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Efficient one-pot synthesis of benzopyranobenzopyrans and naphthopyranobenzopyrans by domino aldol-type reaction/hetero Diels–Alder reaction of resorcinols and naphthols

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ABSTRACT

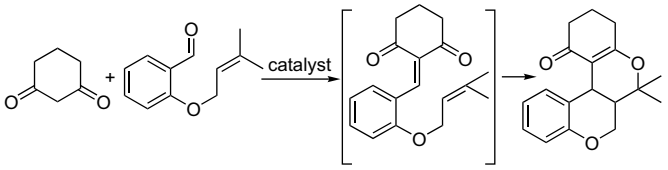
The efficient one-pot synthetic approaches for benzopyranobenzopyrans and naphthopyranobenzopyrans are described. The key strategies involve ethylenediamine diacetate-catalyzed cyclization by domino aldol-type reaction/hetero Diels–Alder reaction of resorcinols and naphthols to benzaldehydes with *O*-allyl ether groups. These reactions provide a rapid route for the synthesis of novel types of polyheterocycles with stereochemically defined quaternary carbon centers.

1. Introduction

The hetero Diels–Alder reaction is a powerful synthetic tool for constructing heterocyclic compounds and natural products.[1] Among these, combination of hetero Diels–Alder reaction with other reactions in a domino fashion has been widely used for the formation of multiple bonds. A number of examples using this strategy have been reported in the last decade.[2] As the pioneering work, Tietze extensively described the domino Knoevenagel/hetero Diels–Alder reaction of 1,3-dicarbonyls to benzaldehydes with *O*-allyl ether groups for the synthesis of tetracycles with a pyran ring, as shown in Scheme 1.[3] These strategies allow for the facile synthesis of polycycles from 1,3-dicarbonyls. However, no examples on combination of aldol-type reaction with hetero Diels–Alder reaction starting from commercially available resorcinols and naphthols have been reported.

Molecules with the benzopyran and naphthopyran moieties are widely found in nature.[4,5] These compounds exhibit a range of biological and pharmacological properties including antioxidant, anticancer, anti-inflammatory, antiviral, antibacterial, and anti-HIV activities.[6] They were also the subject of many studies and numerous applications, such as light sensitive sunglasses,[7] molecular electronics,[8] optical memories,[9] and biological photoswitches,[10] which were reported. This wide range of interesting activities and properties has prompted studies into the development of a convenient and efficient methodology for synthesizing polyheterocycles with benzopyran and naphthopyran moieties.

Recently, Brønsted acids and bases have demonstrated their potential to serve as active catalysts for a variety of synthetically useful reactions in organic chemistry.[11] In particular, we have developed a new and useful methodology for preparing a variety of benzopyrans using ethylenediamine diacetate (EDDA) as effective Brønsted acid and base catalysts.[12] These reactions involve a formal [3+3]-cycloaddition through a 6π-electrocyclization. This methodology provides a rapid route for the synthesis of benzopyran derivatives and biologically active natural products.[13] Very



Scheme 1. Domino Knoevenagel/hetero Diels–Alder reaction.

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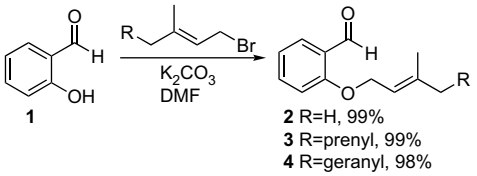
recently, we have also developed a new and efficient synthetic approach for biologically interesting tetrahydroquinoline analogues from 1,3-dicarbonyls to amoinobenzaldehydes through domino Knoevenagel/hetero Diels–Alder reactions.[14] As a part of an ongoing study into the synthetic efficacy of these two methodologies, this study examined the reactions of resorcinols and naphthols to benzaldehydes with *O*-allyl ether groups. We report herein an efficient one-pot synthesis of a variety of benzopyranobenzopyrans and naphthopyranobenzopyrans with substituents on the pyranyl rings using domino aldol-type reaction/hetero Diels–Alder reaction.

2. Results and discussion

As starting materials, benzaldehydes **2**–**4** with *O*-allyl ether groups were prepared from salicylaldehyde (**1**) in one step, as shown in Scheme 2. Treatment of salicylaldehyde (**1**) with prenyl bromide in the presence of K_2CO_3 in DMF at room temperature for 12 h afforded benzaldehyde **2** in 99% yield. A reaction of **1** with geranyl bromide gave benzaldehyde **3** in 99% yield, whereas treatment with *trans*,*trans*-farnesyl bromide afforded compound **4** in 98% yield.

