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Applications of [4 + 2] Anionic Annulation and Carbonyl-Ene Reaction in the Synthesis of Anthraquinones, Tetrahydroanthraquinones and Pyranonaphthoquinones

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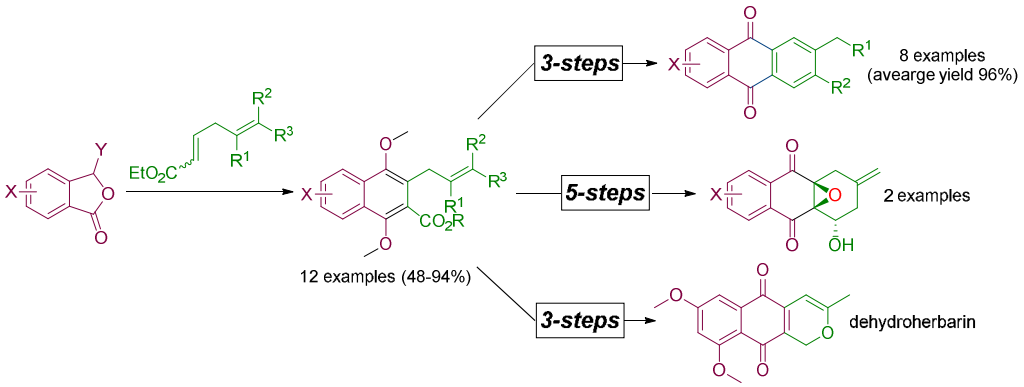
ABSTRACT: Hexa-2,5-dienoates, susceptible to isomerization by acids and bases, are suitable for the [4 + 2] anionic annulation to give 3-(2-alkenyl)naphthoates in regiospecific manner. When combined with intramolecular carbonyl-ene reaction (ICE), the accessibility of the naphthoates culminates in a new synthesis of anthraquinones and diastereoselective synthesis of tetrahydroanthraquinones. This strategy has also resulted in a 3-step synthesis of dehydroherbarin from a 3-methallylnaphthoate.

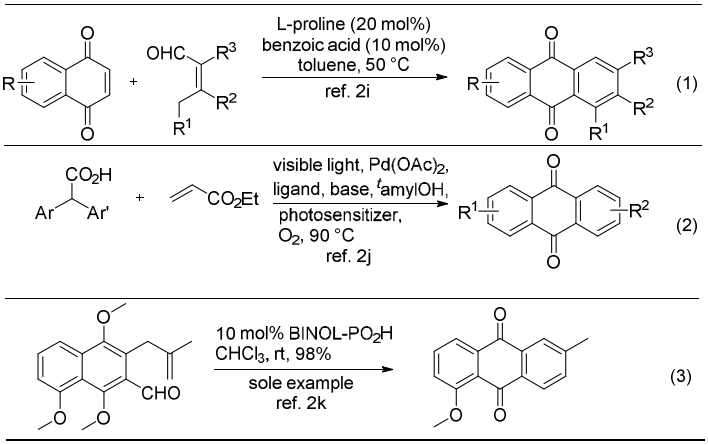


INTRODUCTION

Quinones are one of the largest and most diverse class of natural products, which include several distinguished subclasses like i) anthracyclines, ii) angucyclines, iii) anthraquinones, iv) pyranonaphthoquinones and v) hydroanthraquinones.[1a,b] Many of them have received much attention due to their anticancer activities and other cytotoxicities.[1c] For example, rhein, a natural product, has been found useful in the treatment of degenerative osteoarthritis of the joints.[1d] Furthermore, anthraquinones are useful as chemical sensors,[1e] building blocks for the synthesis of more complex

molecules,[1f] organogelators,[1g] liquid crystals,[1h] and organic semiconductors[1i]. Alkyl anthraquinones are of special interest due to their commercial uses in the production of hydrogen peroxide.[1j]In view of the above importance and usefulness, many synthetic strategies have been developed.[2] These strategies include Friedel–Crafts reaction of benzene derivatives,[2a] Diels-Alder reaction followed by aromatization,[2b–d] cyclization of polyketides,[2e] transition-metal mediated [2 + 2 + 2] cycloaddition,[2f] Diels-Alder reaction followed by aromatization and Friedel-Crafts reaction,[2g] [4 + 2] anionic annulation of phthalides[2h]. Recently, Lee group has developed a method based upon organocatalyzed benzannulation of naphthoquinones with α,β-unsaturated aldehydes at elevated temperature (Scheme 1, eq. (1)).[2i] Hong group combined photooxidation with Heck type of reaction of diarylacetic acids to construct anthraquinones (Scheme 1, eq. (2)).[2j] We reported a single example of one-pot formation of methylanthraquinone from 3-methallylnaphthalene-2-carboxaldehyde (Scheme 1, eq. (3)) via ICE reaction.[2k]

Scheme 1. Recent syntheses of anthraquinones



Furthermore, hydroanthraquinones are of much importance.[3] The structures of few recently isolated hydroanthraquinones, i.e **1**–**6** are displayed in Figure 1.[3a–e] A good majority of them display interesting biological activities, such as antibacterial activity,[3a] antitumor activity,[3b] cytotoxicity,[3d] anticancer activity,[3f] etc (Figure 1). However, very few synthetic strategies have been reported.[2c,4,5]

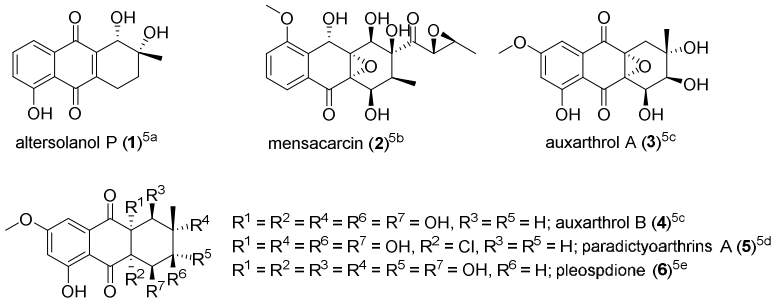
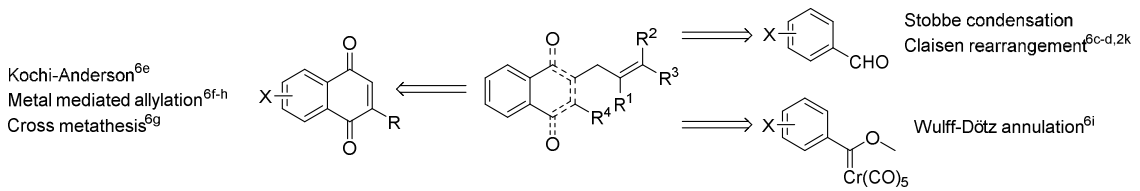


Figure 1. Some recently isolated tetrahydroanthraquinones

Similarly, pyranonaphthoquinones, namely, dehydroherbarin, thysanone, nanaomycin D, have been of synthetic interest and their chemistry is periodically reviewed.[6a–b] Consequently, many synthetic approaches for the titled classes have been reported in the literature. The use of 3-allyl-2-naphthoates as intermediates in the synthesis of tricyclic molecules like pyranonaphthoquinones, anthracenes is an attractive approach.[6a–i] However, the installation of an allyl group *ortho* to an ester group of aromatic ring is often problematic.[6j,k] In some of the approaches, the allyl group attached to an aromatic ring isomerizes under the reaction conditions due to the added stability originating from extended conjugation.[6j,k] Konig synthesis of anthracenes and Dehydroherbarin resorted to Stobbe condensation and Claisen rearrangement for the access to an allylnaphthoate from aromatic aldehydes.[6c,d] Recently, we employed Claisen rearrangement route for the synthesis of 3-methallyl-2-naphthoates.[2k] De Kimpe group utilized Kochi-Anderson reaction of a bromonaphthoquinone.[6e] Other approaches are based on metal mediated allylation of quinones,[6f–h] Wulff-Dötz annulation,[6i] modification of allyl group by cross metathesis reaction[6g] (Scheme 2).

Scheme 2. Previous works on the synthesis allyl naphthoates



In order to generalize our finding (Scheme 1, eq. (3)) on the synthesis of anthraquinones and tetrahydroanthraquinones via ICE, we needed an easy access to 3-allylnaphthoates. It may be mentioned that carbonyl-ene reaction is a fundamentally important atom-economic carbon-carbon single bond forming reaction.[7a–g] Its application has

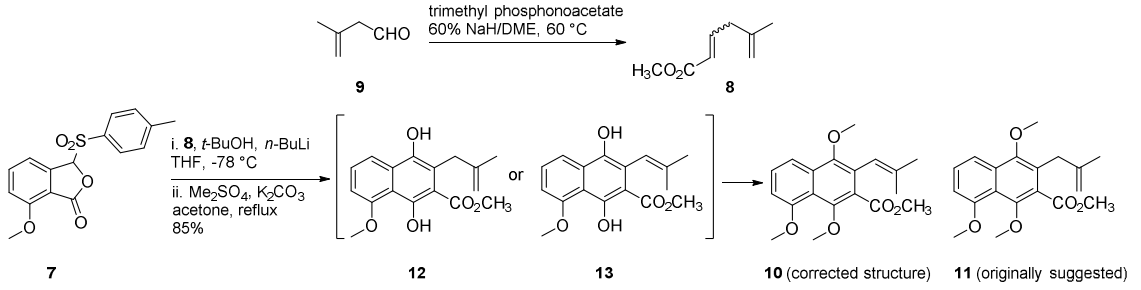
allowed novel synthesis of many natural products including anthracyclinones.[7h–i] The aim of this study was, therefore, two-fold: i) to extend our previous study on the aromatic carbonyl-ene-reaction[2k] for the development of a new synthesis of oxygenated anthraquinones and ii) to develop a general route for the synthesis of tricyclic quinone natural products.

Herein, we report a general and regiospecific synthesis of the 3-allylnaphthoates by [4 + 2] anionic annulations as well as their elaboration into alkylanthraquinones by tandem intramolecular carbonyl-ene reaction-dehydration-photooxidation. We also report diastereoselective synthesis of tetrahydroanthraquinones, and a short synthesis of dehydroherbarin.

RESULTS AND DISCUSSION

In order to resolve the regiochemical problems in the synthesis of 3-allylnaphthoates, we conceived [4 + 2] anionic annulation[8a–c] of 3-nucleofugal phthalides with skipped (1,4-dienes) dienoates. Such a concept was tested by Rho et al. with the sole annulation between sulfone phthalide **7** with dienoate **8** (synthesized from **9**) (Scheme 3).[8d] Unfortunately, isomerized product **10** was obtained and the desired product was not obtained. It may be noted that Rho et al. wrongly proposed the structure **11** for the product. On careful scrutiny of the reported NMR data for the product **11** (**^{1}H NMR data reported by Rho et al.** δ 7.71 (d, *J* = 7.97 Hz, 1H, ArH), 7.47 (t, *J* = 7.97, 1H, ArH), 6.91 (d, *J* = 7.97, 1H, ArH), **6.17 (br s, 1H, CH=)**, 4.01, 3.88, 3.87, 3.77 (3H each, s, OMe), 1.92, 1.75, (3H each, s, CH_3)), we found it to be incorrect. On the basis of the two singlets at δ 1.92 and 1.75 and one singlet at 6.17, we proposed structure **10** as the annulation product (Scheme 3).

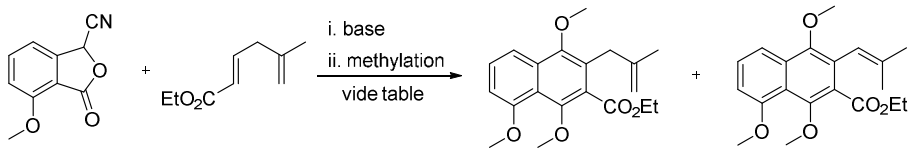
Scheme 3. Reinterpretation of Rho's work



Therefore, we concluded that CC double bond isomerization of the immediate annulation product **12** or its dimethyl derivative **11** or acceptor **8** led to the formation of **13** and then **10**.

Anticipating that the Hauser annulation with 3-cyanophthalides is faster than that of phthalide sulfones (*cf.* **7**), the revisit of the annulation with a cyanophthalide was deemed prudent. Accordingly, we synthesized acceptor **14a** (*cf.* **8**) according to the method of Snider et al.[8e,f] Intermolecular ene reaction of ethyl propiolate with isobutylene in the presence of Et_2AlCl afforded **14a** in 92% yield. When the acceptor **14a** was submitted to annulation with cyanophthalide **15a**[8g] in presence of different bases (vide Table 1), mixtures of two inseparable annulation products **16aa** and **16ab** were formed.

Table 1. Preliminary annulation study

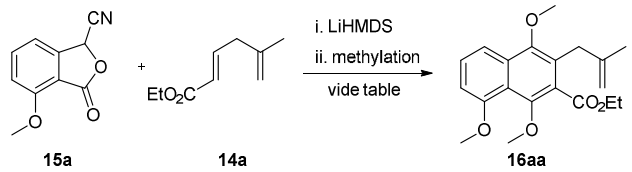


15a **14a** (prepared in 20 g scale) **16aa** **16ab**

Base and Conditions	16aa : 16ab	Yield of mixture of 16aa and 16ab (%)
(i) (a) NaH/0 °C-rt/THF (b) NaH/Me_2SO_4/0 °C-rt	2:1	45
(ii) (a) LiO^tBu/-78 °C-rt/THF (b) K_2CO_3/MeI/acetone/ 0 °C-rt	2:3	25

Thus it is feasible to synthesize 3-methallyl-2-naphthoates (*cf.* **16aa**) by the annulation. To prevent the formation of the isomerized product **16ab** and to identify the step in which methallyl double bond was isomerized, compounds **14a** and **16aa** were separately treated with NaH, LiO^tBu and LiHMDS. The compound **16aa** was found to be resistant to all the three bases. Interestingly, the acceptor **14a** was found to be inert only to LiHMDS. Accordingly, LiHMDS was used for the annulation reaction of the compound **15a** with acrylate **14a** to furnish the desired product **16aa** as the sole product. On optimization, the yield of the annulation product **16aa** could be increased up to 94% by carrying out the reaction in the presence of LiHMDS in MTBE (methyl *tert*-butyl ether)-THF (Table 2).

Table 2. Optimization study of the annulation of 15a with 14a

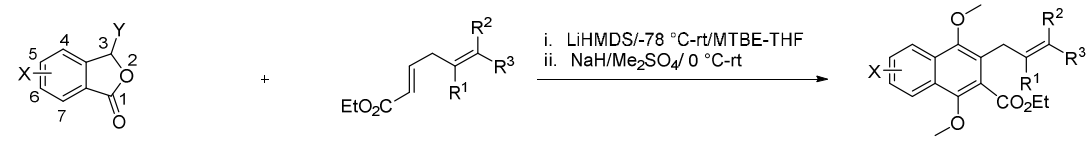


15a **14a** **16aa**

Base and Conditions	16aa
(i) LiHMDS/-78 °C-rt/THF (ii) K_2CO_3/MeI/acetone/ 0 °C-rt	30%
(i) LiHMDS/-78 °C-rt/THF (ii) LiHMDS/Me_2SO_4/ 0 °C-rt	54%
(i) LiHMDS/-78 °C-rt/THF (ii) (After work up) NaH/Me_2SO_4/ 0 °C-rt	28%
(i) LiHMDS/-78 °C-rt/THF (ii) NaH/Me_2SO_4/ 0 °C-rt	70%
(i) LiHMDS/-78 °C-rt/MTBE-THF (ii) NaH/Me_2SO_4/ 0 °C-rt	**94%**

For the evaluation of the substrate scope, cyanophthalides **15a–g**[2h,8g–i] were submitted to the annulation with acceptor **14a**. Expectedly, the desired annulation products **16a–g** were obtained under the optimized conditions in good to excellent yields. Another skipped dienoate i.e. **14b** was prepared by intermolecular ene reaction of ethyl propiolate with 2-ethyl-1-butene in the presence of Et_2AlCl as 1.3:1 diastereomeric mixture in 84% yield.[8e,f] When it was submitted to the annulation with the cyanophthalides **15b** and **15f**, products **16h–i** were obtained in good yields without any isomerization of the CC double bonds. In conjunction with the study, the annulation reactivity of **15h**[8j], which does not have a nucleofuge, was also examined. Its reaction with the acceptor **14a** under the same conditions afforded hydroaromatic products **16ja** and **16jb** (Table 3).

