J_{AB} = 11.9 Hz, 2H, OCH_2Ph); 4.51 (s, 2H, OCH_2Ph); 4.50 (AB, J_{AB} = 12.5 Hz, 2H, C(8)-CH_2O); 3.77 (AB, J_{AB} = 10.4 Hz, 2H, C(4a)-CH_2); 2.45 (AB, J_{AB} = 16.6 Hz, 2H, C(9)H_2); 2.27 (s, 3H, C(5)-CH_3); 2.17 (s, 3H, C(6)-CH_3); 1.97 (q, J = 1.1 Hz, 3H, CH_3); 1.92 (q, J = 1.1 Hz, 3H, CH_3); 1.25 (s, 3H, C(9a)-CH_3).

^{13}C NMR ($CDCl_3$, 125.77 MHz): δ = 199.7 (s, CO); 196.4 (s, CO); 148.6 (s); 143.4 (s); 142.9 (s); 142.8 (s); 137.2 (s); 136.7 (s); 128.6 (d, =*C*H); 128.4 (d, =*C*H); 128.2 (d, =*C*H); 127.9 (d, =*C*H); 127.7 (d, =*C*H); 125.7 (s); 124.1 (s); 115.7 (s); 112.0 (s); 85.3 (s, C(4a)); 73.7 (t, O*C*H$_2$Ph); 73.3 (t, C(4a)-*C*H$_2$O); 72.1 (t, O*C*H$_2$Ph); 66.3 (t, C(8)-*C*H$_2$O); 48.7 (s, C(9a)); 33.8 (t, C(9)); 15.8 (q, C(9a)-*C*H$_3$); 13.1 (q, *C*H$_3$); 13.0 (q, *C*H$_3$); 12.2 (q, *C*H$_3$); 11.8 (q, *C*H$_3$).

CI-MS (CH_4): *m/z* (%) = 541 (22, M^+), 434 (67), 326 (100), 297 (4), 268 (19), 238 (7), 208 (34), 178 (3), 148 (8), 87 (10).

$C_{34}H_{36}O_6$	calcd	C	75.53	H	6.71
(540.65)	found		75.62		6.76

(4aS,9aS*)-8,9a-Bis(benzyloxymethyl)-7-hydroxy-2,3,4a,5,6-pentamethyl-4,4a,9,9a-tetrahydro-1*H*-xanthene-1,4-dione* **(14B)**: orange liquid.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.52 (s, 1H, OH); 7.32–7.11 (m, 10H, 10 arom H); 4.72 (AB, J_{AB} = 12.6 Hz, 2H, C(8)-CH_2O); 4.59 (s, 2H, C(8)-CH$_2$O-CH_2); 4.35 (s, 2H, C(9a)CH$_2$OCH_2); 3.48 (AB, J_{AB} = 6.9 Hz, 2H, C(9a)-CH_2O); 3.33 (d, J = 15.9 Hz, 1H, C(9)H_2); 2.21 (d, J = 15.9 Hz, 1H, C(9)H_2); 2.10 (s, 3H, C(6)-CH_3); 2.03 (q, J = 1.1 Hz, 3H, CH_3); 1.98 (s, 3H, C(5)-CH_3); 1.92 (q, J = 1.1 Hz, 3H, CH_3); 1.37 (s, 3H, C(4a)-CH_3).

^{13}C NMR ($CDCl_3$, 125.77 MHz): δ = 197.8 (s, CO); 194.4 (s, CO); 148.6 (s); 148.2 (s); 144.1 (s); 144.0 (s); 138.4 (s); 137.1 (s); 128.6 (d, =*C*H); 128.3 (d, =*C*H); 128.1 (d, =*C*H); 127.9 (d, =*C*H); 127.6 (d, =*C*H); 126.2 (s); 123.9 (s); 115.8 (s); 113.3 (s); 83.3 (s, C(4a)); 73.7 (t, C(9a)-*C*H$_2$O); 73.5 (t, CH$_2$O*C*H$_2$Ph); 72.2 (t, CH$_2$O*C*H$_2$Ph); 66.6 (t, C(8)-*C*H$_2$O); 54.7 (s, C(9a)); 25.1 (t, C(9)); 15.7 (q, C(4a)-*C*H$_3$); 13.3 (q,*C*H$_3$); 13.1 (q, *C*H$_3$); 12.0 (q, C(5)-*C*H$_3$); 11.7 (q, C(6)-*C*H$_3$).

CI-MS (CH_4): *m/z* (%) = 541 (11, M^+), 511 (43), 481 (100), 390 (18), 299 (13), 269 (4), 239 (11), 209 (9), 105 (34), 53 (4).

$C_{34}H_{36}O_6$	calcd	C	75.53	H	6.71
(540.65)	found		75.84		6.92

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