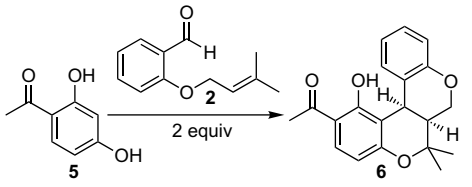


Scheme 2. Preparation of benzaldehydes **2**–**4** with *O*-allyl ether.

To give benzopyranobenzopyrans, reaction of 2,4-dihydroxyacetophenone (**5**) with 2.0 equiv of benzaldehyde **2** under several conditions was first attempted (Table 1). Both indium(III) chloride (20 mol %) and ytterbium(III) triflate (20 mol %) as Lewis acid catalysts in refluxing acetonitrile gave no adducts. With pyridine as a reactant and solvent at 140 °C for 24 h, no products were obtained. However, with triethylamine (excess) or ethylenediamine diacetate (20 mol %) as a catalyst, adduct **6** was obtained as a sole compound. The best yield (64%) was obtained in the presence of EDDA (20 mol %)/TEA (2 mL) as co-catalyst in refluxing xylene for 24 h.

Compound **6** was easily separated by column chromatography and the cis-stereochemistry of **6** is confirmed on the basis of coupling constant of ^{1}H NMR and by direct comparison with reported data.[15,16] The signal of benzylic methine on the pyranyl ring in **6** appears as a doublet (J=4.3 Hz) at δ 4.47. In the cis-fused cycloadducts of these types of other known tetracycles, the signals of benzylic methine showed as a doublet with coupling constant J=4–6 Hz, whereas those of trans-fused adducts appeared as a doublet with coupling constant J=9–11 Hz.[15,16]

Table 1
Reaction of 2,4-dihydroxyacetophenone (**5**) with benzaldehyde **2** under several conditions

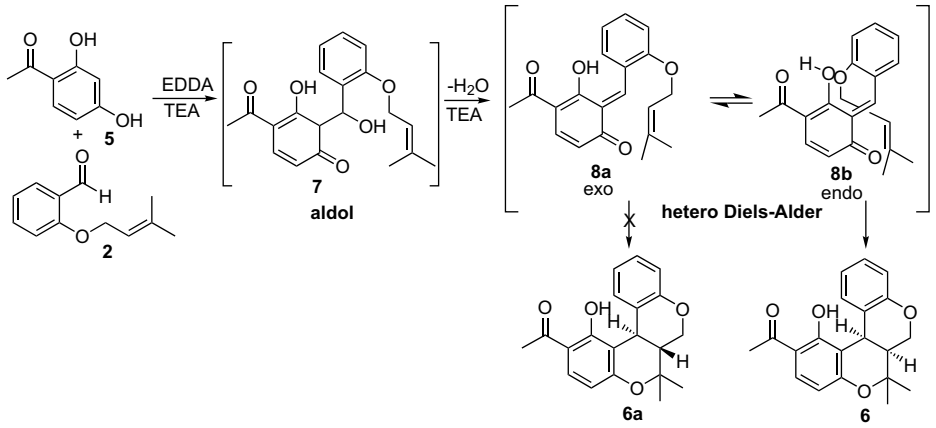


Conditions		Yield (%)
$InCl_3$ (20 mol %)	Acetonitrile, reflux, 12 h	0
Yb $(OTf)_3$ (20 mol %)	Acetonitrile, reflux, 12 h	0
Pyridine (excess)	140 °C, 24 h	0
TEA (excess)	Xylene, reflux, 24 h	20
EDDA (20 mol %)	Chloroform, reflux, 24 h	27
EDDA (20 mol %)	Benzene, reflux, 24 h	33
EDDA (20 mol %)	Xylene, reflux, 24 h	51
EDDA (20 mol %)/TEA (2 ml)	Xylene, reflux, 24 h	64

The stereospecificity of compound **6** may be explained by the *endo*-transition structure as shown in Scheme 3. Reaction of **5** with benzaldehyde **2** in the presence of EDDA/TEA first gives intermediate **7** as an aldol-type product. Such a process was already suggested by Shigemasa to give aldol-type products through a $CaCl_2$/KOH-mediated reaction of resorcinol to aldehydes.[17] TEA likely increases the activity of dehydration of the intermediate **7** to form quinone methide **8a** and **8b**.[18] However, in the final step of cycloaddition, the *endo*-transition structure (**8b**) must have been more favorable than the *exo*-transition structure (**8a**) due to an sp^2-geminal effect according to the phenomenon of 1,3-allylic strain.[19] This explanation has been already proved by Tietze's work, who reported the synthesis of tetracycles using intramolecular hetero Diels–Alder cycloaddition of benzylidene-1,3-dicarbonyl compounds and *O*-allyl ether of salicylic aldehydes.[16,20] The regiospecificity of the sole product **6** may be due to hydrogen bond between the hydroxy group and carbonyl group. Therefore, cyclization of compound **6** is likely to occur on the position without formation of a hydrogen bond. The further structure in relation to cis-stereochemistry and regiochemistry of **6** were confirmed by X-ray single crystal analysis as shown in Figure 1.