Table 3. Scope of Hauser annulation with skipped dienoates 14a–b

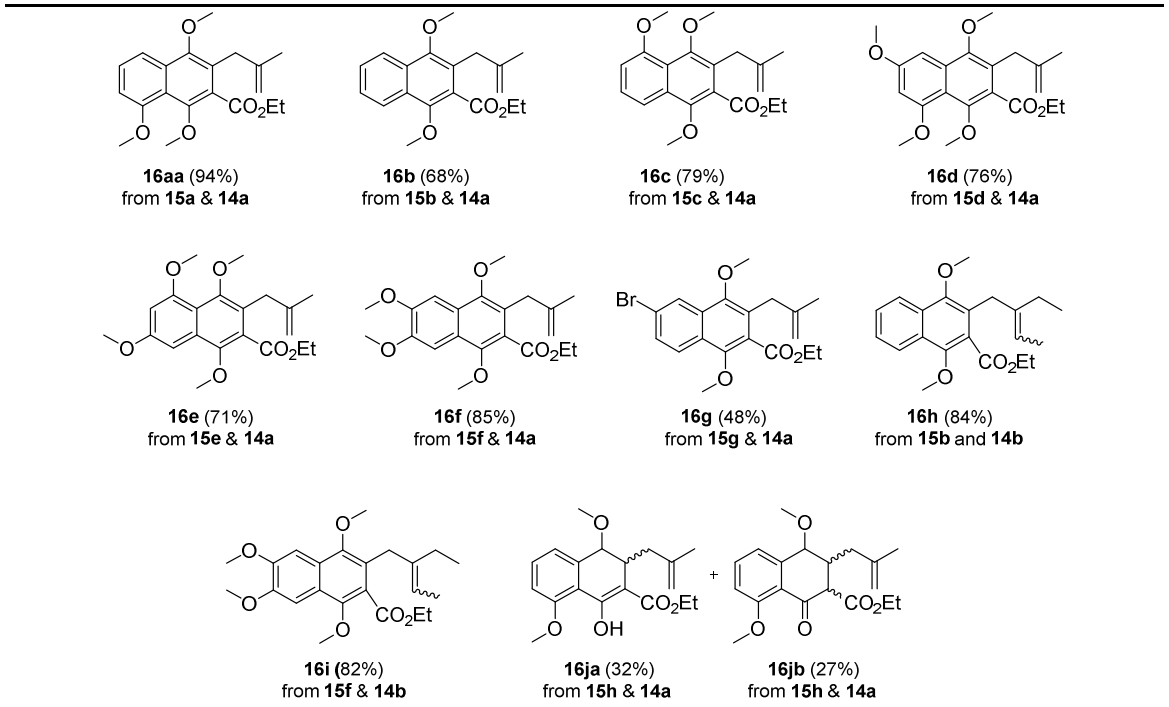


15a-h **14a-b** **16a-j**

X = 7-OMe, Y = CN; **15a**[8g]
X = H, Y = CN; **15b**[8g]
X = 4-OMe, Y = CN; **15c**[8g]
X = 5,7-OMe, Y = CN; **15d**[8g]
X = 4,6-OMe, Y = CN; **15e**[2h]
X = 5,6-OMe, Y = CN; **15f**[8h]
X = 5-Br, Y = CN; **15g**[8i]
X = 7-OMe, Y = H; **15h**[8j]

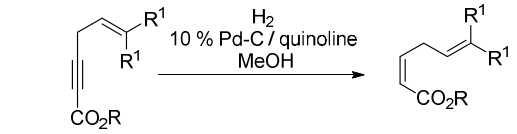
R^1 = Me, R^2 = R^3 = H; **14a**
R^1 = Et, (R^2 = Me, R^3 = H) or (R^2 = H, R^3 = Me); **14b**

R^1 = Me, Et ; R^2 = H, Me; R^3 = H, Me



To examine the scope of the acceptors, skipped dienoates **14c–d** were synthesized from **17a–b** by selective hydrogenation with 10% Pd-C/H_2 poisoned with quinoline or Lindlar catalyst (Scheme 4).

Scheme 4. Synthesis of acceptor 14c–d



R = Me, R^1 = Me; **17a**
R = Et, R^1 = H; **17b**

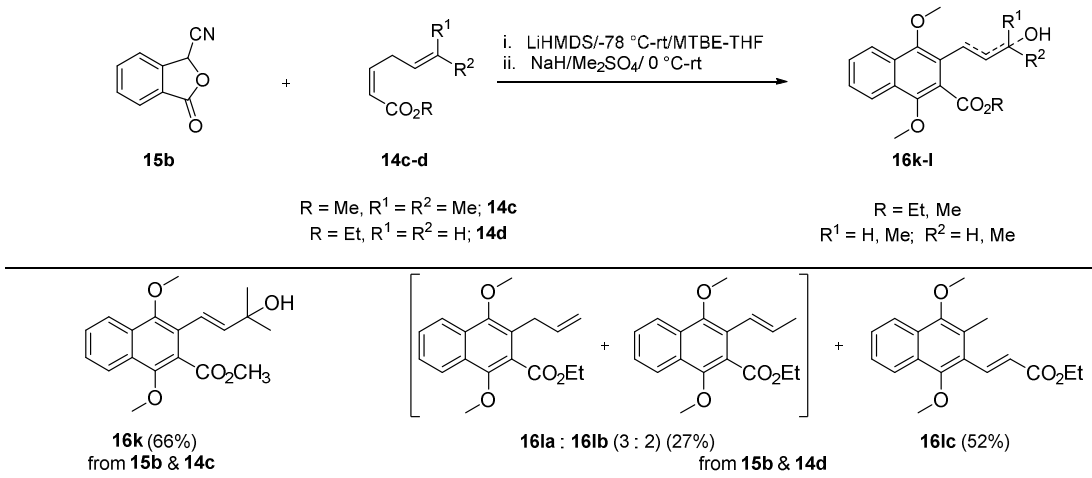
R = Me, R^1 = Me; **14c** (70%)
R = Et, R^1 = H; **14d** (90%)

An interesting result was obtained when the cyanophthalide **15b** was reacted with the acceptor **14c** (vide Table 4). Autooxidized annulation product **16k** was isolated in 66% yield. This kind of oxidation is invoked in the biogenesis of complex dimeric *Rubiaceae* natural products.[6g,9a–b] Furthermore, it is to be noted that the corresponding napthoquinone of the naphthoate **16k** is the putative intermediate for these natural products.

For the simple allylacrylate **14d**, the annulation with **15b** afforded an inseparable mixture of products **16la, 16lb** and **16lc**. The formation of product **16la** is the result of the annulation between cyanophthalide **15b** and skipped dienoate **14d** and the products **16lb** and

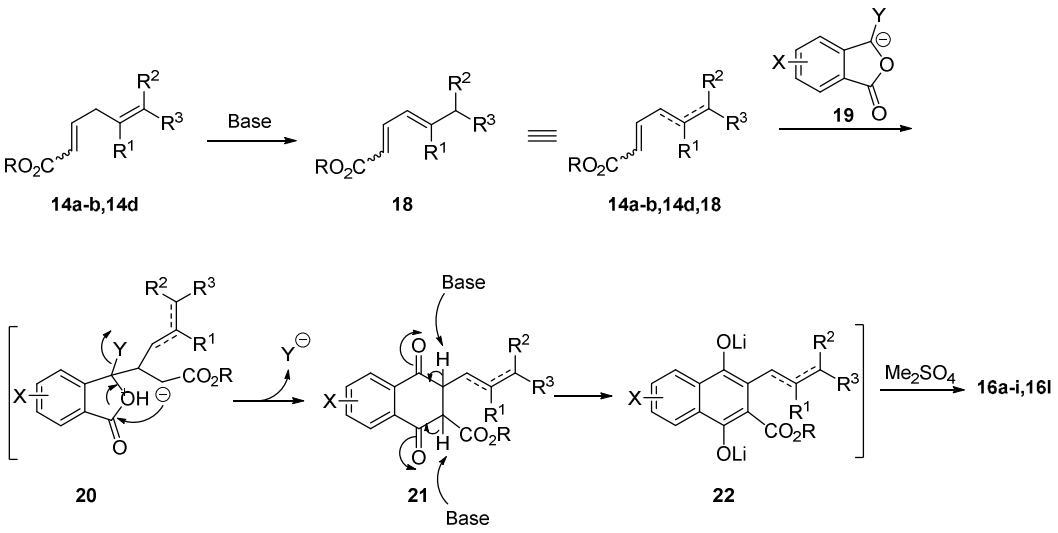
16lc from the annulation between **15b** and the acceptor which is isomerized product of **14d** (Table 4)**.**

Table 4. Scope of Hauser annulation with skipped dienoates 14c–d



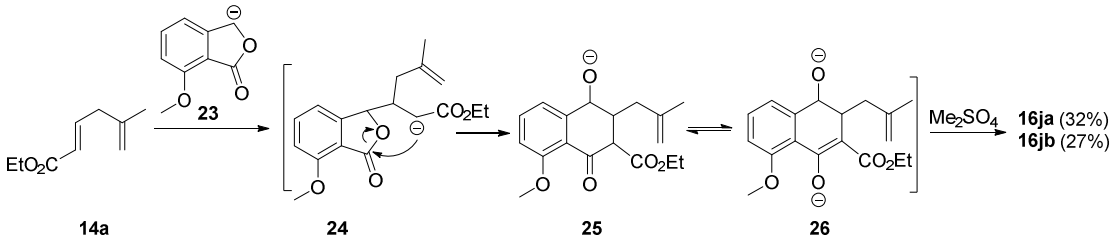
The mechanism of the annulation between 3-nucleofugal phthalides (**15a–g**) and skipped dienoates (**14a–b**,**14d**) is shown in Scheme 5. Under basic conditions of the annulation, 2,5-hexadienoates (**14a–b**,**14d**) may be in equilibrium with their isomers, i.e. 2,4-hexadienoates **18**. At low temperature, the incipient phthalide anions **19** add to the acrylates **14a–b**,**14d**,**18** in Michael addition mode to form new anions **20**. These anions **20** then undergo ring closure at the phthalide carbonyl group resulting in the displacement of nucleofuge Y as anion to produce dihydronaphthoquinones **21**. The deprotonation of **21** by bases give enolate intermediates **22**, which upon *in situ* methylation with Me_2SO_4, form the products **16a–i,16l** (Scheme 5).

Scheme 5. Mechanism of annulation between 3-nucleofugal phthalides and skipped dienoates



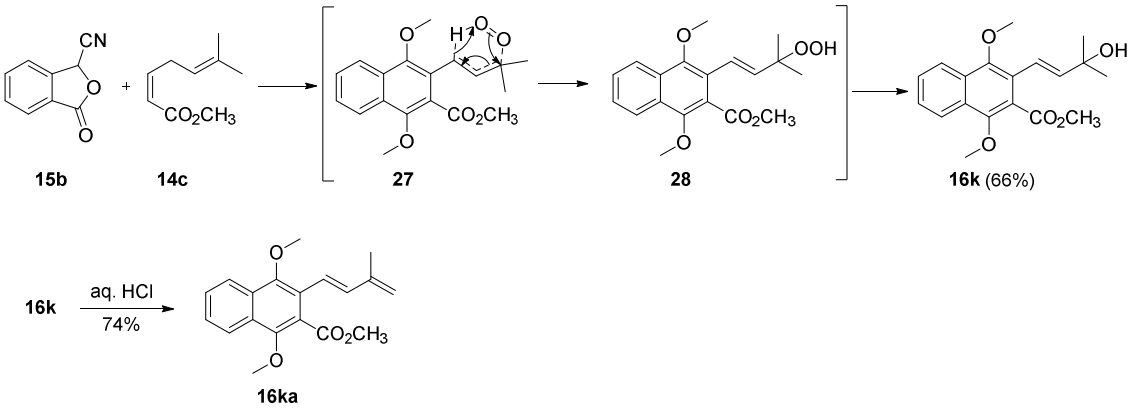
The mechanism of annulation between phthalide **15h** and skipped dienoate **14a** is presented in Scheme 6. At low temperature, the phthalide anion **23** undergoes Michael addition to the acrylate **14a** give anion **24**. This anion **24** then attacks at the phthalide carbonyl group resulting in the formation of anions **25** and **26**, which upon *in situ* methylation form the keto and enol products **16ja** and **16jb** (Scheme 6).

Scheme 6. Mechanism of annulation between phthalide 15h and skipped dienoate 14a



The formation of **16k** from **15b** and **14c** is accounted for by the brief mechanism presented in Scheme 7. The initial annulation product **27** is transformed to peroxo intermediate **28** after the ene reaction of the prenyl side chain with singlet oxygen. The intermediate **28** then undergoes disproportion to furnish the product **16k**. To confirm the structure of the product **16k** and presence of hydroxyl group, we performed acid catalyzed dehydration on **16k**, affording the dehydrated product **16ka** (Scheme 7).

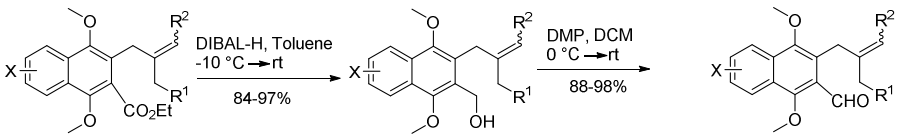
Scheme 7. Proposed mechanism for the formation of 16k and dehydration experiment on 16k



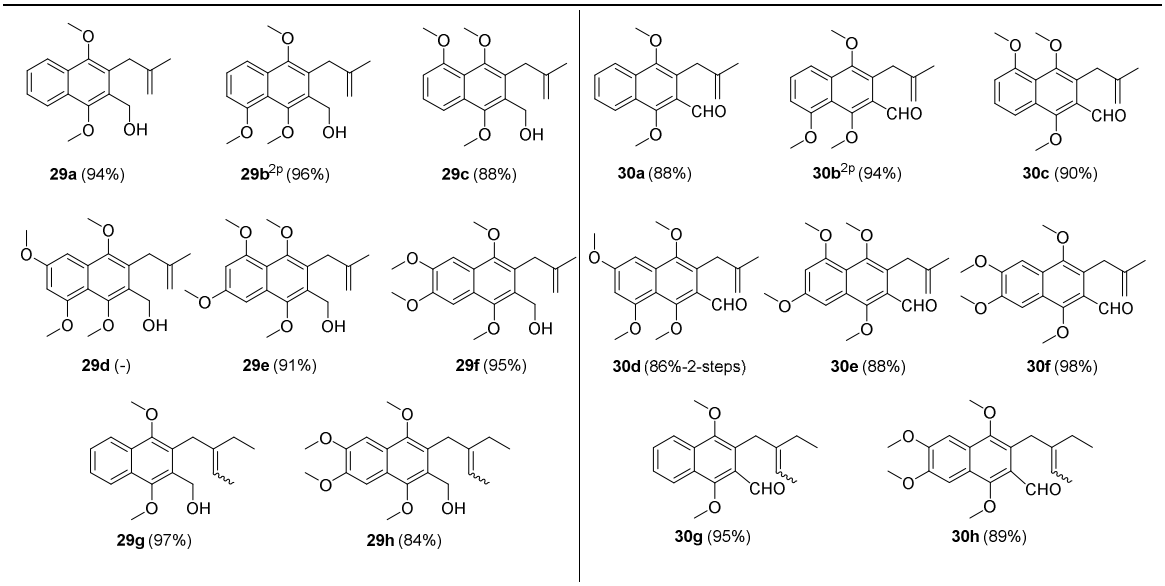
Synthesis of anthraquinones from 3-allylnaphthoates:

In an earlier study, we reported only one example of a novel formation of anthraquinone based upon ICE reaction of 3-methallylnaphthalene-2-carboxaldehyde.[2k] Generalization of the finding was impeded by the accessibility of the precursor aldehydes. With naphthoates **16a**–**f**, **16h–i** (Table 3) in hand, we elaborated them to the respective anthraquinones. The naphthoates **16a**–**f**, **16h–i** were transformed to alcohols **29a**–**h** by DIBAL-H (diisobutylaluminium hydride) reduction and then to aldehydes **30a**–**h** by DMP (Dess–Martin periodinane) oxidation (Table 5) in good yields.

Table 5. Preparation of *o*-allyl naphthalaldehyde

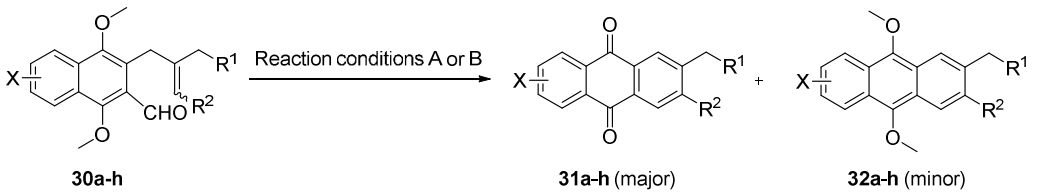


X = H, OCH_3; R^1 = H, Me; R^2= H, Me



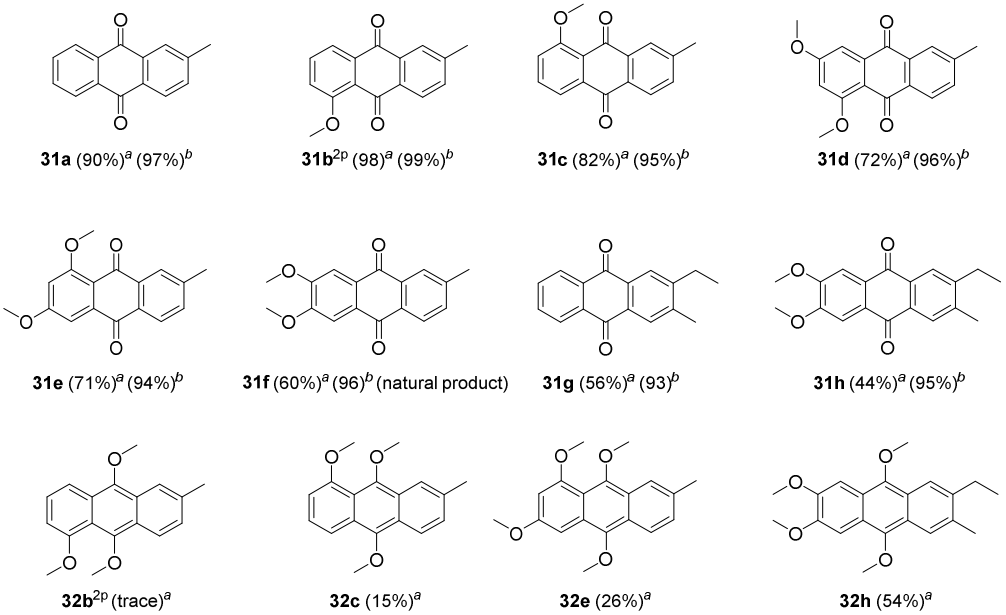
The aldehydes **30a–h** were then treated with BINOL-PO_2H (*rac*-BINOL phosphoric acid) in chloroform at rt in the presence of air. The corresponding anthraquinones **31a–h** were formed. But, along with some amounts of anthracenes **32a–h** were also formed in the range trace-54% yield. Since, the anthracenes were not stable to light and air, their full characterizations were difficult. However, we could characterize four anthracenes **32b**, **32c**, **32e** and **32h** (vide Table 6 for yields of **32b**, **32c**, **32e** and **32h**; vide experimental section for yields of unidentified anthracenes). According to the mechanism,[2k] earlier proposed by us, for the formation of anthraquinones **31a–h**, water and light are needed along with air (Scheme 8). Therefore, we repeated the reactions of **30a–h** with BINOL-PO_2H in the presence of water, air under the exposure of 100 W lamp. In each case, the corresponding anthraquinone (**31a–h**) was obtained almost in quantitative yield (Table 6).

Table 6. Substrate scope for the new anthraquinone synthesis



Reaction conditions A: 10 mol% of BINOL-PO_2H added to a stirred solution of *o*-propenyl naphthalene aldehydes in a screw capped vial and stirred for 4–5 d.

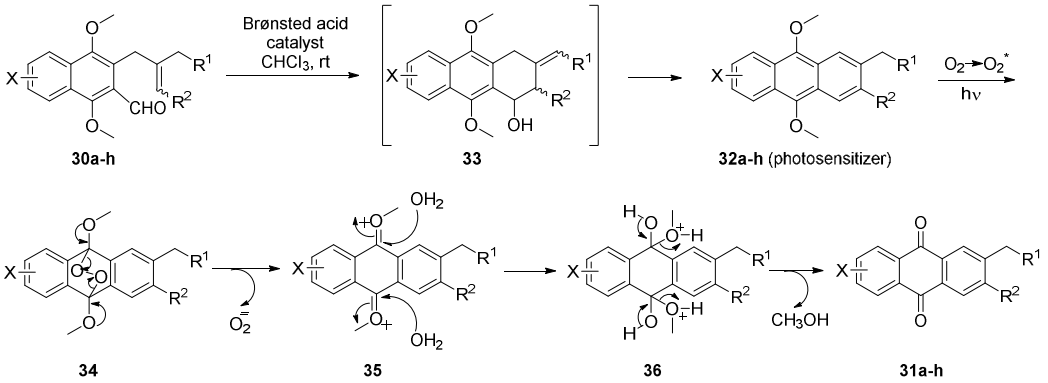
Reaction conditions B: 10 mol% of BINOL-PO_2H added to a stirred solution of *o*-propenyl naphthalene aldehydes in a screw capped vial and stirred for 4–5 d. After completion of reaction, water (2 mL/mmol) was added and stirred under the exposure of 100 W lamp for 15 h.



[a]Yields refer to the conditions A in the discussion above, [b]Yields refer to the conditions B in the discussion above

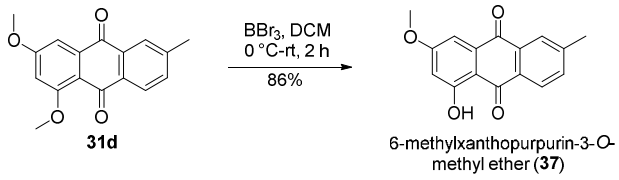
Akin to the already proposed mechanism,[2k] the aldehydes **30a**–**h** undergo carbonyl-ene reaction to form ene cyclized products **33**, followed by dehydration under acidic conditions to furnish the anthracenes **32a**–**h**. These anthracenes act as photosensitizers and react with *in situ* generated singlet oxygen to form cycloaddition adducts **34**. The cycloaddition adducts break down to form bisoxocarbenium ions **35**, which on water addition form **36**. Loss of methanol from **36** furnishes anthraquinones **31a**–**h** (Scheme 8).

Scheme 8. Proposed mechanism for the formation of 31a−h



To prepare the natural product **37,** the anthraquinone **31d** was treated with BBr_3 in DCM. Expectedly, natural product **37** was formed in 86% yield (Scheme 9).

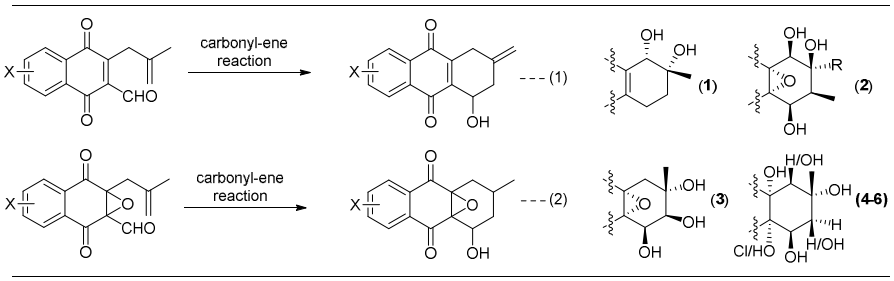
Scheme 9. Synthesis of natural product 6-methylxanthopurpurin-3-*O*-methyl ether (37)



Synthesis of tetrahydroanthraquinones from 3-allylnaphthoates:

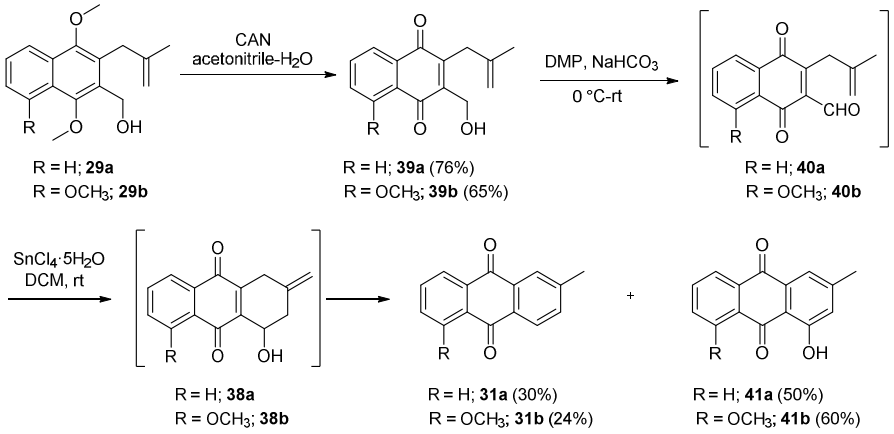
This part of the study was directed to the utilization of the naphthoates (*cf.* **16aa**, **16b**) in the synthesis of hydroanthraquinone embedded natural products. It may be noted that the synthesis of these natural products (**1–6**) (Figure 1, Scheme 10) are of interest due to their complex and varied oxygen functionalities. The carbonyl-ene reaction of electronically rich methoxy naphthoxaldehydes **30a–h** directly leads to the formation of anthraquinones (Table 6). Alternatively, we conceived the strategies presented in Scheme 10, where affording the non-aromatized ene products is much more feasible.

Scheme 10. Strategies for the synthesis of tetrahydroanthraquinones



First, we contemplated the access to anthracenones **38a–b** as key intermediates so as to fabricate the corresponding hydroaromatics. When alcohols **39a**–**b**, obtained by CAN (ceric ammonium nitrate) oxidation of the alcohols **29a**–**b**, were treated with DMP, aldehydes **40a**-**b** were obtained. Due to their instability in silica gel, they were as such subjected to reaction with $SnCl_4{\cdot}5H_2O$. These reactions afforded anthraquinones **31a–b** and **41a–b** in moderate yields. Isolation of the immediate ene products **38a–b** were of no avail (Scheme 11).

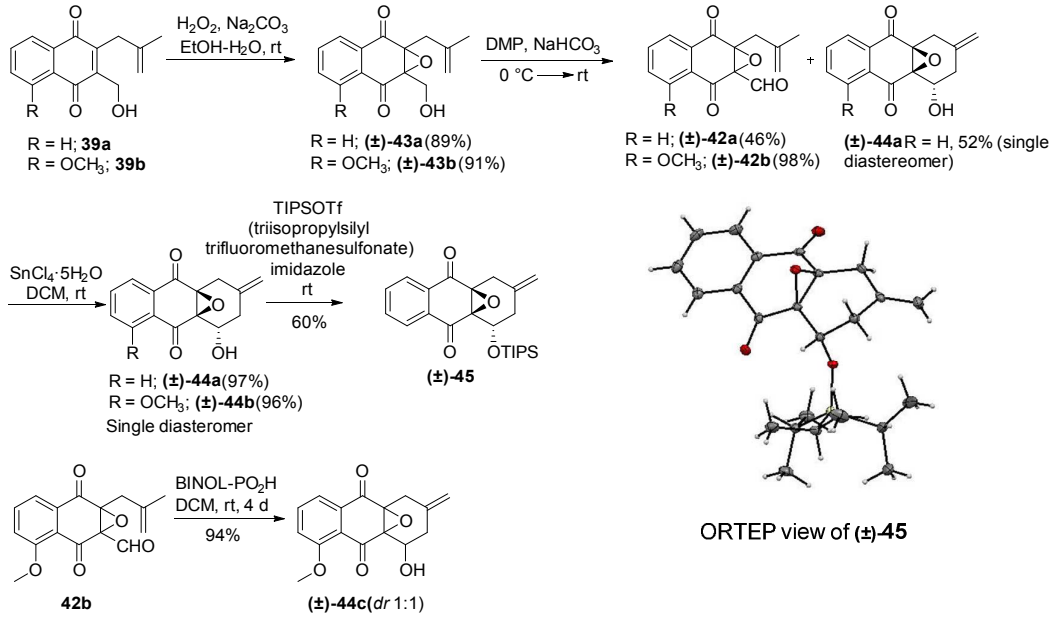
Scheme 11. Intramolecular carbonyl-ene reactivity of naphthoquinonyl carboxaldehyde



Alternatively, we explored ene-chemistry of epoxy aldehydes (±)-**42a**–**b**. The epoxy alcohols (±)-**43a–b** were prepared by epoxidation of naphthoquinones **39a–b**. Treatment of epoxy alcohol (±)-**43a** with DMP provided aldehyde (±)-**42a** along with ene product (±)-**44a** as single diastereomer. The epoxy alcohol (±)-**43b,** however, furnished aldehyde (±)-**42b** as the sole product on oxidation with DMP. When the aldehydes (±)-**42a**–**b** were treated with $SnCl_4{\cdot}5H_2O$ in DCM, ene products (±)-**44a**–**b** were obtained in almost quantitative yields as single diastereomers. The *trans* stereochemistry of the ene cyclized products were confirmed from the crystal structure of the silylated product of (±)-**44a** i.e. (±)-**45**. Most notably, many hydroanthraquinone natural products bear this kind *trans* stereochemistry (*cf.* **2**–**6**; Figure 2,

Scheme 10). On the contrary, treatment of (±)-**42b** with BINOL-PO_2H gave 1:1 diastereomeric mixture (±)-**44c** (Scheme 12).

Scheme 12. Intramolecular ene-reaction of epoxydihydronaphthoquinone carboxaldehydes



Explanation for the anomaly in stereoselectivity observed in ene reaction of (±)-42a–b: Excess $NaHCO_3$ was used during the DMP-oxidation of (±)-**43a** to quench acetic acid by-product. So, acetic acid catalyzed ene reaction of (±)-**42a** during DMP-oxidaion is ruled out. The aldehyde **(±)-42a** is stable at room temperature and we carried out the DMP-oxidation on (±)-**43a** at 0 °C-rt. Therefore, the thermal ene reaction of (±)-**42a** at room temperature is also ruled out. We, therefore, propose that diastereoselectivity of the reaction of (±)-**42a** under DMP-oxidation conditions is due to DMP or acetoxy iodinane. This kind of ene reaction is not observed for the substrate (±)-**42b** under the DMP-oxidation conditions, probably due to the *peri*-effect originating from the methoxy group in the substrate (±)-**42b**. The substrates **30a–h** are also stable under DMP-oxidation conditions. This must be due to the reduced reactivity arising from conjugation with aromatic ring in **30a–h**.

When Lewis acid catalysts are employed for the ene reaction, there may be a continuum between concerted and stepwise mechanisms.[7b] However, we have conceived transition states for the concerted mechanism for explaining the product diastereoselectivity. During $SnCl_4·5H_2O$ catalyzed ene reaction of (±)-**42a–b** or DMP/acetoxy iodinane catalyzed

ene reaction of (±)-**42a**, 6-membered chelation occurs as shown in transition states **46** and **47**, providing conformational bias in the transition states. For the requirement of lower activation energy, reaction occurs in such a conformation that hydroxyl group becomes *trans* to epoxy group in product (±)-**44a–b**. Representative orbital picture of the transition states is shown as **48**. For BINOL-PO_2H catalyzed reaction of (±)-**42b**, the only driving force is weaker H-bonding so conformational restriction of aldehyde functionality does not occur. Ene reaction of (±)-**42b** occurs with two different conformations of aldehyde functionality with BINOL-PO_2H as shown in transition states **49**, **50** producing two different diastereomers in 1:1 ratio (Figure 2).

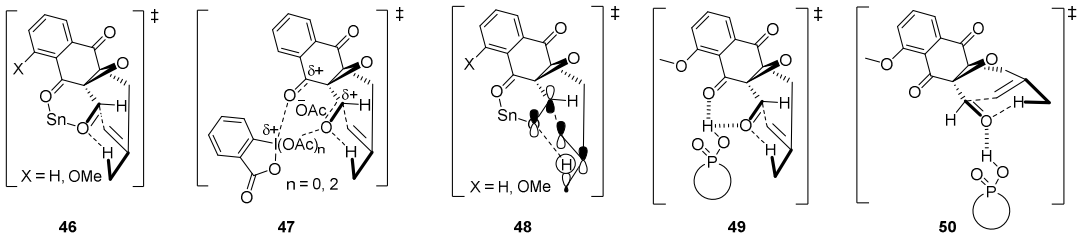
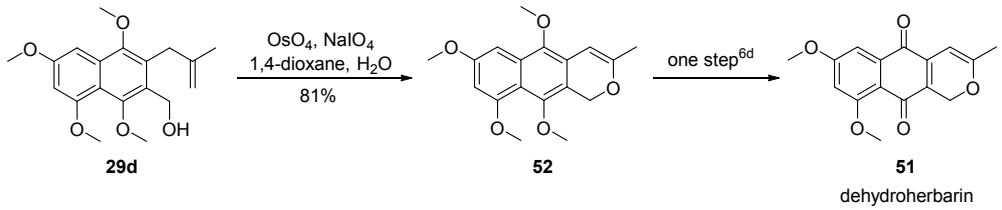


Figure 2. Plausible transition states for the diastereselective ene reaction of (±)-**42a–b**

Synthesis of pyaranonaphthoquinone natural product dehydroherbarin (51):

With the naphthylmethanol **29d** in hand, we were tempted to achieve a short synthesis of pyranonapthaquinone natural product, dehydroherbarin (**51**). It was isolated from dematiaceous fungus *Torula herbarum*[10a] and shown to exhibit antimicrobial and antiamoebic activity, as well as inhibit both metastatic prostate and breast cancers (PC-3M and MDA-MB-231 respectively).[6f,10b] Till date, three total syntheses[10c–d,6d] of **51** have been reported. When alcohol **29d** was subjected to OsO_4 catalyzed Lemieux-Johnson oxidation, tricyclic product **52** was formed in 81% yield, thus constituting a formal short synthesis of **51**[6d] (Scheme 13).

Scheme 13. Synthesis of dehydroherbarin (51)



CONCLUSION

A regiospecific synthesis of 3-(2-alkenyl)naphthoates is achieved, by the use of [4 + 2] anionic annulations. An autooxidized annulation product, i.e. **16k** was obtained when annulation was performed with prenyl chain containing dienoate. The ready accessibility of the naphthoates has allowed development of a room temperature synthesis of anthraquinones via a sequence of intramolecular carbonyl-ene reaction-dehydration-photooxidation. Diastereoselective synthesis of tetrahydroanthraquinones has been feasible with similar strategy. A short synthesis of dehydroherbarin (**51**) is accomplished utilizing one of the methallylnaphthoates.

EXPERIMENTAL SECTION

General Procedures. All reactions utilizing moisture-sensitive reagents were performed under an inert atmosphere. All solvents were dried prior to use, according to the standard protocols. Benzene, toluene, diethyl ether, THF, MTBE were distilled from Na/benzophenone. CH_3CN, $CHCl_3$ and DCM were dried over CaH_2. EtOH and MeOH were dried over CaO and then over magnesium turnings. Ethyl acetate, hexane, petroleum ether and acetone were distilled from $CaCl_2$. Melting points were determined in open capillary tubes and are reported as uncorrected. TLC was carried out on precoated plates (silica gel 60 F_{254}), and the spots were visualized with UV and fluorescent lights or by staining with iodine, *p*-anisaldehyde, $KMnO_4$ stains. Column chromatography was performed on silica gel (60–120 or 230–400 mesh). ^1H and ^{13}C NMR spectra for all the compounds were recorded at 400/600 and 100/150 MHz (Bruker Ultrashield^{TM} 400, Ascend^{TM} 600), respectively. The following abbreviations are used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublets of doublets, m = multiplet. Coupling constants, *J*, are reported in Hertz (Hz). IR spectra were recorded with a Perkin–Elmer FTIR instrument using a KBr pellet. The phrase "usual work-up" refers to washing of the organic phase with water (2 x 1/4 of the volume of the organic phase) and brine (1 x 1/4 of the volume of the organic phase), drying (Na_2SO_4), filtration, and concentration under reduced pressure.