In order to extend the utility of this methodology, further reactions of several types of resorcinols to benzaldehydes **2**–**4** were carried out in the presence of ethylenediamine diacetate (20 mol %)/TEA (2 mL) in refluxing xylene. The results are summarized in Table 2. First, reactions of orcinol (**9**) and olivetol (**10**) were examined. Reaction of orcinol (**9**) with 2.0 equiv of benzaldehyde **2** in refluxing xylene for 18 h afforded adduct **16** in 56% yield, whereas that of olivetol (**10**) gave product **17** in 52% yield (entries 1 and 2). Similarly, reactions of resorcinols with ester group on benzene ring were successful. Reactions of methyl 2,4-dihydroxybenzoate (**11**) and ethyl 2,4-dihydroxybenzoate (**12**) in refluxing xylene for 18 h afforded the desired products **18** and **19** in 57 and 62% yields, respectively (entries 3 and 4). Similarly, treatment of ethyl 2,4-dihydroxy-6-methylbenzoate (**13**) in refluxing xylene for 18 h afforded product **20** in 60% yield (entry 5). In other resorcinols with carbonyl group on the benzene ring, such as 2,4-dihydroxypropiophenone (**14**) and 2,4-dihydroxybenzophenone (**15**), cycloaddition reactions were also successful. Treatment of **14** with benzaldehyde **2** in refluxing xylene for 12 h afforded product **21** in 63% yield, whereas reaction of **15** gave adduct **22** in 71% yield (entries 6 and 7). We also studied the reactions of compound **15** with benzaldehydes **3** and **4** with long chains under the optimized reaction conditions. In these cases, a longer reaction time (24 h) was required and products **23** and **24** were obtained in 64% and 60% yields, respectively, as sole products (entries 8 and 9). As shown in Scheme 4, stereospecific construction of quaternary carbon centers on compounds **23** and **24** may also be explained through the *endo*-transition state of structures **25** and **26**. The stereochemical assignment of compounds **23** and **24** was also confirmed by comparison with X-ray structure of the compound **36**, which was obtained by other domino hetero Diels–Alder reaction.[21] These reactions provided a rapid route for the synthesis of a variety of benzopyranobenzopyrans with substituents on the benzopyranyl ring.

On the basis of these successful results, we examined additional reactions between naphthols **27**–**29** and benzaldehydes **2**–**4** to



Scheme 3. Possible explanation of the stereochemistry and regiochemistry of compound **6**.

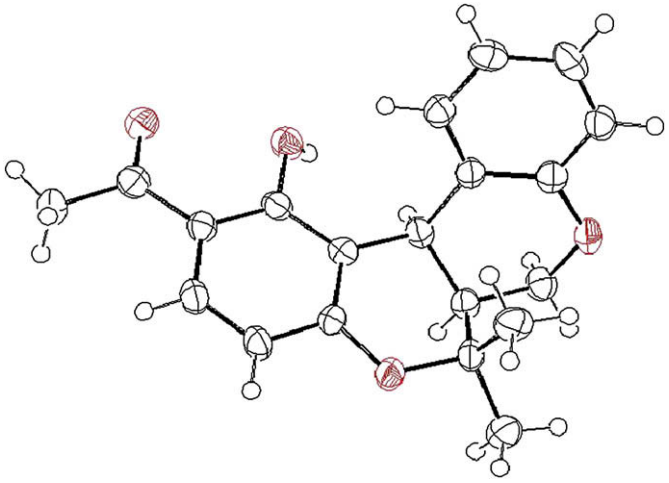


Figure 1. X-ray structure of compound **6**.

afford naphthopyranobenzopyrans as shown in Table 3. Reaction of 1-naphthol (**27**) with benzaldehyde **2** using 20 mol % of ethylenediamine diacetate/TEA (2 ml) in refluxing xylene for 12 h gave product **30** (94%) (entry 1), whereas reactions with aldehydes **3** and **4** provided adducts **31** and **32** in 83 and 70% yields, respectively, as sole products (entries 2 and 3). The stereochemistry of quaternary carbon centers having a long chain on compounds **31** and **32** was determined in a similar manner as shown in Scheme 4. With other naphthols containing substituents, cycloaddition reactions were also successful. Reaction of 4-methoxy-1-naphthol (**28**) with benzaldehyde **2** in the presence of 20 mol % of ethylenediamine diacetate/TEA (2 mL) in refluxing xylene for 18 h gave product **33** (68%), whereas with 4-chloro-1-naphthol (**29**) adduct **34** was produced in 73% yield. These reactions also provided a rapid entry to the synthesis of naphthopyranobenzopyrans with substituents on the benzochromene ring.