Preparation of skipped dienoates

*Ethyl (E)-5-methylhexa-2,5-dienoate (**14a**).*[8e–f] Ethylaluminium dichloride (40.8 mL 25 wt % in toluene, 80.0 mmol) was added to a solution of ethyl propiolate (7.84 g, 80.0 mmol) in 30 mL DCM in 250 mL sealed tube. An excess of isobutylene gas was then condensed into

the solution at -25 °C and the tube was sealed and stirred at 25 °C for 1 day. The reaction mixture was poured into saturated sodium bicarbonate solution and filtered to remove precipitated aluminum salts. The filtrate was then extracted with DCM (3 x 100 mL). The combined extracts were washed with brine (2 x 100 mL), dried over Na_2SO_4 and concentrated to afford crude product **14a** in 92% yield (11.3 g, 73.6 mmol). The crude product was of high purity to perform reactions. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.98–6.93 (m, 1H), 5.84 (d, *J* = 15.5 Hz, 1H), 4.82 (s, 1H), 4.74 (s, 1H), 4.18 (q, *J* = 7.0 Hz, 2H), 2.87 (d, *J* = 7.2 Hz, 2H), 1.73 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.7, 146.5, 142.4, 122.8, 112.7, 60.4, 40.7, 22.7, 14.5.

*Ethyl (2E)-5-ethylhepta-2,5-dienoate (**14b**).*[8e–f] The compound **14b** was obtained as 1.3:1 diastereomeric mixture from intermolecular ene reaction between ethyl propiolate (1.94 g, 20 mmol) and 2-ethyl-1-butene (2.36 g, 28 mmol) as yellowish liquid (3.06 g, 16.8 mmol) in 84% yield. Experimental procedure is similar to that described for the synthesis of the compound **14a**. Crude product was of high purity to perform reactions. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.92–6.83 (m, 1H), 5.79–5.75 (m, 1H), 5.34–5.17 (m, 1H), 4.16–4.11 (m, 2H), 2.89–2.81 (m, 2H), 2.02–1.94 (m, 2H), 1.58 – 1.52 (m, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 0.95–0.90 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.8, 166.7, 147.8, 146.7, 138.3, 137.3, 122.2, 121.6, 121.1, 120.1, 60.3, 60.2, 39.4, 33.2, 30.0, 23.1, 14.4, 13.4, 13.2, 12.7.

*Methyl 6-methylhept-5-en-2-ynoate (**17a**).*[11a] The compound **17a** was prepared from ethyl propiolate and prenyl bromide following the literature procedure.[11a] ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.17–5.14 (m, 1H), 3.74 (s, 3H), 3.02 (d, *J* = 7.0 Hz, 2H), 1.71 (d, J = 1.2 Hz, 3H), 1.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 135.8, 115.9, 88.2, 72.1, 52.4, 25.4, 17.7. IR (KBr): $\tilde{\nu}$ = 3422, 2957, 2219, 1717, 1437, 1251, 1098, 963, 750 cm^{-1}. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_9H_{13}O_2$ 153.0916; Found 153.0902.

*Methyl (Z)-6-methylhepta-2,5-dienoate (**14c**).*[11b] The compound **17a** (1.01 g, 6.5 mmol) was dissolved in 10 mL methanol. Catalytic amount of 10 % Pd-C (50 mg) and quinoline (50 mg) was added and stirred for 24 h at rt under atmospheric pressure of H_2. The reaction mixture was filtered through celite and methanol was evaporated carefully under reduced pressure at low temperature. The crude product was purified by column chromatography on silica gel with petroleum ether as solvent to obtain pure compound **14c** in 70% yield (0.7 g, 4.55 mmol) as sole product. Colourless liquid; R_f (hexane) 0.3; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.20–6.13 (m, 1H), 5.77–5.73 (m, 1H), 5.17–5.13 (m, 1H), 3.71 (s, 3H), 3.38–3.35 (m, 2H),

1.71 (s, 3H), 1.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 149.3, 134.1, 120.8, 118.7, 51.2, 28.5, 25.8, 18.0.

*Ethyl hex-5-en-2-ynoate (**17b**).*[11a] The compound **17b** was prepared following the literature procedure.[11a] ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.78–5.72 (m, 1H), 5.33–5.30 (m, 1H), 5.17–5.14 (m, 1H), 4.19 (q, J = 7.2 Hz, 2H), 3.09–3.07 (m, 2H), 1.27 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.8, 129.9, 117.9, 85.6, 75.2, 62.0, 23.0, 14.2. IR (KBr): $\tilde{\nu}$ = 3416, 2986, 2238, 1714, 1370, 1262, 1098, 1014, 860, 752 cm^{-1}. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ Calcd for $C_8H_{11}O_2$ 139.0759; Found 139.0735.

*Ethyl (Z)-hexa-2,5-dienoate (**14d**).*[11c] The compound **17b** (1.1 g, 8 mmol) was dissolved in 10 mL methanol. Catalytic amount of Lindlar catalyst was added and stirred for 24 h at rt under atmospheric pressure of H_2. The reaction mixture was filtered through celite and methanol was evaporated carefully under reduced pressure at low temperature. The crude product was purified by column chromatography on silica gel with petroleum ether as solvent to obtain pure compound **14d** in 90% yield (1.0 g, 7.2 mmol) as sole product. Colourless liquid; R_f (hexane) 0.3; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.23–6.14 (m, 1H), 5.89 – 5.72 (m, 2H), 5.12 – 4.97 (m, 2H), 4.14 (q, J = 7.1 Hz, 2H), 3.41–3.37 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 146.9, 135.4, 120.4, 116.2, 60.0, 33.3, 14.4. IR (KBr): $\tilde{\nu}$ = 2982, 1720, 1640, 1412, 1182, 1036, 916, 818 cm^{-1}. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ Calcd for $C_8H_{13}O_2$ 141.0916; Found 141.0922.

*Ethyl 1,4,8-trimethoxy-3-(2-methylallyl)-2-naphthoate (**16aa**) and ethyl 1,4,8-trimethoxy-3-(2-methylprop-1-en-1-yl)-2-naphthoate (**16ab**).*

Annulation with NaH. A suspension of NaH (60% in oil, 40 mg, 1.0 mmol) in THF (5 mL) was added to a solution of methoxycyanophthalide **15a** (94.5 mg, 0.5 mmol) and **14a** (84.1 mg, 0.6 mmol) in 8 mL THF at 0 °C. The reaction mixture was warmed to rt and stirred for 2 h. The reaction mixture was cooled to 0 °C and NaH (60% in oil, 40 mg, 1.0 mmol) was added to the reaction mixture followed by addition of Me_2SO_4 (0.47 mL, 5 mmol). The reaction mixture was allowed to warm to rt and stirred for 4 h. The reaction mixture was again cooled to 0 °C and quenched with saturated NH_4Cl. THF was evaporated under reduced pressure. The residue was then extracted with EtOAc (3 x 20 mL). The combined extracts were washed with brine (3 x 10 mL), dried over Na_2SO_4 and concentrated to afford crude product. This crude product was purified by column chromatography on silica gel with

EtOAc/petroleum ether (1:20) as solvent to obtain mixture of **16aa** and **16ab** in 45% yield (78 mg, 0.23 mmol) in 2:1 ratio.

Annulation with LiO^{t}Bu. A solution of 3-cyanophthalide **15a** (94.5 mg, 0.5 mmol) in dry THF (2 mL) was added to stirred suspension of LiO^{t}Bu (240 mg, 3 mmol) in dry THF (8 mL) at -60 °C under an inert atmosphere. The resulting solution was stirred at -60 °C for 30 min after which a solution of **14a** (84.1 mg, 0.6 mmol) in dry THF (2 mL) was added. The reaction mixture was stirred for another 30 min at -60 °C followed by 6–8 h stirring at room temperature. The reaction mixture was cooled to 0 °C and NaH (60% in oil, 40 mg, 1.0 mmol) was added to the reaction mixture followed by addition of Me_2SO_4 (0.47 mL, 5 mmol). The reaction mixture was again cooled to 0 °C and quenched with saturated NH_4Cl. THF was evaporated under reduced pressure. The residue was then extracted with EtOAc (3 x 20 mL). The combined extracts were washed with brine (3 x 10 mL), dried over Na_2SO_4 and concentrated to afford crude product. This crude product was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:20) as solvent to obtain mixture of **16aa** and **16ab** in 25% yield (43 mg, 0.13 mmol) in 2:3 ratio.

Optimized general annulation procedure with LiHMDS. A solution of 3-cyanophthalide (1.0 mmol) in dry THF (5 mL) was added to stirred solution of LiHMDS (3 mmol) in mixture of dry THF (5 mL) and MTBE (5 mL) at -78 °C under an inert atmosphere. The resulting solution was stirred at -78 °C for 30 min after which a solution of skipped dienoate acceptor (1.2 mmol) in dry THF (2 mL) was added. The reaction mixture was stirred for another 30 min at -78 °C followed by 6–8 h stirring at room temperature. The reaction mixture was cooled to 0 °C and NaH (60% in oil, 160 mg, 4.0 mmol) was added to the reaction mixture followed by addition of Me_2SO_4 (0.95 mL, 10 mmol). The reaction mixture was again cooled to 0 °C and quenched with saturated NH_4Cl. THF was evaporated under reduced pressure. The residue was then extracted with EtOAc (3 x 40 mL). The combined extracts were washed with brine (3 x 15 mL), dried over Na_2SO_4 and concentrated to afford crude product. This crude product was purified by column chromatography on silica gel with EtOAc/petroleum ether as solvent to obtain pure compound.

Data for 16aa. Annulation reaction was performed between **15a** and **14a** with LiHMDS following the optimized procedure. Annulation crude product was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:15) as solvent to obtain pure compound **16aa** in 94% yield (323.5 mg, 0.94 mmol) as sole product. Yellowish liquid; R_f

(1:15 EtOAc (Ethyl acetate)/hexane) 0.25; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.69 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.47–7.43 (m, 1H), 6.88 (dd, *J* = 7.7, 1.0 Hz, 1H), 4.82–4.78 (m, 1H), 4.54–4.53 (m, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 4.00 (s, 3H), 3.86 (s, 3H), 3.85 (s, 3H), 3.54 (s, 2H), 1.75 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.1, 156.8, 150.6, 150.2, 143.8, 131.9, 127.8, 127.5, 126.1, 119.8, 115.3, 112.1, 106.4, 64.1, 62.3, 61.3, 56.3, 35.2, 23.1, 14.4. IR (KBr): $\tilde{\nu}$ = 2933, 2842, 1726, 1573, 1448, 1372, 1341, 1272, 1251, 1220, 1190, 1109, 1072, 1048, 772 cm^{-1}. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{20}H_{25}O_5$ 345.1702; Found 345.1711.

Data for 16ab.[8d] As the compound **16ab** was obtained as a mixture with the compound **16aa** from annulation reaction with NaH and Li*O*^{t}Bu, we determined the data of the compound **16ab** comparing the NMR of pure **16aa** and NMR of mixture of **16aa** and **16ab**. R_f (1:20 EtOAc/hexane) 0.1; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.4 Hz, 1H), 7.45–7.42 (m, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.17–6.16 (m, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 4.00 (s, 3H), 3.87 (s, 3H), 3.76 (s, 3H), 1.91 (s, 3H), 1.59 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (600 MHz, $CDCl_3$): δ 168.0, 156.7, 149.8, 149.3, 139.6, 132.1, 127.9, 127.3, 125.6, 119.8, 117.8, 115.4, 106.6, 64.1, 61.2, 61.1, 56.4, 25.8, 20.4, 14.5.

*Ethyl 1,4-dimethoxy-3-(2-methylallyl)-2-naphthoate (**16b**).* Annulation reaction was performed between **15b** (240 mg, 1.5 mmol) and **14a** (277 mg, 1.8 mmol) with LiHMDS (4.5 mmol) following the general procedure. Annulation crude product was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:20) as solvent to obtain pure compound **16b** in 68% yield (314 mg, 1.0 mmol) as sole product. Yellowish liquid; R_f (1:20 EtOAc/hexane) 0.4; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.12–8.08 (m, 2H), 7.59–7.50 (m, 2H), 4.81–4.80 (m, 1H), 4.51 (s, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.99 (s, 3H), 3.89 (s, 3H), 3.61 (s, 2H), 1.77 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 150.8, 150.3, 144.2, 129.6, 127.9, 127.4, 126.4, 125.9, 125.7, 123.2, 122.9, 112.0, 63.7, 62.5, 61.5, 34.9, 23.1, 14.4. IR (KBr): $\tilde{\nu}$ = 2979, 2938, 1727, 1590, 1457, 1418, 1356, 1283, 1233, 1158, 1087, 1047, 968, 891, 777, 754 cm^{-1}. HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{19}H_{22}O_4Na$ 337.1416, $[M + H]^+$ Calcd for $C_{19}H_{23}O_4$ 315.1596; Found 337.1415, 315.1599.

*Ethyl 1,4,5-trimethoxy-3-(2-methylallyl)-2-naphthoate (**16c**).* Annulation reaction was performed between **15c** (189 mg, 1.0 mmol) and **14a** (185 mg, 1.2 mmol) with LiHMDS (3.0 mmol) following the general procedure. Annulation crude product was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:10) as solvent to obtain pure

compound **16c** in 79% yield (272 mg, 1.0 mmol) as sole product. Yellowish liquid; R_f (1:10 EtOAc/hexane) 0.4; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.70 (d, J = 8.4 Hz, 1H), 7.42–7.38 (m, 1H), 6.91 (d, J = 7.6 Hz, 1H), 4.78 (s, 1H), 4.50 (s, 1H), 4.37 (q, J = 7.1 Hz, 2H), 3.99 (s, 3H), 3.94 (s, 3H), 3.77 (s, 3H), 3.59 (s, 2H), 1.76 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 156.2, 151.0, 149.5, 144.4, 130.3, 126.6, 126.5, 126.4, 121.6, 115.4, 111.8, 107.5, 63.4, 62.7, 61.4, 56.4, 34.7, 23.1, 14.3. IR (KBr): $\tilde{\nu}$ = 2934, 2841, 1727, 1573, 1460, 1370, 1337, 1269, 1156, 1065, 1048, 980, 890, 769 cm^{-1}. HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{20}H_{24}O_5Na$ 367.1521, $[M + H]^+$ Calcd for $C_{20}H_{25}O_5$ 345.1702; Found 367.1524, 345.1714.

*Ethyl 1,4,6,8-tetramethoxy-3-(2-methylallyl)-2-naphthoate (**16d**).* Annulation reaction was performed between **15d** (217 mg, 1.0 mmol) and **14a** (185 mg, 1.2 mmol) with LiHMDS (3.0 mmol) following the general procedure. Annulation crude product was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:10) as solvent to obtain pure compound **16d** in 76% yield (284 mg, 0.76 mmol) as sole product. Yellowish liquid; R_f (1:10 EtOAc/hexane) 0.5; ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.99 (d, J = 2.4 Hz, 1H), 6.54 (d, J = 2.4 Hz, 1H), 4.83–4.75 (m, 1H), 4.54 (s, 1H), 4.33 (q, J = 7.1 Hz, 2H), 3.96 (s, 3H), 3.93 (s, 3H), 3.84 (s, 3H), 3.83 (s, 3H), 3.52 (s, 2H), 1.75 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.2, 159.4, 158.1, 150.6, 149.6, 143.9, 132.7, 126.8, 125.5, 115.6, 112.0, 99.4, 93.5, 64.1, 61.6, 61.2, 56.3, 55.6, 35.3, 23.0, 14.4. IR (KBr): $\tilde{\nu}$ = 2928, 2851, 1725, 1619, 1582, 1411, 1381, 1346, 1240, 1213, 1189, 1155, 1058, 973, 834 cm^{-1}. HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{21}H_{26}O_6Na$ 397.1627, $[M + H]^+$ Calcd for $C_{21}H_{27}O_6$ 375.1808; Found 397.1605, 375.1812.

*Ethyl 1,4,5,7-tetramethoxy-3-(2-methylallyl)-2-naphthoate (**16e**).* Annulation reaction was performed between **15e** (325.5 mg, 1.5 mmol) and **14a** (277.2 mg, 1.8 mmol) with LiHMDS (4.5 mmol) following the general procedure. Annulation crude product was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:10) as solvent to obtain pure compound **16e** in 71% yield (398 mg, 1.1 mmol) as sole product. Yellowish liquid; R_f (1:10 EtOAc/hexane) 0.3; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 (d, J = 2.4 Hz, 1H), 6.57 (d, J = 2.4 Hz, 1H), 4.80–4.73 (m, 1H), 4.51–4.46 (m, 1H), 4.36 (q, J = 7.1 Hz, 2H), 3.95 (s, 3H), 3.92 (s, 3H), 3.90 (s, 3H), 3.74 (s, 3H), 3.54 (s, 2H), 1.74 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 158.6, 157.5, 151.3, 148.5, 144.6, 130.9, 127.2, 123.9, 117.5, 111.6, 100.3, 93.4, 62.8, 62.7, 61.3, 56.3, 55.5, 34.5, 23.0, 14.3.

IR (KBr): $\tilde{\nu}$ = 2941, 2842, 1719, 1618, 1591, 1468, 1448, 1411, 1342, 1251, 1342, 1219, 1155, 1047, 960, 849, 668 cm^{-1}. HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{21}H_{26}O_6Na$ 397.1627, $[M + H]^+$ Calcd for $C_{21}H_{27}O_6$ 375.1808; Found 397.1603, 375.1815.

*Ethyl 1,4,6,7-tetramethoxy-3-(2-methylallyl)-2-naphthoate (**16f**).* Annulation reaction was performed between **15f** (325 mg, 1.5 mmol) and **14a** (277 mg, 1.8 mmol) with LiHMDS (4.5 mmol) following the general procedure. Annulation crude product was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:5) as solvent to obtain pure compound **16f** in 85% yield (477 mg, 1.3 mmol) as sole product. Yellowish liquid; R_f (1:5 EtOAc/hexane) 0.3; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 (s, 1H), 7.34 (s, 1H), 4.79–4.78 (m, 1H), 4.51–4.50 (m, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 4.02 (s, 3H), 4.01 (s, 3H), 3.95 (s, 3H), 3.86 (s, 3H), 3.57 (s, 2H), 1.75 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.1, 150.9, 150.1, 149.7, 149.3, 144.4, 125.4, 124.2, 124.1, 123.3, 111.7, 101.9, 101.6, 63.2, 62.0, 61.3, 56.2, 56.1, 34.9, 23.1, 14.4. IR (KBr): $\tilde{\nu}$ = 3448, 2937, 1720, 1450, 1332, 1259, 1231, 1209, 1169, 1093, 1046, 1013, 859 cm^{-1}. HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{21}H_{26}O_6Na$ 397.1627, $[M + H]^+$ Calcd for $C_{21}H_{27}O_6$ 375.1808; Found 397.1620, 375.1792.

*Ethyl 6-bromo-1,4-dimethoxy-3-(2-methylallyl)-2-naphthoate (**16g**).* Annulation reaction was performed between **15g** (237 mg, 1.0 mmol) and **14a** (185 mg, 1.2 mmol) with LiHMDS (3.0 mmol) following the general procedure. Annulation crude product was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:15) as solvent to obtain pure compound **16g** in 48% yield (188 mg, 0.48 mmol) as sole product. Yellowish liquid; R_f (1:15 EtOAc/hexane) 0.3; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.23 (d, *J* = 2.1 Hz, 1H), 7.97 (d, *J* = 8.9 Hz, 1H), 7.59 (dd, *J* = 9.0, 2.1 Hz, 1H), 4.84–4.76 (m, 1H), 4.49 (s, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 3.96 (s, 3H), 3.87 (s, 3H), 3.59 (s, 2H), 1.75 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 150.5, 149.9, 143.9, 130.7, 129.9, 127.3, 126.4, 126.3, 125.3, 125.2, 122.3, 112.2, 63.8, 62.7, 61.6, 35.0, 23.1, 14.4. IR (KBr): $\tilde{\nu}$ = 2975, 2937, 2850, 1772, 1730, 1616, 1582, 1449, 1367, 1341, 1274, 1225, 1092, 1046, 968, 889, 825 cm^{-1}. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{19}H_{22}BrO_4$ 393.0701; Found 393.0711.

*Ethyl 3-(2-ethylbut-2-en-1-yl)-1,4-dimethoxy-2-naphthoate (**16h**).* Annulation reaction was performed between **15b** (159 mg, 1.0 mmol) and **14b** (219 mg, 1.2 mmol) with LiHMDS (3.0 mmol) following the general procedure. Annulation crude product was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:10) as solvent to obtain

1.3:1 diastereomeric mixture of compound **16h** in 84% yield (288 mg, 0.84 mmol). Yellowish liquid; R_f (1:10 EtOAc/hexane) 0.3; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.11–8.08 (m, 4.6H), 7.56–7.49 (m, 4.6H), 5.35 (q, *J* = 6.6 Hz, 1.3H), 4.95 (q, *J* = 6.6 Hz, 1H), 4.38–4.32 (m, 4.6H), 3.98 (s, 3H), 3.97 (s, 3.9H), 3.89 (s, 3.9H), 3.87 (s, 3H), 3.73 (s, 2.6H), 3.63 (s, 2H), 2.08 (q, *J* = 7.8 Hz, 2H), 1.79 (q, *J* = 7.2 Hz, 2.6H), 1.75 (d, *J* = 6.6 Hz, 3.9H), 1.56 (d, *J* = 6.6 Hz, 3H), 1.40–1.36 (m, 6.9H), 1.02 (t, *J* = 7.8 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3.9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.9, 167.9, 151.0, 150.8, 150.1, 150.0, 140.0, 139.3, 129.5, 129.4, 127.7, 127.6, 127.3, 127.3, 126.4, 126.2, 126.2, 126.1, 126.1, 123.1, 123.0, 122.8, 122.8, 119.8, 118.7, 63.5, 62.5, 62.2, 61.4, 61.3, 33.4, 28.4, 27.5, 23.8, 14.3, 14.2, 13.7, 13.2, 12.9, 12.6. IR (KBr): $\tilde{\nu}$ = 3448, 2964, 2936, 1727, 1458, 1419, 1355, 1280, 1234, 1158, 1086, 1039, 969, 778, 749 cm^{-1}. HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{21}H_{26}O_4Na$ 365.1729, $[M + H]^+$ Calcd for $C_{21}H_{27}O_4$ 343.1909; Found 365.1731, 343.1921.

*Ethyl (E)-3-(2-ethylbut-2-en-1-yl)-1,4,6,7-tetramethoxy-2-naphthoate (**16i**).* Annulation reaction was performed between **15f** (219 mg, 1.0 mmol) and **14b** (218 mg, 1.2 mmol) with LiHMDS (3.0 mmol) following the general procedure. Annulation crude product was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:5) as solvent to obtain 1:1 diastereomeric mixture of compound **16i** in 82% yield (330 mg, 0.82 mmol). Yellowish liquid; R_f (1:5 EtOAc/hexane) 0.4; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 (s, 3H), 7.31 (s, 1H), 5.30 (q, *J* = 6.6 Hz, 1H), 4.90 (q, *J* = 6.6 Hz, 1H), 4.36–4.23 (m, 4H), 4.01 (s, 3H), 4.00 (s, 3H), 3.98 (s, 6H), 3.93 (s, 3H), 3.92 (s, 3H), 3.85 (s, 3H), 3.83 (s, 3H), 3.65 (s, 2H), 3.55 (s, 2H), 2.03 (q, *J* = 7.4 Hz, 2H), 1.75 (q, *J* = 7.5 Hz, 2H), 1.71 (d, *J* = 6.8 Hz, 3H), 1.51 (d, *J* = 6.7 Hz, 3H), 1.36–1.33 (m, 6H), 0.97 (t, *J* = 7.5 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.2, 168.1, 150.8, 150.0, 149.9, 149.7, 149.1, 148.9, 140.2, 139.5, 125.3, 125.2, 124.8, 124.6, 124.5, 124.5, 123.0, 128.9, 119.6, 118.4, 101.8, 101.7, 101.6, 101.6, 63.0, 62.0, 61.8, 61.3, 61.2, 56.1, 56.0, 33.3, 28.4, 27.4, 23.7, 14.3, 14.2, 13.7, 13.2, 12.8, 12.6. IR (KBr): $\tilde{\nu}$ = 3448, 2935, 1724, 1507, 1475, 1428, 1332, 1259, 1231, 1207, 1170, 1092, 1039, 1016, 975, 859 cm^{-1}. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{23}H_{31}O_6$ 403.2121; Found 403.2139.

*Ethyl 4,8-dimethoxy-3-(2-methylallyl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**16ja**) and Ethyl 1-hydroxy-4,8-dimethoxy-3-(2-methylallyl)-3,4-dihydronaphthalene-2-carboxylate (**16jb**).* Annulation reaction was performed between **15h** (246 mg, 1.5 mmol) and **14a** (277 mg, 1.8 mmol) with LiHMDS (4.5 mmol) following

the general procedure. Annulation crude product was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:10) as solvent to obtain two products **16ja** in 32% yield (160 mg, 0.48 mmol) and **16jb** in and 27% yield (135 mg, 0.41 mmol) respectively.

Data for 16ja. Yellowish liquid; R_f (1:3 EtOAc/hexane) 0.40; ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.14 (s, 1H), 7.40–7.36 (m, 1H), 7.03 (d, J = 8.8 Hz, 1H), 6.86 (d, J = 7.2 Hz, 1H), 4.75 (s, 1H), 4.50 (s, 1H), 4.39 – 4.26 (m, 1H), 4.26 – 4.18 (m, 1H), 3.98–3.94 (m, 1H), 3.94 (s, 3H), 3.29–3.25 (m, 1H), 3.21 (s, 3H), 2.08–2.04 (m, 1H), 1.80 (s, 3H), 1.77–1.68 (m, 1H), 1.34 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 166.0, 159.1, 143.4, 137.5, 131.6, 123.5, 117.6, 113.9, 112.8, 99.8, 79.3, 60.7, 56.7, 56.2, 39.5, 35.3, 22.1, 14.4. IR (KBr): $\tilde{\nu}$ = 3430, 2928, 1736, 1638, 1610, 1472, 1376, 1270, 1250, 1094, 1076, 962, 894, 770 cm^{-1}. HRMS (ESI-TOF) m/z: $[M - 2H_2O + H]^+$ Calcd for $C_{19}H_{21}O_3$ 297.1491; Found 297.1499.

Data for 16jb. Yellowish liquid; R_f (1:3 EtOAc/hexane) 0.35; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.44 (m, 1H), 6.98 (d, J = 8.4 Hz, 1H), 6.92 (d, J = 7.2 Hz, 1H), 4.78 (s, 1H), 4.60 (s, 1H), 4.38 (d, J = 5.6 Hz, 1H), 4.06 (q, J = 7.2 Hz, 2H), 3.91 (s, 3H), 3.83 (d, J = 5.2 Hz, 1H), 3.17 (s, 3H), 2.56–2.51 (m, 1H), 2.14–2.10 (m, 1H), 2.02–1.98 (m, 1H), 1.75 (s, 3H), 1.11 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 172.8, 158.9, 143.4, 143.1, 133.4, 122.2, 120.2, 113.0, 112.2, 79.5, 61.1, 56.5, 56.2, 45.1, 38.3, 23.7, 21.9, 14.1. IR (KBr): $\tilde{\nu}$ = 3451, 2922, 1736, 1594, 1470, 1376, 1276, 1074, 960, 892, 772 cm^{-1}. HRMS (ESI-TOF) m/z: $[M - 2H_2O + H]^+$ Calcd for $C_{19}H_{21}O_3$ 297.1491; Found 297.1499.

*Methyl (E)-3-(3-hydroxy-3-methylbut-1-en-1-yl)-1,4-dimethoxy-2-naphthoate (**16k**).* Annulation reaction was performed between **15b** (159 mg, 1.0 mmol) and **14c** (168 mg, 1.2 mmol) with LiHMDS (3.0 mmol) following the general procedure. Annulation crude product was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:7) as solvent to obtain pure compound **16k** in 66% yield (218 mg, 0.66 mmol) as sole product. Yellowish liquid; R_f (1:5 EtOAc/hexane) 0.5; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.14–8.06 (m, 2H), 7.58–7.52 (m, 2H), 6.81 (d, J = 16.4 Hz, 1H), 6.33 (d, J = 16.4 Hz, 1H), 3.99 (s, 3H), 3.94 (s, 3H), 3.85 (s, 3H), 1.69 (bs, 1H), 1.43 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 150.5, 150.1, 143.5, 129.7, 127.9, 127.7, 126.9, 124.6, 123.7, 123.0, 123.0, 119.8, 71.4, 63.8, 61.5, 52.6, 30.0. IR (KBr): $\tilde{\nu}$ = 3448, 2970, 1734, 1441, 1356, 1296, 1226, 1160, 1086, 1048, 968, 777, 743 cm^{-1}. HRMS (ESI-TOF) m/z: $[M - H_2O + H]^+$ Calcd for $C_{19}H_{21}O_4$ 313.1440; Found 313.1444.

*Methyl (E)-1,4-dimethoxy-3-(3-methylbuta-1,3-dien-1-yl)-2-naphthoate (**16ka**).* To a stirred solution of **16k** (106 mg, 0.32 mmol) in 5 ml of THF was added dropwise 1 N aqueous

HCl (1 mL) at 0 °C. Then the reaction mixture was allowed to warm and stirred at rt for 1 h. THF was evaporated at reduced pressure. Then the reaction mixture was extracted with DCM (15 mL x 3) and dried over Na_2SO_4. Evaporation of solvent under reduced pressure afforded crude product, which was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:10) as solvent to obtain pure compound **16ka** in 74% yield (74 mg, 0.24 mmol) as sole product. Yellowish liquid; R_f (1:10 EtOAc/hexane) 0.4. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 8.1, 1.4 Hz, 1H), 8.09–8.06 (m, 1H), 7.58–7.52 (m, 2H), 6.90 (d, *J* = 16.5 Hz, 1H), 6.72 (d, *J* = 16.5 Hz, 1H), 5.12 (s, 2H), 4.00 (s, 3H), 3.94 (s, 3H), 3.86 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.9, 150.8, 150.2, 142.6, 137.1, 129.8, 127.9, 127.7, 126.9, 124.5, 123.9, 123.0, 122.0, 118.5, 63.9, 61.6, 52.7, 18.5. IR (KBr): $\tilde{\nu}$ = 3448, 2936, 1734, 1438, 1356, 1286, 1225, 1160, 1086, 1045, 970, 777 cm^{-1}. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{19}H_{21}O_4$ 313.1440; Found 313.1416.

*Mixture of ethyl 3-allyl-1,4-dimethoxy-2-naphthoate (**16la**) and 7-(ethoxycarbonyl)-5,8-dimethoxy-6-(prop-1-en-1-yl)naphthalen-2-ylium (**16lb**), and ethyl (E)-3-(1,4-dimethoxy-3-methylnaphthalen-2-yl)acrylate (**16lc**).* Annulation reaction was performed between **15b** (238 mg, 1.5 mmol) and **14d** (252 mg, 1.8 mmol) with LiHMDS (4.5 mmol) following the general procedure. Annulation crude product was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:50) as solvent to obtain 3:2 mixture of **16la** and **16lb** in 27% yield (122 mg, 0.41 mmol) and pure **16lc** in 52% yield (234 mg, 0.78 mmol).

Data for mixture of 16la and 16lb. Yellowish liquid; R_f (1:15 EtOAc/hexane) 0.3; **16la:** ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.12–8.09 (m, 2H), 7.57–7.4.9 (m, 2H), 6.01–5.94 (m, 1H), 5.07 (dq, *J* = 8.4, 1.8 Hz, 1H), 5.05 (t, *J* = 1.8 Hz, 1H), 4.43 (q, *J* = 7.2 Hz, 2H), 4.00 (s, 3H), 3.91 (s, 3H), 3.64 (dt, J = 6.0, 1.8 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.9, 150.6, 150.3, 129.7, 129.7, 127.4, 126.4, 125.8, 125.6, 123.1, 122.9, 122.8, 116.1, 63.7, 62.7, 61.6, 31.7, 14.4. **16lb:** ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09–8.05 (m, 2H), 7.57–7.4.9 (m, 2H), 6.60 (dq, *J* = 16.2, 1.8 Hz, 1H), 6.26 (dq, *J* = 16.2, 6.6 Hz, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 3.99 (s, 3H), 3.85 (s, 3H), 1.93 (dd, *J* = 6.6, 1.8 Hz, 3H), 1.41 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 150.1, 149.8, 136.6, 131.8, 127.8, 127.6, 127.4, 126.5, 125.1, 124.3, 124.2, 122.9, 63.8, 61.6, 61.4, 19.6, 14.5. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{18}H_{21}O_4$ 301.1440; Found 301.1436.

Data for 16lc. Colourless liquid; R_f (1:15 EtOAc/hexane) 0.3; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.12–8.11 (m, 2H), 8.00 (d, *J* = 16.3 Hz, 1H), 7.54–7.47 (m, 2H), 6.75 (d, *J* = 16.2 Hz, 1H),

4.31 (q, J = 7.2 Hz, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 2.50 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.7, 152.6, 150.4, 139.2, 129.3, 127.6, 127.4, 126.0, 124.6, 123.9, 123.2, 122.4, 61.6, 61.5, 60.7, 14.5, 13.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{21}O_4$ 301.1440; Found 301.1442.

General procedure for reduction with DIBAL-H. A solution of 1 M DIBAL-H in cyclohexanes (4 equiv) was added to a solution of corresponding esters (1 equiv) in toluene (20 mL/mmol) at -20 °C. The reaction mixture was allowed to warm slowly and stirred for 10 h at rt. When the reaction is complete, excess DIBAL-H was quenched with aqueous saturated Na_2SO_4 solution. Then it was filtered through celite pad. Residue part was thoroughly washed with EtOAc. Crude product was obtained after removal of solvent. Flash column chromatography was done on silica gel with EtOAc/hexane to afford pure alcohols.

*(1,4-Dimethoxy-3-(2-methylallyl)naphthalen-2-yl)methanol (**29a**).* General procedure for reduction with DIBAL-H was performed on **16b** to afford the alcohol **29a** in 94% yield (182 mg, 0.67 mmol). Yellowish liquid; R_f (1:3 EtOAc/hexane) 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16–8.00 (m, 2H), 7.58–7.46 (m, 2H), 4.83–4.82 (m, 1H), 4.81 (s, 2H), 4.34 (s, 1H), 4.00 (s, 3H), 3.88 (s, 3H), 3.67 (s, 2H), 2.20 (bs, 1H), 1.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 150.9, 147.0, 129.6, 128.9, 128.01, 128.0, 126.6, 126.1, 122.8, 122.7, 111.1, 63.5, 62.5, 57.9, 34.4, 23.8. IR (KBr): $\tilde{\nu}$ = 3432, 2936, 1592, 1448, 1355, 1271, 1194, 1100, 1061, 1030, 1003, 970, 891, 774, 719 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{20}O_3Na$ 295.1310; Found 295.1317.