3. Conclusion

We have demonstrated a new and efficient methodology for biologically interesting benzopyranobenzopyrans and naphthopyranobenzopyrans by domino aldol-type/hetero Diels–Alder reactions from commercially available resorcinols and naphthols. These reactions provide a rapid route for the synthesis of novel types of polycycles with stereochemically defined quaternary carbon centers.

4. Experimental section

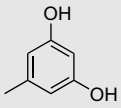
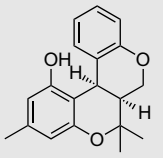
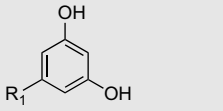
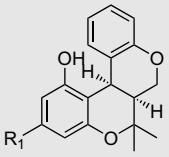
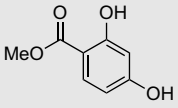
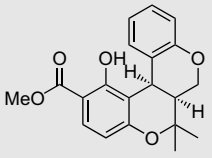
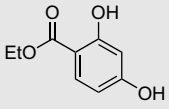
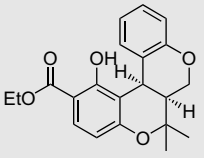
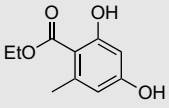
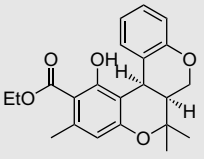
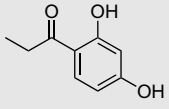
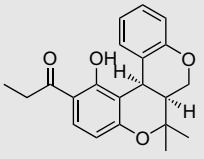
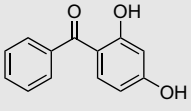
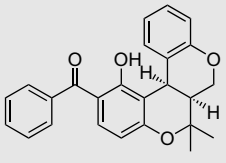
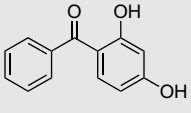
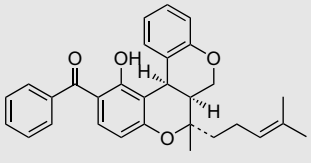
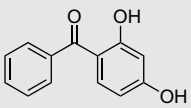
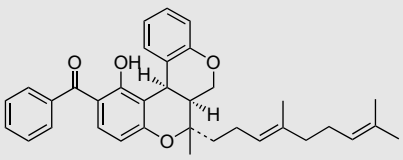
4.1. 2-(3-Methylbut-2-enyloxy)benzaldehyde (2)

To a solution of **1** (1.807 g, 14.8 mmol) in DMF (20 mL) was added sodium hydride (1.776 g, 60%, 44.4 mmol) at 0 °C. After 20 min, prenyl bromide (2.426 g, 16.3 mmol) in DMF (3 mL) was added dropwise. The reaction mixture was stirred at room temperature for 12 h and water (30 mL) was added slowly at 0 °C. The reaction mixture was extracted with ethyl acetate (30 mL×3), washed with water (30 mL) and saturated NH_4Cl solution (30 mL), dried over $MgSO_4$, and evaporated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, 20:1) to give **2** (2.787 g, 99%) as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.54 (1H, s), 7.80 (1H, dd, J=7.6, 1.7 Hz), 7.70 (1H, ddd, J=8.0, 7.6, 1.7 Hz), 7.00–6.95 (2H, m), 5.50–5.45 (1H, m), 4.64 (2H, d, J=6.6 Hz), 1.78 (3H, s), 1.73 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.9, 161.3, 138.6, 135.7, 128.2, 125.1, 120.5, 118.9, 112.9, 65.4, 25.7, 18.2; IR (neat) 2976, 2861, 1688, 1599, 1481, 1458, 1383, 1287, 1236, 1190, 1161, 1101, 1044, 993, 758 cm^{-1}; m/z (EI) 190 (M^+, 4), 148 (6), 147 (6), 123 (8), 122 (100), 121 (46), 120 (7), 69 (97), 68 (13), 65 (13), 53 (6); HRMS m/z (M^+) calcd for $C_{12}H_{14}O_2$: 190.0994. Found: 190.0992.