*(1,4,5-Trimethoxy-3-(2-methylallyl)naphthalen-2-yl)methanol (**29c**).* General procedure for reduction with DIBAL-H was performed on **16c** to afford the alcohol **29c** in 96% yield (224 mg, 0.74 mmol). Yellowish liquid; R_f (1:2 EtOAc/hexane) 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, J = 8.4, 1.0 Hz, 1H), 7.44–7.35 (m, 1H), 6.90 (dd, J = 7.7, 1.0 Hz, 1H), 4.81–4.80 (m, 1H), 4.79 (s, 2H), 4.34–4.30 (m, 1H), 4.00 (s, 3H), 3.97 (s, 3H), 3.77 (s, 3H), 3.66 (s, 2H), 2.33 (bs, 1H), 1.91 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.3, 151.5, 151.0, 147.6, 130.5, 130.3, 129.0, 126.2, 121.0, 115.3, 111.0, 106.8, 63.3, 62.7, 58.1, 56.4, 34.2, 23.8. IR (KBr): $\tilde{\nu}$ = 3448, 2933, 2838, 1594, 1575, 1461, 1448, 1369, 1336, 1265, 1118, 1073, 982, 899, 764 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{22}O_4Na$ 325.1416, $[M - H_2O + H]^+$ Calcd for $C_{18}H_{21}O_3$ 285.1491; Found 325.1429, 285.1508.

(1,4,6,8-Tetramethoxy-3-(2-methylallyl)naphthalen-2-yl)methanol (***29d***). General procedure for reduction with DIBAL-H was performed on **16d** to afford the alcohol **29d**, which could not be purified by column chromatography. So impure product, obtained after column chromatography, was directly used for the next step. Yellowish liquid; R_f (1:1 EtOAc/hexane) 0.5.

(1,4,5,7-Tetramethoxy-3-(2-methylallyl)naphthalen-2-yl)methanol (***29e***). General procedure for reduction with DIBAL-H was performed on **16e** to afford the alcohol **29e** in 91% yield (269 mg, 0.81 mmol). Yellowish liquid; R_f (1:1 EtOAc/hexane) 0.5. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.00 (d, J = 2.3 Hz, 1H), 6.55 (d, J = 2.3 Hz, 1H), 4.79–4.78 (m, 1H), 4.76 (s, 2H), 4.32–4.31 (m, 1H), 3.96 (s, 3H), 3.95 (s, 3H), 3.93 (s, 3H), 3.74 (s, 3H), 3.61 (s, 2H), 2.41 (bs, 1H), 1.89 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.4, 157.6, 151.2, 150.6, 147.7, 131.0, 130.7, 126.5, 116.8, 110.9, 99.7, 93.3, 62.7, 62.6, 58.1, 56.3, 55.5, 34.0, 23.7. IR (KBr): $\tilde{\nu}$ = 3449, 2930, 2838, 1620, 1598, 1449, 1410, 1379, 1340, 1262, 1235, 1204, 1158, 1121, 1083, 1059, 998, 889, 833 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{25}O_5$ 333.1702; Found 333.1717.

(1,4,6,7-Tetramethoxy-3-(2-methylallyl)naphthalen-2-yl)methanol (***29f***). General procedure for reduction with DIBAL-H was performed on **16f** to afford the alcohol **29f** in 95% yield (229 mg, 0.69 mmol). Yellowish liquid; R_f (1:1 EtOAc/hexane) 0.5. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.34 (s, 1H), 4.81 (t, J = 2.0 Hz, 1H), 4.77 (s, 2H), 4.35 (d, J = 2.2 Hz, 1H), 4.02 (d, J = 2.0 Hz, 6H), 3.99 (s, 3H), 3.86 (s, 3H), 3.62 (s, 2H), 2.19 (s, 1H), 1.90 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.0, 150.3, 149.9, 149.8, 147.4, 128.0, 126.3, 124.5, 123.5, 111.0, 101.7, 63.1, 62.0, 58.0, 56.2, 56.1, 34.4, 23.7. $\tilde{\nu}$ = 3428, 2820, 1590, 1508, 1476, 1428, 1382, 1320, 1258, 1220, 1170, 772 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{24}O_5Na$ 355.1521, $[M - H_2O + H]^+$ Calcd for $C_{19}H_{23}O_4$ 315.1596; Found 355.1518, 315.1594.

(3-(2-Ethylbut-2-en-1-yl)-1,4-dimethoxynaphthalen-2-yl)methanol (***29g***). General procedure for reduction with DIBAL-H was performed on **16h** to afford 1:1 diastereomeric mixture of the alcohol **29g** in 97% yield (228 mg, 0.76 mmol). Yellowish liquid; R_f (1:3 EtOAc/hexane) 0.3. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15–8.01 (m, 4H), 7.54–7.48 (m, 4H), 5.41 (q, J = 6.8 Hz, 1H), 4.83 (s, 2H), 4.80 (s, 2H), 4.75 (q, J = 6.7 Hz, 1H), 4.01 (s, 3H), 4.00 (s, 3H), 3.89 (s, 3H), 3.87 (s, 3H), 3.83 (s, 2H), 3.68 (s, 2H), 2.37 (s, 1H), 2.22 (q, J = 7.6 Hz, 2H), 1.86 (d, J = 6.8 Hz, 3H), 1.79 (q, J = 7.4 Hz, 2H), 1.54 (d, J = 6.7 Hz, 3H), 1.14

(t, J = 7.6 Hz, 3H), 0.91 (t, J = 7.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.0, 151.8, 151.3, 151.0, 142.9, 141.8, 129.9, 129.9, 128.9, 128.9, 128.9, 128.8, 128.2, 128.0, 128.0, 126.6, 126.6, 126.0, 126.0, 122.9, 122.9, 122.8, 122.7, 118.9, 118.3, 63.6, 63.5, 62.44, 62.2, 57.9, 57.6, 32.9, 28.4, 27.5, 24.7, 13.6, 13.1, 13.0, 12.9. IR (KBr): $\tilde{\nu}$ = 3432, 2934, 1591, 1458, 1355, 1269, 1193, 1100, 1054, 1000, 972, 772, 727 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{24}O_3Na$ 323.1623, $[M - H_2O + H]^+$ Calcd for $C_{19}H_{23}O_2$ 283.1698; Found 323.1616, 283.1704.

(3-(2-Ethylbut-2-en-1-yl)-1,4,6,7-tetramethoxynaphthalen-2-yl)methanol ***(29h)***. General procedure for reduction with DIBAL-H was performed on **16i** to afford 1:1 diastereomeric mixture of the alcohol **29h** in 84% yield (321mg, 0.89 mmol). Yellowish liquid; R_f (1:2 EtOAc/hexane) 0.4. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (s, 0.7H), 7.34 (s, 2H), 7.33 (s, 0.7H), 5.38 (q, J = 6.8 Hz, 1H), 4.78 (s, 2H), 4.75 (s, 1.4H), 4.74 (q, J = 6.6 Hz, 0.7H), 4.02 (s, 3H), 4.01 (s, 2.1H), 4.01 (s, 2.1H), 4.01 (s, 3H), 3.98 (s, 2.1H), 3.96 (s, 3H), 3.86 (s, 3H), 3.83 (s, 2.1H), 3.76 (s, 2H), 3.62 (s, 1.4H), 2.19 (q, J = 7.2 Hz, 1.4H), 1.83 (d, J = 6.8 Hz, 3H), 1.77 (q, J = 7.2 Hz, 2H), 1.52 (d, J = 6.6 Hz, 2.1H), 1.11 (t, J = 7.2 Hz, 2.1H), 0.89 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.0, 150.8, 150.3, 150.2, 150.2, 149.9, 149.8, 149.7, 143.1, 142.1, 128.2, 128.1, 127.2, 126.5, 124.5, 124.3, 123.4, 123.3, 118.7, 118.1, 101.7, 101.7, 101.6, 101.6, 63.1, 63.1, 61.9, 61.7, 57.9, 57.6, 56.1, 56.1, 32.8, 28.3, 27.3, 24.6, 13.6, 13.1, 13.0, 12.8. IR (KBr): $\tilde{\nu}$ = 3518, 2930, 1626, 1600, 1507, 1473, 1457, 1428, 1325, 1258, 1207, 1192, 1170, 1107, 1027, 1012, 979, 853, 779 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{28}O_5Na$ 383.1834; Found 383.1844.

General procedure for oxidation with DMP. To a stirred solution of alchols (1 equiv) in dry DCM (20 mL/ mmol) was added $NaHCO_3$ (5 equiv), DMP (1.3 equiv) at 0 °C. The reaction mixture was allowed to warm and stirred for 4 h at rt. The reaction mixture was diluted with DCM. The extract was washed with $Na_2S_2O_3$, $NaHCO_3$ and brine solution and dried over Na_2SO_4. Removal of the solvent under reduced pressure followed by flash column chromatography on silica gel with EtOAc/haxane afforded the desired aldehydes in very good yields.

1,4-Dimethoxy-3-(2-methylallyl)-2-naphthaldehyde ***(30a)***. General procedure for oxidation with DMP was performed on alcohol **29a** to afford the aldehyde **30a** in 88% yield (154 mg, 0.57 mmol). Yellowish liquid; R_f (1:20 EtOAc/hexane) 0.3. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.60 (s, 1H), 8.23 (d, J = 8.3 Hz, 1H), 8.11 (d, J = 8.3 Hz, 1H), 7.67 (t, J = 7.6 Hz,

1H), 7.58 (t, J = 7.6 Hz, 1H), 4.69 (s, 1H), 4.14 (s, 1H), 4.06 (s, 3H), 3.89 (s, 3H), 3.88 (s, 2H) 1.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 159.9, 151.2, 146.6, 132.0, 129.5, 128.0, 127.8, 126.8, 124.9, 123.6, 123.1, 109.8, 65.5, 62.7, 33.4, 24.1. IR (KBr): $\tilde{\nu}$ = 3435, 2935, 1686, 1458, 1410, 1355, 1274, 1194, 1103, 1061, 969, 886, 777, 722 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{19}O_3$ 271.1334; Found 271.1346.

*1,4,5-Trimethoxy-3-(2-methylallyl)-2-naphthaldehyde (**30c**).* General procedure for oxidation with DMP was performed on alcohol **29c** to afford the aldehyde **30c** in 90% yield (204 mg, 0.68 mmol). Yellowish liquid; R_f (1:15 EtOAc/hexane) 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.57 (s, 1H), 7.83 (d, J = 8.5 Hz, 1H), 7.49–7.45 (m, 1H), 7.04 (d, J = 7.8 Hz, 1H), 4.69–4.68 (m, 1H), 4.13 (s, 1H), 4.01 (s, 6H), 3.87 (s, 2H), 3.77 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 158.7, 156.3, 151.3, 146.9, 130.4, 128.6, 127.0, 125.4, 123.8, 115.8, 109.8, 109.6, 65.2, 62.9, 56.6, 32.9, 24.1. IR (KBr): $\tilde{\nu}$ = 3448, 2933, 2840, 1692, 1576, 1449, 1396, 1357, 1331, 1266, 1062, 972, 767 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{21}O_4$ 301.1440, $[M - H_2O + H]^+$ Calcd for $C_{18}H_{19}O_3$ 283.1334; Found 301.1428, 283.1330.

*1,4,6,8-Tetramethoxy-3-(2-methylallyl)-2-naphthaldehyde (**30d**).* General procedure for oxidation with DMP was performed on crude alcohol **29d** to afford the aldehyde **30d** in 86% overall yield (191 mg, 0.58 mmol) in two steps. Yellowish liquid; R_f (1:10 EtOAc/hexane) 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.56 (s, 1H), 7.03 (d, J = 2.4 Hz, 1H), 6.57 (d, J = 2.4 Hz, 1H), 4.70–4.59 (m, 1H), 4.17–4.09 (m, 1H), 4.02 (s, 3H), 3.96 (s, 3H), 3.90 (s, 3H), 3.86 (s, 2H), 3.83 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.5, 161.5, 161.2, 158.9, 145.0, 146.5, 135.6, 129.4, 123.8, 115.1, 109.3, 99.6, 94.1, 65.3, 61.8, 56.5, 55.7, 33.5, 24.2. IR (KBr): $\tilde{\nu}$ = 3444, 2928, 1692, 1610, 1590, 1430, 1420, 1263, 1210, 1155, 1090, 840 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{22}O_5Na$ 353.1365, $[M + H]^+$ Calcd for $C_{19}H_{23}O_5$ 331.1545, $[M - H_2O + H]^+$ Calcd for $C_{19}H_{21}O_4$ 313.1440; Found 353.1351, 331.1530, 313.1428.

*1,4,5,7-Tetramethoxy-3-(2-methylallyl)-2-naphthaldehyde (**30e**).* General procedure for oxidation with DMP was performed on alcohol **29e** to afford the aldehyde **30e** in 88% yield (172 mg, 0.52 mmol). Yellowish liquid; R_f (1:7.5 EtOAc/hexane) 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.55 (s, 1H), 7.11 (d, J = 2.4 Hz, 1H), 6.68 (d, J = 2.4 Hz, 1H), 4.68–4.66 (m, 1H), 4.13–4.12 (m, 1H), 4.00 (s, 3H), 3.98 (s, 3H), 3.95 (s, 3H), 3.81 (s, 2H), 3.74 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 158.9, 157.5, 151.5, 147.1, 131.0, 126.3, 125.8,

119.7, 109.8, 102.2, 93.7, 64.7, 62.9, 56.5, 55.7, 32.7, 24.1. IR (KBr): $\tilde{\nu}$ = 3448, 2933, 1690, 1617, 1584, 1447, 1407, 1338, 1266, 1235, 1205, 1160, 1081, 1060, 835 cm^{-1}. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{19}H_{23}O_5$ 331.1545; Found 331.1561.

*1,4,6,7-Tetramethoxy-3-(2-methylallyl)-2-naphthaldehyde (**30f**).* General procedure for oxidation with DMP was performed on alcohol **29f** to afford the aldehyde **30f** in 98% yield (218 mg, 0.66 mmol). Yellowish liquid; R_f (1:7.5 EtOAc/hexane) 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.54 (s, 1H), 7.46 (s, 1H), 7.37 (s, 1H), 4.68–4.67 (m, 1H), 4.17–4.14 (m, 1H), 4.05 (s, 3H), 4.04 (s, 3H), 4.03 (s, 3H), 3.86 (s, 3H), 3.84 (s, 2H), 1.91 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.6, 158.8, 152.6, 150.3, 150.1, 146.7, 128.4, 126.7, 123.3, 123.2, 109.6, 102.1, 101.9, 65.0, 62.2, 56.3, 56.3, 33.4, 24.1. IR (KBr): $\tilde{\nu}$ = 1686, 1618, 1508, 1474, 1426, 1324, 1264, 1218, 1172, 1014, 772 cm^{-1}. HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{19}H_{22}O_5Na$ 353.1365, $[M + H]^+$ Calcd for $C_{19}H_{23}O_5$ 331.1545, $[M - H_2O + H]^+$ Calcd for $C_{19}H_{21}O_4$ 313.1440; Found 353.1351, 331.1530, 313.1428.

*3-(2-Ethylbut-2-en-1-yl)-1,4-dimethoxy-2-naphthaldehyde (**30g**).* General procedure for oxidation with DMP was performed on alcohol **29g** to afford 1:1 diastereomeric mixture of the aldehyde **30g** in 95% yield (242 mg, 0.81 mmol). Yellowish liquid; R_f (1:20 EtOAc/hexane) 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.58 (s, 1H), 10.54 (s, 1H), 8.21 (t, *J* = 8.3 Hz, 2H), 8.10 (d, *J* = 8.4 Hz, 2H), 7.65 (t, *J* = 7.6 Hz, 2H), 7.58–7.53 (m, 2H), 5.31 (q, *J* = 6.6 Hz, 1H), 4.57 (q, *J* = 6.6 Hz, 1H), 4.05 (s, 3H), 4.03 (s, 3H), 4.02 (s, 2H), 3.90 (s, 3H), 3.89 (s, 2H) 3.87 (s, 3H), 2.20 (q, *J* = 7.6 Hz, 2H), 1.76 (d, *J* = 6.6 Hz, 3H), 1.69 (q, *J* = 7.4 Hz, 2H), 1.48 (d, *J* = 6.6 Hz, 3H), 1.12 (t, *J* = 7.6 Hz, 3H), 0.85 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 192.0, 158.8, 158.4, 151.5, 151.1, 142.1, 140.0, 131.8, 131.6, 129.3, 128.7, 128.2, 127.9, 127.8, 126.6, 126.0, 125.2, 123.6, 123.6, 123.0, 123.0, 118.0, 117.9, 65.2, 62.6, 62.2, 31.8, 28.4, 26.7, 24.9, 13.7, 13.2, 12.8, 12.8. IR (KBr): $\tilde{\nu}$ = 3422, 2962, 2933, 1690, 1455, 1409, 1354, 1270, 1193, 1101, 1055, 967, 779, 721, 595 cm^{-1}. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{19}H_{23}O_3$ 299.1647; Found 299.1639.