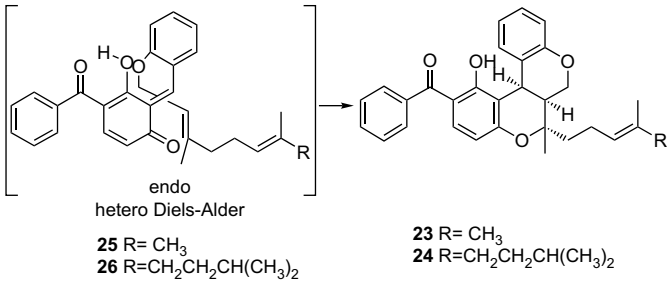
4.2. (*E*)-2-(3,7-Dimethylocta-2,6-dienyloxy)benzaldehyde (3)

To a solution of **1** (0.904 g, 7.4 mmol) in DMF (20 mL) was added sodium hydride (0.888 g, 60%, 22.2 mmol) at 0 °C. After 20 min, geranyl bromide (1.770 g, 8.2 mmol) in DMF (3 mL) was added dropwise. The reaction mixture was stirred at room temperature for 12 h and water (30 mL) was added slowly at 0 °C. The mixture was extracted with ethyl acetate (30 mL×3), washed with water (30 mL) and saturated NH_4Cl solution (30 mL), dried over $MgSO_4$, and evaporated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, 20:1) to give **3** (1.893 g, 99%) as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.48 (1H, s), 7.80 (1H, dd, J=7.5, 1.7 Hz), 7.49 (1H, ddd, J=8.0, 7.5, 1.7 Hz), 7.00–6.94 (2H, m), 5.49–5.44 (1H, m), 5.14–5.11 (1H, m), 4.63 (2H, d, J=6.4 Hz), 1.72 (3H, s), 2.16–2.00 (4H, m), 1.64 (3H, s), 1.57 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.9, 161.3, 141.8, 135.8, 135.7, 131.9, 128.2, 123.6, 120.5, 118.8, 113.0, 65.5, 39.4, 26.2, 25.6, 17.6, 16.7; IR (neat) 2969, 2920, 2859, 1690, 1599, 1481, 1456, 1383, 1287, 1236, 1190, 1161, 1103, 992, 833, 758 cm^{-1}; m/z (EI) 258 (M^+, 2), 137 (26), 136 (15), 122 (31), 121 (21), 95 (13), 93 (18), 81 (49), 69 (100), 68 (13), 67 (13); HRMS m/z (M^+) calcd for $C_{17}H_{22}O_2$: 258.1620. Found: 258.1623.

Table 2
Reactions of resorcinols with benzaldehydes **2**–**4**[a]

Entry	Resorcinol	Benzaldehyde	Time (h)	Product	Yield (%)
1	 **9**	**2**	18	 **16**	56
2	 **10** R_1=n-C_5H_{11}	**2**	18	 **17**	52
3	 **11**	**2**	18	 **18**	57
4	 **12**	**2**	18	 **19**	62
5	 **13**	**2**	18	 **20**	60
6	 **14**	**2**	12	 **21**	63
7	 **15**	**2**	12	 **22**	71
8	 **15**	**3**	24	 **23**	64
9	 **15**	**4**	24	 **24**	60

[a] Resorcinols (1.0 mmol) and benzaldehydes **2**–**4** (2.0 mmol) under EDDA (20 mol %)/TEA (2 mL) in refluxing xylene.



Scheme 4. Explanation for construction of stereochemically defined quaternary carbon centers on compounds **23** and **24**.

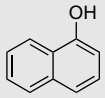
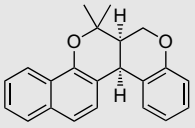
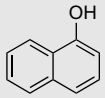
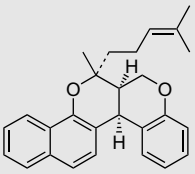
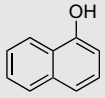
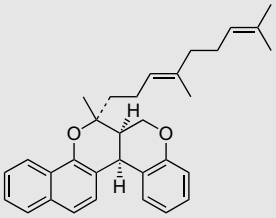
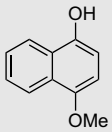
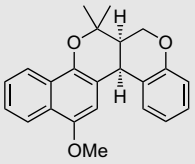
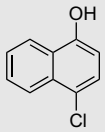
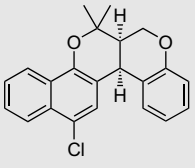
4.3. (*E*),(*E*)-2-(3,7,11-Trimethyldodeca-2,6,10-trienyloxy)benzaldehyde (4)

To a solution of **1** (0.904 g, 7.4 mmol) in DMF (20 mL) was added sodium hydride (0.888 g, 60%, 22.2 mmol) at 0 °C. After 20 min, *trans*,*trans*-farnesyl bromide (2.325 g, 8.2 mmol) in DMF (3 mL) was added dropwise. The reaction mixture was stirred at room temperature for 12 h and water (30 mL) was added slowly at 0 °C. The mixture was extracted with ethyl acetate (30 mL×3), washed with water (30 mL) and saturated NH_4Cl solution (30 mL), dried over $MgSO_4$, and evaporated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, 20:1) to give **4** (2.368 g, 98%) as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.48 (1H, s), 7.80 (1H, dd, J=7.5, 1.7 Hz), 7.49 (1H, ddd, J=8.0, 7.5, 1.7 Hz), 7.01–6.94 (2H, m), 5.50–5.46 (1H, m), 5.11–5.04 (1H, m), 4.64 (2H, d, J=6.4 Hz), 2.18–1.91 (8H, m), 1.73 (3H, s), 1.65 (3H, s), 1.58 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.9, 161.3, 141.8, 135.7, 135.5, 131.2, 128.2, 125.1, 124.2, 123.5, 120.5, 118.8, 112.9, 65.5, 39.6, 39.4, 26.6, 26.1, 25.6, 17.6, 16.7, 16.0; IR (neat) 2967, 2922, 2857, 1690, 1599, 1481, 1456, 1383, 1287, 1236, 1190, 1161, 1103, 992, 833, 758 cm^{-1}; m/z (EI) 326 (M^+, 2), 207 (7), 189 (6), 161 (9), 149 (10), 137 (34), 122 (30), 121 (24), 93 (33), 81 (95), 69 (100), 55 (20); HRMS m/z (M^+) calcd for $C_{22}H_{30}O_2$: 326.2246. Found: 326.2244.

4.4. General procedure for the synthesis of benzopyranobenzopyrans and naphthopyranobenzopyrans

Ethylenediamine diacetate (36 mg, 0.2 mmol) and TEA (2 mL) were added to a solution of resorcinol or naphthol (1.0 mmol) and benzaldehyde (2.0 mmol) in xylene (10 mL) at room temperature. The reaction mixture was stirred in refluxing xylene for 12–24 h. The removal of the solvent under reduced pressure left an oily

Table 3
Reactions of naphthols with benzaldehydes **2**–**4**[a]

Entry	Naphthols	Benzaldehyde	Time (h)	Product	Yield (%)
1	 **27**	**2**	12	 **30**	94
2	 **27**	**3**	24	 **31**	83
3	 **27**	**4**	24	 **32**	70
4	 **28**	**2**	18	 **33**	68
5	 **29**	**2**	18	 **34**	73

[a] Naphthols (1.0 mmol) and benzaldehydes **2**–**4** (2.0 mmol) under EDDA (20 mol %)/TEA (2 mL) in refluxing xylene.

residue, which was then purified by column chromatography on silica gel to give the product.

4.4.1. 1-(1-Hydroxy-6,6-dimethyl-6a,12b-dihydro-6H,7H-5,8-dioxabenzo[c]phenanthren-2-yl)ethanone (**6**)

A reaction of 2,4-dihydroxyacetophenone (**5**) (0.152 g, 1.0 mmol) with benzaldehyde **2** (0.380 g, 2.0 mmol) in refluxing xylene (10 mL) for 24 h and purification by column chromatography on silica gel (hexane/ethyl acetate, 10:1) afforded compound **6** (0.208 g, 64%) as a solid: mp 152–153 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.47 (1H, s), 7.59 (1H, d, J=8.9 Hz), 7.23 (1H, d, J=8.0 Hz), 7.06 (1H, dd, J=8.0, 7.5 Hz), 6.80 (1H, dd, J=7.8, 7.5 Hz), 6.70 (1H, d, J=7.8 Hz), 6.37 (1H, d, J=8.9 Hz), 4.50 (2H, dd, J=12.0, 4.2 Hz), 4.47 (1H, d, J=4.3 Hz), 2.58 (3H, s), 2.24–2.18 (1H, m), 1.53 (3H, s), 1.08 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.6, 163.5, 160.0, 153.9, 130.9, 129.2, 127.6, 122.3, 120.7, 115.8, 112.9, 110.7, 109.3, 78.6, 65.5, 38.5, 29.0, 28.8, 26.1, 23.8; IR (KBr) 2969, 1618, 1487, 1449, 1412, 1373, 1323, 1267, 1127, 1084, 1059, 893, 828, 804, 758 cm^{-1}; m/z (EI) 324 (M^+, 100), 325 (21), 324 (100), 309 (16), 282 (11), 281 (50), 268 (9), 255 (13), 240 (11), 239 (67), 159 (13), 69 (8); HRMS m/z (M^+) calcd for $C_{20}H_{20}O_4$: 324.1362. Found: 324.1363.