*3-(2-Ethylbut-2-en-1-yl)-1,4,6,7-tetramethoxy-2-naphthaldehyde (**30h**).* General procedure for oxidation with DMP was performed on alcohol **29h** to afford 1.5:1 diastereomeric mixture of the aldehyde **30h** in 89% yield (265 mg, 0.74 mmol). Yellowish liquid; R_f (1:10 EtOAc/hexane) 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.53 (s, 1.5H), 10.48 (s, 1H), 7.46 (s, 1H), 7.44 (s, 1.5H), 7.35 (s, 1H), 7.35 (s, 1.5H), 5.29 (q, *J* = 6.8 Hz, 1.5H), 4.58 (q, *J* = 6.6 Hz, 1H), 4.04 (s, 7.5H), 4.04 (s, 3H), 4.03 (s, 4.5H), 4.02 (s, 3H), 4.01 (s, 4.5H),

4.00 (s, 3H), 3.88 (s, 4.5H), 3.85 (s, 2H), 3.84 (s, 3H) 2.18 (q, J = 7.4 Hz, 2H), 1.75 (d, J = 6.8 Hz, 4.5H), 1.69 (q, J = 7.4 Hz, 3H), 1.47 (d, J = 6.6 Hz, 3H), 1.11 (t, J = 7.4 Hz, 3H), 0.83 (t, J = 7.4 Hz, 4.5H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.1, 191.6, 157.7, 157.5, 152.6, 152.5, 150.4, 150.3, 150.3, 150.0, 142.2, 140.3, 128.3, 128.1, 127.6, 127.1, 124.4, 123.6, 123.2, 123.1, 117.8, 117.6, 102.2, 102.1, 101.8, 101.8, 64.7, 64.7, 62.0, 61.7, 56.3, 31.9, 28.3, 26.7, 24.8, 13.6, 13.2, 12.8. IR (KBr): $\tilde{\nu}$ = 2935, 1685, 1620, 1587, 1507, 1474, 1426, 1329, 1264, 1210, 1192, 1172, 1037, 1015, 973, 860, 761 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{27}O_5$ 359.1858, $[M - H_2O + H]^+$ Calcd for $C_{21}H_{25}O_4$ 341.1753; Found 359.1871, 341.1759.

General procedures for the BINOL-PO_2H catalyzed one pot ene-reaction and photolytic aerial oxidation for the synthesis of anthraquinones.

General procedure A: 10 mol% of BINOL-PO_2H was added to a stirred solution of *o*-propenyl naphthalene aldehydes (1 equiv) in $CHCl_3$ (10 mL/mmol) in a screw capped vial and stirred for 4–5 d. Reaction was monitored by TLC. The reaction mixture was diluted with $CHCl_3$. The extract was washed with brine solution and dried over Na_2SO_4. Removal of the solvent under reduced pressure followed by flash column chromatography on silica gel with EtOAc/haxane afforded the anthraquinones as major products and anthracenes as minor products.

General Procedure B: 10 mol% of BINOL-PO_2H was added to a stirred solution of *o*-propenyl naphthalene aldehydes (1 equiv) in $CHCl_3$ (10 mL/mmol) in a screw capped vial and stirred for 4–5 d. Reaction was monitored by TLC. After completion of reaction, water (2 mL/mmol) was added and stirred under the exposure of visible light (480–600 nm) from 100 Watt incandescent light bulb (100 Watt-A19-Clear-1600 Lumens) for 15 h. The reaction mixture was diluted with $CHCl_3$. The extract was washed with brine solution and dried over Na_2SO_4. Removal of the solvent under reduced pressure followed by flash column chromatography on silica gel with EtOAc/haxane afforded the desired anthraquinones in very excellent yields.

*2-Methylanthracene-9,10-dione (**31a**).*[2i] General procedures A was performed on the substrate **30a** to afford the anthraquinone **31a** in 90% yield (90 mg, 0.41 mmol) along with trace amount of the corresponding anthracene, which could not be characterized. When general procedure B was performed on the substrate **30a**, anthraquinone **31a** was obtained in

97% yield (110 mg, 0.50 mmol) as sole product. Yellowish solid; R_f (1:50 EtOAc/hexane) 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32–8.30 (m, 2H), 8.21 (d, J = 7.8 Hz, 1H), 8.13–8.08 (m, 1H), 7.83–7.75 (m, 2H), 7.64–7.57 (m, 1H), 2.54 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 183.7, 183.2, 145.5, 135.2, 134.3, 134.2, 133.9, 133.8, 133.7, 131.6, 127.7, 127.7, 127.4, 127.4, 22.1.

*1-Methoxy-7-methylanthracene-9,10-dione (**31c**)*[11d] *1,9,10-Trimethoxy-7-methylanthracene (**32c**).* General procedures A was performed on the substrate **30c** to afford the anthraquinone **31c** in 82% yield (60 mg, 0.24 mmol) along with the corresponding anthracene **32c** in 15% yield (12 mg, 0.04 mmol). When general procedure B was performed on the substrate **30c**, the anthraquinone **31c** was obtained in 95% yield (100 mg, 0.40 mmol) as sole product.

Data for 31c. Yellow solid; R_f (1:5 EtOAc/hexane) 0.5. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, J = 7.8 Hz, 1H), 8.10–8.01 (m, 1H), 7.96 (m, 1H), 7.73–7.70 (t, J = 8.0 Hz, 1H), 7.57–7.49 (m, 1H), 7.33 (d, J = 8.4 Hz, 1H), 4.05 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 183.5, 183.1, 160.6, 145.6, 136.1, 135.2, 135.1, 134.3, 130.5, 127.7, 127.0, 121.9, 120.0, 118.1, 56.8, 22.2.

Data for 32c. Yellowish liquid; R_f (1:20 EtOAc/hexane) 0.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22–8.09 (m, 2H), 7.87 (d, J = 8.8 Hz, 1H), 7.42–7.29 (m, 2H), 6.77 (d, J = 7.2 Hz, 1H), 4.07 (s, 6H), 4.01 (s, 3H), 2.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 148.6, 148.2, 135.1, 128.9, 126.7, 126.6, 124.9, 124.1, 122.3, 121.7, 118.6, 115.2, 103.9, 63.6, 63.1, 56.4, 22.5. IR (KBr): $\tilde{\nu}$ = 3432, 2929, 1586, 1449, 1361, 1262, 1065, 975, 822, 769 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{19}O_3$ 283.1334; Found 283.1347.

*1,3-Dimethoxy-6-methylanthracene-9,10-dione (**31d**).*[11e] General procedures A was performed on the substrate **30d** to afford the anthraquinone **31d** in 72% yield (75 mg, 0.26 mmol) along with the corresponding anthracene in 18% yield (20 mg, 0.06 mmol), which could not be characterized. When general procedures B was performed on the substrate **30d**, the anthraquinone **31d** was obtained in 96% yield (81 mg, 0.28 mmol) as sole product. Yellow solid; R_f (1:2 EtOAc/hexane) 0.5. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, J = 7.8 Hz, 1H), 8.01 (s, 1H), 7.61–7.52 (m, 1H), 7.47 (d, J = 2.4 Hz, 1H), 6.79 (d, J = 2.4 Hz, 1H), 4.01 (s, 3H), 3.99 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 184.0, 181.6, 164.8, 162.8, 144.0, 137.8, 135.4, 133.2, 132.5, 127.7, 126.9, 116.4, 105.0, 103.5, 56.8, 56.2, 21.9.

*1,3-Dimethoxy-7-methylanthracene-9,10-dione (**31e**)*[11f] and *1,3,9,10-Tetramethoxy-7-methylanthracene (**32e**).* General procedures A was performed on the substrate **30e** to afford the anthraquinone **31e** in 71% yield (97 mg, 0.34 mmol) along with the corresponding anthracene **32e** in 26% yield (39 mg, 0.12 mmol). When general procedure B was performed on the substrate **30e**, the anthraquinone **31e** was obtained in 94% yield (92 mg, 0.33 mmol) as sole product.

Data for 31e. Yellow solid; R_f (1:3 EtOAc/hexane) 0.4. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, J = 7.9 Hz, 1H), 8.08–8.02 (m, 1H), 7.53–7.48 (m, 1H), 7.47 (d, J = 2.5 Hz, 1H), 6.79 (d, J = 2.5 Hz, 1H), 4.01 (s, 3H), 3.98 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 183.5, 181.8, 164.9, 162.8, 145.7, 137.9, 135.3, 133.9, 130.4, 127.7, 127.0, 116.5, 104.9, 103.5, 56.8, 56.2, 22.3.

Data for 32e. Yellowish semisolid; R_f (1:5 EtOAc/hexane) 0.5. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12–8.05 (m, 2H), 7.34 (dd, J = 8.8, 1.7 Hz, 1H), 7.08 (d, J = 2.2 Hz, 1H), 6.47 (d, J = 2.2 Hz, 1H), 4.04 (s, 6H), 3.99 (s, 3H), 3.98 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.0, 157.4, 149.0, 146.6, 134.1, 129.1, 127.0, 125.2, 124.6, 121.8, 121.8, 115.6, 99.0, 91.2, 63.6, 62.2, 56.4, 55.5, 22.4. IR (KBr): $\tilde{\nu}$ = 3447, 2929, 1635, 1563, 1453, 1362, 1285, 1237, 1207, 1154, 1066, 1007, 974, 828, 790 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{21}O_4$ 313.1440; Found 313.1428.

*2,3-Dimethoxy-6-methylanthracene-9,10-dione (**31f**).*[2g] General procedures A was performed on the substrate **30f** to afford the anthraquinone **31f** in 60% yield (63 mg, 0.22 mmol) along with the corresponding anthracene in 34% yield (39 mg, 0.12 mmol), which could not be characterized. When general procedure B was performed on the substrate **30f** the anthraquinone **31f** was obtained in 96% yield (95 mg, 0.34 mmol) as sole product. Yellow solid; R_f (1:10 EtOAc/hexane) 0.4. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, J = 7.9 Hz, 1H), 8.07 (d, J = 1.7 Hz, 1H), 7.72 (d, J = 1.7 Hz, 2H), 7.55 (dd, J = 8.0, 1.7 Hz, 1H), 4.07 (s, 3H), 4.07 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 183.1, 182.7, 154.0, 153.9, 145.1, 134.7, 133.7, 131.6, 128.8, 128.7, 127.6, 127.5, 108.6, 108.6, 56.77, 22.10.

*2-Ethyl-3-methylanthracene-9,10-dione (**31g**).* General procedures A was performed on the substrate **30g** to afford the anthraquinone **31g** in 56% yield (74 mg, 0.30 mmol) along with the corresponding anthracene in 30% yield (45 mg, 0.16 mmol), which could not be characterized. When general procedure B was performed on the substrate **30g**, the

anthraquinone **31g** was obtained in 93% yield (85 mg, 0.34 mmol) as sole product. Yellow solid; R_f (1:10 EtOAc/hexane) 0.4. Yellow solid; mp 136 °C; R_f (1:10 EtOAc/hexane) 0.3. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30–8.27 (m, 2H), 8.08 (s, 1H), 8.04 (s, 1H), 7.78–7.75 (m, 2H), 2.78 (q, J = 7.6 Hz, 2H), 2.47 (s, 3H), 1.31 (t, J = 7.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 183.6, 183.5, 149.8, 143.6, 134.0, 133.9, 133.9, 132.0, 131.6, 128.8, 127.3, 127.3, 126.7, 26.7, 19.9, 14.0. IR (KBr): $\tilde{\nu}$ = 3440, 1672, 1594, 1330, 1302, 1218, 956, 716 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}O_2$ 251.1072; Found 251.1071.

*6-Ethyl-2,3-dimethoxyanthracene-9,10-dione (**31h**) and 2-Ethyl-6,7,9,10-tetramethoxy-3-methylanthracene (**32h**).* General procedures A was performed on the substrate **30h** to afford the anthraquinone **31h** in 44% yield (44 mg, 0.14 mmol) along with the corresponding anthracene **32h** in 54% yield (58 mg, 0.17 mmol). When the general procedure B was performed on the substrate **30h**, the anthraquinone **31h** was obtained in 95% yield (103 mg, 0.33 mmol) as sole product.

Data for 31h. Yellow solid; mp 178 °C; R_f (1:10 EtOAc/hexane) 0.4. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (s, 1H), 8.01 (s, 1H), 7.71 (s, 1H), 7.70 (s, 1H), 4.07 (s, 3H), 4.06 (s, 3H), 2.78 (q, J = 7.6 Hz, 2H), 2.47 (s, 3H), 1.31 (t, J = 7.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 183.0, 183.0, 153.9, 149.4, 143.1, 132.0, 131.6, 128.9, 128.8, 128.7, 126.7, 108.6, 108.6, 56.8, 26.7, 19.8, 14.1. IR (KBr): $\tilde{\nu}$ = 3434, 2928, 1661, 1578, 1376, 1325, 1224, 1049, 740 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{19}O_4$ 311.1283; Found 311.1291.

Data for 32h. Yellowish semisolid; R_f (1:5 EtOAc/hexane) 0.45. ^{1}H NMR (600 MHz, $CDCl_3$) 8.00–7.94 (m, 2H), 7.44–7.43 (m, 2H), 4.09 (s, 3H), 4.08 (s, 3H), 4.08 (s, 6H), 2.85 (q, J = 7.5 Hz, 2H), 2.54 (s, 3H), 1.38 (t, J = 7.5 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.1, 140.6, 134.4, 123.6, 123.4, 121.8, 121.3, 121.2, 119.6, 99.9, 62.5, 62.5, 56.1, 26.8, 20.3, 14.6. IR (KBr): $\tilde{\nu}$ = 3434, 2926, 1635, 1577, 1496, 1455, 1348, 1335, 1247, 1220, 1196, 1168, 1132, 1054, 1006, 849, 798, 728 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{25}O_4$ 341.1753; Found 341.1759.

*1-Hydroxy-3-methoxy-6-methylanthracene-9,10-dione (**37**).*[11g] To a stirred solution of **31d** (50 mg, 0.18 mmol) in 10 ml of dry DCM was added dropwise 1 M solution of BBr_3 in DCM (0.9 mL, 0.9 mmol) under inert atmosphere at 0 °C. Then the reaction mixture was allowed to warm and stirred at rt for 2 h. The reaction mixture was quenched with water and extracted with DCM (15 mL x 3) and dried over Na_2SO_4. Evaporation of solvent under

reduced pressure afforded crude product, which was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:15) as solvent to obtain pure compound **37** in 86% yield (42 mg, 0.15 mmol) as sole product. Yellowish solid; R_f (1:10 EtOAc/hexane) 0.5. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.94 (s, 1H), 8.19 (d, J = 7.8 Hz, 1H), 8.11–8.04 (m, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.37 (d, J = 2.4 Hz, 1H), 6.71 (d, J = 2.4 Hz, 1H), 3.94 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.1, 183.0, 166.4, 165.6, 145.6, 135.4, 135.3, 133.6, 131.4, 128.0, 127.2, 111.0, 107.8, 106.9, 56.3, 22.1.

*2-(Hydroxymethyl)-3-(2-methylallyl)naphthalene-1,4-dione (**39a**).* To a stirred solution of **29a** (280 mg, 1.03 mmol) in acetonitrile (10 mL) and water (10 mL), solution of cerric ammonium nitrate (1.7 g, 3.09 mmol) was added portion-wise and stirred for 1 h at room temperature. Then the reaction mixture was extracted with EtOAc (2 x 50 mL). The combined extracts were washed successively with water (25 mL), brine (25 mL), dried (anhydrous Na_2SO_4), filtered and concentrated under reduced pressure. Column chromatography of the residue on silica gel with EtOAc/petroleum ether (1:2) as solvent afforded **39a** in 76% yield (190 mg, 0.78 mmol). Yellow liquid; R_f (1:2 EtOAc/hexane) 0.5; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.15–8.03 (m, 2H), 7.75–7.72 (m, 2H), 4.82–4.81 (m, 1H), 4.64 (s, 2H), 4.61–4.56 (m, 1H), 3.43 (s, 2H), 2.89 (bs, 1H), 1.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.4, 184.8, 145.4, 144.3, 142.6, 134.1, 133.9, 132.1, 132.0, 126.8, 126.3, 112.0, 58.2, 33.4, 23.5. IR (KBr): $\tilde{\nu}$ = 3448, 2936, 1664, 1595, 1355, 1331, 1291, 1226, 1026, 956, 894, 790, 730 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{15}O_3$ 243.1021; Found 243.1025.

*3-(Hydroxymethyl)-5-methoxy-2-(2-methylallyl)naphthalene-1,4-dione (**39b**).* The compound **39b** was obtained from **29b** in 65% yield (410 mg, 1.51 mmol). Experimental procedure is similar to that described for the transformation **29a**→**39a**. Yellow liquid; R_f (1:2 EtOAc/hexane) 0.3; ^{1}H NMR (600 MHz, $CDCl_3$): δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.6 Hz, 1H), 7.67–7.63 (m, 1H), 7.28 (d, J = 8.8 Hz, 1H), 4.84–4.73 (m, 1H), 4.58 (s, 2H), 4.56 (s, 1H), 4.00 (s, 3H), 3.37 (s, 2H), 2.98 (bs, 1H), 1.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.2, 185.1, 159.7, 146.0, 143.1, 142.5, 135.3, 134.4, 119.9, 119.7, 117.8, 111.9, 58.7, 56.7, 33.2, 23.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{17}O_4$ 273.1127; Found 273.1120.