4.4.2. 3,6,6-Trimethyl-6a,12b-dihydro-6H,7H-5,8-dioxabenzo[c]phenanthren-1-ol (**16**)

A reaction of orcinol (**9**) (0.124 g, 1.0 mmol) with benzaldehyde **2** (0.380 g, 2.0 mmol) in refluxing xylene (10 mL) for 18 h and purification by column chromatography on silica gel (hexane/ethyl acetate, 10:1) afforded compound **16** (0.166 g, 56%) as a solid: mp 140–141 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.01 (1H, s), 7.30 (1H, d, J=7.8 Hz), 7.11 (1H, d, J=7.8, 7.4 Hz), 6.84 (1H, dd, J=8.0, 7.4 Hz), 6.76 (1H, d, J=8.0 Hz), 6.29 (1H, s), 6.24 (1H, s), 4.47 (1H, dd, J=11.8, 4.6 Hz), 4.35 (1H, dd, J=11.8, 4.6 Hz), 4.33 (1H, d, J=4.6 Hz), 2.27–2.20 (1H, m), 2.22 (3H, s), 1.46 (3H, s), 1.09 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.9, 154.4, 153.9, 139.0, 129.3, 128.1, 123.3, 120.9, 116.4, 110.6, 108.3, 106.8, 76.2, 65.8, 39.2, 30.2, 28.5, 24.0, 21.1; IR (KBr) 3428, 3036, 2982, 2942, 1618, 1584, 1489, 1450, 1240, 1175, 1132, 1080, 1049, 995, 885, 853, 816, 748 cm^{-1}; m/z (EI) 296 (M^+, 60), 281 (7), 253 (17), 227 (20), 212 (15), 211 (100), 159 (13); HRMS m/z (M^+) calcd for $C_{19}H_{20}O_3$: 296.1412. Found: 296.1411.

4.4.3. 6,6-Dimethyl-3-pentyl-6a,12b-dihydro-6H,7H-5,8-dioxabenzo[c]phenanthren-1-ol (**17**)

A reaction of olivetol (**10**) (0.180 g, 1.0 mmol) with benzaldehyde **2** (0.380 g, 2.0 mmol) in refluxing xylene (10 mL) for 18 h and purification by column chromatography on silica gel (hexane/ethyl acetate, 20:1) afforded compound **17** (0.183 g, 52%) as a solid: mp 113–114 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.51 (1H, s), 7.31 (1H, d, J=7.8 Hz), 7.10 (1H, d, J=7.8, 7.4 Hz), 6.84 (1H, dd, J=8.0, 7.4 Hz), 6.75 (1H, d, J=8.0), 6.29 (1H, s), 6.25 (1H, s), 4.48 (1H, dd, J=11.8, 4.6 Hz), 4.35 (1H, dd, J=11.8, 4.6 Hz), 4.33 (1H, d, J=4.6 Hz), 2.46 (2H, t, J=7.5 Hz), 2.26–2.21 (1H, m), 1.62–1.52 (3H, m), 1.46 (3H, s), 1.37–1.29 (3H, m), 1.09 (3H, s), 0.87 (3H, t, J=6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8, 154.4, 153.8, 144.0, 129.1, 128.0, 123.3, 120.8, 116.3, 109.8, 107.6, 107.0, 76.2, 65.8, 39.2, 35.6, 31.5, 30.6, 30.2, 28.5, 24.0, 22.5, 14.0; IR (KBr) 3368, 2930, 1624, 1487, 1452, 1429, 1348, 1246, 1171, 1136, 1078, 1043, 889, 790, 754 cm^{-1}; HRMS m/z (M^+) calcd for $C_{23}H_{28}O_3$: 352.2038. Found: 352.2034.