*1-Hydroxy-3-methylanthracene-9,10-dione (**41a**).*[11h] To a stirred solution of the compound **39a** (100 mg, 0.42 mmol) in dry DCM (10 mL) was added $NaHCO_3$ (174 mg, 2.1 mmol), DMP (228 mg, 0.54 mmol) at 0 °C. The reaction mixture was allowed to warm and

stirred for 1 h at rt. The reaction mixture was diluted with DCM (40 mL). The extract was washed with $Na_2S_2O_3$, $NaHCO_3$ and brine solution and dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded the desired crude aldehyde (**40a**). This crude aldehyde was dissolved in dry DCM (10 mL) and was added $SnCl_4 \cdot 5H_2O$ (148 mg, 0.42 mmol). The reaction mixture was stirred for 2 h at rt. The reaction was quenched with aqueous saturated $NaHCO_3$ (10 mL) and was extracted with DCM (30 mL x 3). The extracts were dried over Na_2SO_4 and evaporated under reduced pressure to obtain crude product, which was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:50) as solvent to obtain pure compound **41a** in 50% yield (50 mg, 0.21 mmol) along with **31a** in 30% yield (28 mg, 0.13 mmol). Yellowish solid; R_f (1:20 EtOAc/hexane) 0.6. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.59 (s, 1H), 8.36–8.24 (m, 2H), 7.82–7.79 (m, 2H), 7.66 (s, 1H), 7.12 (s, 1H), 2.47 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 188.3, 183.0, 163.1, 148.9, 134.7, 134.4, 133.9, 133.6, 133.4, 127.6, 127.0, 124.4, 121.1, 114.4, 22.5.

*1-Hydroxy-8-methoxy-3-methylanthracene-9,10-dione (**41b**).*[3b] The compound **41b** was obtained from **39b** in 60% yield (65 mg, 0.24 mmol) along with the compound **31b** in 24% yield (24 mg, 0.10 mmol). Experimental procedure is similar to that described for the transformation **39a→41a**. Yellow solid; R_f (1:10 EtOAc/hexane) 0.3; ^{1}H NMR (600 MHz, $CDCl_3$): δ 12.92 (s, 1H), 7.96 (dd, J = 7.6, 1.0 Hz, 1H), 7.76–7.72 (m, 1H), 7.59 (d, J = 1.8 Hz, 1H), 7.36 (d, J = 8.5 Hz, 1H), 7.09 (s, 1H), 4.07 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 188.8, 183.2, 162.9, 161.0, 147.8, 136.1, 135.9, 132.6, 124.9, 121.1, 120.4, 120.3, 118.4, 115.2, 56.9, 22.3.

*1a-(Hydroxymethyl)-7a-(2-methylallyl)-1a,7a-dihydronaphtho[2,3-b]oxirene-2,7-dione (**(±)-43a**).* To a solution of **39a** (242 mg, 1.00 mmol) in 95% ethanol (40 mL) and H_2O (2 mL) was added sodium carbonate (160 mg, 1.5 mmol) and 30% H_2O_2 (0.9 mL). The yellow mixture was stirred for 30 min at room temperature during which time it turned colorless. Water (45 mL) was added to precipitate the product which was extracted into EtOAc (3 x 20 mL) and dried over Na_2SO_4. After removal of the solvent under reduced pressure and purification by column chromatography on silica gel and EtOAc/petroleum ether (1:2) as solvent, **(±)-43a** was obtained as a sole product in 89% yield (230 mg, 0.89 mmol). Colourless liquid; R_f (1:2 EtOAc/hexane) 0.4. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10–7.93 (m, 2H), 7.82–7.71 (m, 2H), 4.89–4.88 (m, 1H), 4.7–4.69 (m, 1H), 4.25 (dd, J = 12.9, 7.9 Hz, 1H), 4.17 (dd, J = 12.9, 6.8 Hz, 1H), 3.30 (d, J = 16.5 Hz, 1H), 2.62 (d, J = 16.5 Hz, 1H), 2.62 (t, J = 7.8 Hz, 1H), 1.84 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.9, 190.6, 140.8, 135.0, 134.7, 132.2, 131.9, 127.8, 127.2, 112.9, 67.0, 65.8, 59.4, 32.9, 23.9. IR (KBr): $\tilde{\nu}$ =

2924, 2852, 1700, 1560, 1458, 1298, 1224, 1058, 960, 896, 782 cm^{-1}. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{15}H_{15}O_4$ 259.0970; Found 259.0970.

*1a-(Hydroxymethyl)-3-methoxy-7a-(2-methylallyl)-1a,7a-dihydronaphtho[2,3-b]oxirene-2,7-dione (**(±)-43b**).* The compound **(±)-43b** was obtained from **39b** in 91% yield (370 mg, 1.28 mmol). Experimental procedure is similar to that described for the transformation **39a→(±)-43a**.Colourless liquid; R_f (1:1 EtOAc/hexane) 0.4; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.64 (m, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 4.92–4.84 (m, 1H), 4.71 (s, 1H), 4.20 (dd, *J* = 7.0, 2.6 Hz, 2H), 3.97 (s, 3H), 3.07 (d, *J* = 16.3 Hz, 1H), 2.77 (d, *J* = 16.3 Hz, 1H), 2.70 (t, *J* = 7.4 Hz, 1H), 1.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 192.0, 159.1, 140.5, 135.5, 134.4, 120.3, 119.7, 117.9, 113.0, 66.8, 65.8, 59.7, 56.7, 32.5, 23.9. IR (KBr): $\tilde{\nu}$ = 3447, 2936, 1700, 1571, 1459, 1277, 1068, 977, 895, 730 cm^{-1}. HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{16}H_{16}O_5Na$ 311.0895, $[M + H]^+$ Calcd for $C_{16}H_{17}O_5$ 289.1076; Found 311.0899, 289.1085.

*7a-(2-Methylallyl)-2,7-dioxo-7,7a-dihydronaphtho[2,3-b]oxirene-1a(2H)-carbaldehyde (**(±)-42a**) and (±)-1-hydroxy-3-methylene-1,2,3,4-tetrahydro-4a,9a-epoxyanthracene-9,10-dione (**(±)-44a**-single diastereomer).* To a stirred solution of the compound **(±)-43a** (150 mg, 0.58 mmol) in dry DCM (20 mL) was added $NaHCO_3$ (487 mg, 5.8 mmol), DMP (594 mg, 1.4 mmol) at 0 °C. The reaction mixture was allowed to warm and stirred for 1 h at rt. The reaction mixture was diluted with DCM (50 mL). The extract was washed with $Na_2S_2O_3$, $NaHCO_3$ and brine solution and dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded the crude product, which was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:10) as solvent to obtain pure aldehyde **(±)-42a** in 46% yield (68 mg, 0.27 mmol) along with cyclized product **(±)-44a** in 52% yield (78 mg, 0.30 mmol) as single diastereomer.

Data for (±)-42a. Yellowish liquid; R_f (1:10 EtOAc/hexane) 0.6 (it trails in TLC). ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.24 (s, 1H), 8.11–7.98 (m, 2H), 7.87–7.74 (m, 2H), 4.87–4.80 (m, 1H), 4.53 (s, 1H), 3.32 (d, *J* = 16.7 Hz, 1H), 2.31 (d, *J* = 16.7 Hz, 1H), 1.76 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.0, 190.7, 188.1, 141.1, 135.5, 135.1, 131.8, 131.6, 128.2, 127.3, 112.8, 68.7, 65.5, 31.7, 24.1. IR (KBr): $\tilde{\nu}$ = 3444, 2930, 1702, 1676, 1630, 1625, 1530, 1526, 1479, 1380 cm^{-1}. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{15}H_{13}O_4$ 257.0814, $[M - H_2O + H]^+$ Calcd for $C_{15}H_{11}O_3$ 239.0708; Found 257.0820, 239.0710.

The compound **(±)-42a** (60 mg, 0.23 mmol) was dissolved in dry DCM (5 mL) and was added $SnCl_4 \cdot 5H_2O$ (82 mg, 0.23 mmol). The reaction mixture was stirred for 1 h at rt. The reaction was quenched with aqueous saturated $NaHCO_3$ (5 mL) and was extracted with DCM

(10 mL x 3). The extracts were dried over Na_2SO_4 and evaporated under reduced pressure to obtain crude product, which was purified by column chromatography on silica gel with EtOAc/petroleum ether (1:5) as solvent to obtain pure compound **(±)-44a** in 97% yield (57 mg, 0.22 mmol) as single diastereomer.

Data for (±)-44a. Yellowish semisolid; R_f (1:5 EtOAc/hexane) 0.4. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08–7.95 (m, 2H), 7.78–7.73 (m, 2H), 5.06 (s, 1H), 5.01–4.96 (m, 2H), 3.49 (d, J = 17.8 Hz, 1H), 2.97 (dq, J = 17.9, 2.2 Hz, 1H), 2.91 (bs, 1H), 2.56 (dq, J = 14.6, 1.9 Hz, 1H), 2.40 (dd, J = 14.3, 3.1 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.3, 190.9, 135.8, 135.0, 134.6, 132.0, 131.9, 127.8, 127.2, 115.2, 64.7, 64.5, 63.7, 35.5, 27.8. IR (KBr): $\tilde{\nu}$ = 3480, 1692, 1675, 1596, 1470, 1382, 1290, 1271, 1220, 950, 899, 727 cm^{-1}. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{15}H_{13}O_4$ 257.0814, $[M - H_2O + H]^+$ Calcd for $C_{15}H_{11}O_3$ 239.0708; Found 257.0818, 239.0714.

*3-Methoxy-7a-(2-methylallyl)-2,7-dioxo-7,7a-dihydronaphtho[2,3-b]oxirene-1a(2H)-carbaldehyde (**(±)-42b**).* The compound **(±)-42b** was obtained from **(±)-43b** in 98% yield (295 mg, 1.03 mmol). Experimental procedure is similar to that described for the transformation **(±)-43a→(±)-42a**. Yellowish semisolid; R_f (1:10 EtOAc/hexane) 0.5 (it trails in TLC). ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.41 (s, 1H), 7.73–7.69 (m, 1H), 7.59 (dd, J = 7.7, 1.1 Hz, 1H), 7.32 (dd, J = 8.5, 1.0 Hz, 1H), 4.86–4.85 (m, 1H), 4.54 (s, 1H), 3.97 (s, 3H), 3.15 (d, J = 16.6 Hz, 1H), 2.34 (d, J = 16.6 Hz, 1H), 1.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 190.3, 189.3, 159.4, 141.2, 136.0, 135.7, 134.0, 120.0, 118.3, 112.7, 69.0, 65.2, 56.8, 31.5, 24.1. IR (KBr): $\tilde{\nu}$ = 3444, 2930, 1700, 1684, 1670, 1653, 1617, 1559, 1540, 1522, 1473, 1385 cm^{-1}. HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{16}H_{14}O_5Na$ 309.0739, $[M + H]^+$ Calcd for $C_{16}H_{15}O_5$ 287.0919, $[M - H_2O + H]^+$ Calcd for $C_{16}H_{13}O_4$ 269.0814; Found 309.0747, 287.0923, 269.0819.

*(±)-1-Hydroxy-8-methoxy-3-methylene-1,2,3,4-tetrahydro-4a,9a-epoxyanthracene-9,10-dione (**(±)-44b**-single diastereomer).* The compound **(±)-44b** was obtained from **(±)-42b** in 96% yield (230 mg, 0.80 mmol) as single diasteremer. Experimental procedure is similar to that described for the transformation **(±)-42a→(±)-44a**. Colourless semisolid; R_f (1:2 EtOAc/hexane) 0.4; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.69–7.60 (m, 1H), 7.55 (dd, J = 7.7, 1.0 Hz, 1H), 7.26 (dd, J = 8.4, 1.0 Hz, 1H), 5.02–5.01 (m, 1H), 4.96–4.95 (m, 2H), 3.94 (s, 3H), 3.50 (d, J = 18.0 Hz, 1H), 3.30 (s, 1H), 2.93–2.83 (m, 1H), 2.53–2.42 (m, 1H), 2.38 (dd, J = 14.5, 3.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.5, 191.7, 159.4, 135.7, 135.6, 134.2, 120.2, 119.8, 118.0, 114.8, 64.6, 64.1, 64.0, 56.7, 35.2, 27.0. IR (KBr): $\tilde{\nu}$ = 3483,

2953, 1697, 1677, 1588, 1473, 1291, 1277, 1264, 1224, 1210, 1064, 957, 934, 897, 729 cm^{-1}. HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{16}H_{14}O_5Na$ 309.0739, $[M + H]^+$ Calcd for $C_{16}H_{15}O_5$ 287.0919, $[M - H_2O + H]^+$ Calcd for $C_{16}H_{13}O_4$ 269.0814; Found 309.0747, 287.0923, 269.0819.

*8-Methoxy-3-methylene-1-((triisopropylsilyl)oxy)-1,2,3,4-tetrahydro-4a,9a-epoxyanthracene-9,10-dione (**(±)-45**).* Imidazole (850.9 mg, 12.5 mmol) was added to a stirred solution of compound **(±)-44a** (358 mg, 1.25 mmol) in 10 mL DCM at 0 °C. After 5 min stirring at 0 °C, TIPSOTf (1.7 mL, 6.25 mmol) was added. Reaction completed in 12 h. Usual work up done with DCM to get the crude product. Flash column chromatography was done on silica gel with hexane to afford pure silyl protected product **(±)-45** in 60 % yield (332 mg, 0.75 mmol). The pure product **(±)-45** was crystallized from EtOAc/hexane solvent. Yellow crystalline solid; mp 58 °C; R_f (hexane) 0.55; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.13–7.97 (m, 2H), 7.80–7.68 (m, 2H), 5.29 (t, *J* = 3.0 Hz, 1H), 5.02 (t, *J* = 2.0 Hz, 1H), 4.9 –4.82 (m, 1H), 3.39–3.20 (m, 2H), 2.59–2.40 (m, 2H), 1.17–1.09 (m, 3H), 1.05 (d, *J* = 7.4 Hz, 9H), 1.00 (d, *J* = 7.4 Hz, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.6, 190.0, 136.8, 134.7, 134.6, 132.2, 132.0, 127.6, 127.3, 114.5, 64.6, 64.3, 63.6, 36.0, 27.1, 18.3, 18.3, 12.8. IR (KBr): $\tilde{\nu}$ = 3378, 2941, 1696, 1595, 1466, 1324, 1304, 1285, 1195, 1109, 1069, 878, 711, 680 cm^{-1}. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{25}H_{35}O_5Si$ 443.2254; Found 443.2261.

*(±)-1-Hydroxy-8-methoxy-3-methylene-1,2,3,4-tetrahydro-4a,9a-epoxyanthracene-9,10-dione (**(±)-44c**-1:1 diastereomeric mixture).* 10 mol% of BINOL-PO_2H (3.6 mg, 0.0105 mmol) was added to a stirred solution of aldehydes **(±)-42b** (30 mg, 0.105 mmol) in $CHCl_3$ (5 mL) in a screw capped vial and stirred for 5 d. Reaction was monitored by TLC. After completion of reaction, the solvent was evaporated and the reaction mixture was directly charged onto silica gel and subjected to flash column chromatography with EtOAc/petroleum ether (1:2). The 1:1 diastereomeric mixture of product **(±)-44c** was afforded in 94% yield (28 mg, 0.099 mmol). Colourless semisolid; R_f (1:2 EtOAc/hexane) 0.4; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.69–7.65 (m, 2H), 7.58 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.55 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.30–7.28 (m, 2H), 5.05 (s, 1H), 4.99 (s, 2H), 4.96 (s, 2H), 4.88 (bs, 1H), 3.97 (s, 3H), 3.96 (s, 3H), 3.54 (d, *J* = 18.0 Hz, 1H), 3.37 (d, *J* = 17.1 Hz, 1H), 3.27 (bs, 1H), 3.02 (bs, 1H), 2.94–2.87 (m, 1H), 2.83–2.79 (m, 1H), 2.56–2.44 (m, 2H), 2.43–2.27 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 192.6, 191.9, 191.8, 159.4, 159.3, 137.4, 135.7, 135.7, 135.5, 134.2, 134.2, 120.4, 120.1, 119.9, 119.7, 118.1, 118.0, 114.9, 114.8, 66.4, 66.1, 65.5, 64.6, 64.2, 64.0, 56.7, 36.3, 35.2, 28.2, 27.0. IR (KBr): $\tilde{\nu}$ = 3480, 2951, 1695, 1680,

1583, 1475, 1293, 1276, 1264, 1225, 1214, 1061, 955, 936, 896, 730 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{14}O_5Na$ 309.0739, $[M + H]^+$ Calcd for $C_{16}H_{15}O_5$ 287.0919, $[M - H_2O + H]^+$ Calcd for $C_{16}H_{13}O_4$ 269.0814; Found 309.0749, 287.0921, 269.0818.

*5,7,9,10-Tetramethoxy-3-methyl-1H-benzo[g]isochromene (**52**).*[6c,6e] To a solution of the compound **29d** (90 mg, 0.27 mmol) in water (3 mL) and dioxane (10 mL) was first added a catalytic amount of osmium(VIII) tetroxide (7 mg), and then sodium periodate (115 mg, 0.54 mmol) was added portionwise over a period of 1 h. The suspension formed was stirred for 3 days, poured into water, extracted with ether, washed with brine, dried over Na_2SO_4, and evaporated at reduced pressure. Flash chromatography on silica gel with 1:7 EtOAc/Hexane afforded the product **52** in 81% yield (70 mg, 0.22 mmol). Yellowish semisolid; R_f (1:7 EtOAc/hexane) 0.3; ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.95 (d, *J* = 2.3 Hz, 1H), 6.45 (d, *J* = 2.3 Hz, 1H), 5.94 (q, *J* = 1.0 Hz, 1H), 5.27 (s, 2H), 3.95 (s, 3H), 3.92 (s, 3H), 3.84 (s, 3H), 3.76 (s, 3H), 2.00 (d, *J* = 1.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.6, 157.8, 156.3, 147.7, 143.2, 132.0, 122.4, 117.1, 115.1, 98.4, 95.8, 93.2, 64.2, 62.5, 61.4, 56.3, 55.5, 20.3.

ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra of the synthesized compounds and X-ray crystallographic data (PDF)

X-ray crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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