4.4.4. 1-Hydroxy-6,6-dimethyl-6a,12b-dihydro-6H,7H-5,8-dioxabenzo[c]phenanthrene-2-carboxylic acid methyl ester (**18**)

A reaction of methyl 2,4-dihydroxybenzoate (**11**) (0.168 g, 1.0 mmol) with benzaldehyde **2** (0.380 g, 2.0 mmol) in refluxing xylene (10 mL) for 18 h and purification by column chromatography on silica gel (hexane/ethyl acetate, 20:1) afforded compound **18** (0.194 g, 57%) as a solid: mp 123–124 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.62 (1H, s), 7.70 (1H, d, J=8.9 Hz), 7.25 (1H, d, J=7.7 Hz), 7.07 (1H, d, J=7.7, 7.4 Hz), 6.80 (1H, dd, J=8.0, 7.4 Hz), 6.72 (1H, d, J=8.0 Hz), 6.38 (1H, d, J=8.9 Hz), 4.53–4.46 (3H, m), 3.92 (3H, s), 2.24–2.18 (1H, m), 1.53 (3H, s), 1.07 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 161.9, 159.4, 154.0, 129.7, 129.2, 127.6, 122.5, 120.7, 115.9, 110.5, 109.5, 104.3, 78.2, 65.7, 52.0, 38.6, 29.3, 28.9, 23.8; IR (KBr) 2980, 1664, 1622, 1584, 1489, 1439, 1345, 1267, 1217, 1134, 1061, 997, 889, 791, 752 cm^{-1}; m/z (EI) 340 (M^+, 92), 309 (26), 308 (100), 293 (11), 281 (11), 280 (48), 239 (17), 224 (10), 223 (59), 159 (20); HRMS m/z (M^+) calcd for $C_{20}H_{20}O_5$: 340.1311. Found: 340.1313.

4.4.5. 1-Hydroxy-6,6-dimethyl-6a,12b-dihydro-6H,7H-5,8-dioxabenzo[c]phenanthrene-2-carboxylic acid ethyl ester (**19**)

A reaction of ethyl 2,4-dihydroxybenzoate (**12**) (0.182 g, 1.0 mmol) with benzaldehyde **2** (0.380 g, 2.0 mmol) in refluxing xylene (10 mL) for 18 h and purification by column chromatography on silica gel (hexane/ethyl acetate, 20:1) afforded compound **19** (0.220 g, 62%) as a solid: mp 134–135 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.60 (1H, s), 7.64 (1H, d, J=8.9 Hz), 7.17 (1H, d, J=7.8 Hz), 6.99 (1H, d, J=7.8, 7.4 Hz), 6.72 (1H, dd, J=8.0, 7.4 Hz), 6.63 (1H, d, J=8.0 Hz), 6.29 (1H, d, J=8.9 Hz), 4.46–4.28 (5H, m), 2.32–2.20 (1H, m), 1.44 (3H, s), 1.33 (3H, t, J=7.2 Hz), 0.99 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 162.0, 159.3, 154.0, 129.7, 129.2, 127.6, 122.5, 120.7, 115.9, 110.4, 109.3, 104.6, 78.2, 65.7, 61.0, 38.7, 29.3, 28.9, 23.8, 14.3; IR (KBr) 2980, 1661, 1584, 1489, 1373, 1265, 1136, 1061, 1020, 910, 793, 752 cm^{-1}; HRMS m/z (M^+) calcd for $C_{21}H_{22}O_5$: 354.1467. Found: 354.1469.

4.4.6. 1-Hydroxy-3,6,6-trimethyl-6a,12b-dihydro-6H,7H-5,8-dioxabenzo[c]phenanthrene-2-carboxylic acid ethyl ester (**20**)

A reaction of ethyl 2,4-dihydroxy-6-methylbenzoate (**13**) (0.196 g, 1.0 mmol) with benzaldehyde **2** (0.380 g, 2.0 mmol) in refluxing xylene (10 mL) for 18 h and purification by column chromatography on silica gel (hexane/ethyl acetate, 20:1) afforded compound **20** (0.221 g, 60%) as a solid: mp 126–127 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.55 (1H, s), 7.27 (1H, d, J=7.7 Hz), 7.06 (1H, d, J=7.7, 7.4 Hz), 6.80 (1H, dd, J=8.0, 7.4 Hz), 6.71 (1H, d, J=8.0 Hz), 6.24 (1H, s), 4.53–4.39 (5H, m), 2.51 (3H, s), 2.23–2.16 (1H, m), 1.52 (3H, s), 1.43 (3H, t, J=7.1 Hz), 1.06 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.3, 163.7, 157.7, 154.0, 141.6, 129.3, 127.5, 122.8, 120.7, 115.8, 112.5, 108.5, 104.4, 78.1, 65.7, 61.2, 38.9, 29.3, 28.9, 24.2, 23.8, 14.3; IR (KBr) 3038, 2980, 2936, 1644, 1397, 1489, 1453, 1397, 1368, 1323, 1269, 1246, 1136, 1090, 1009, 806, 752 cm^{-1}; m/z (EI) 368 (M^+, 55), 323 (27), 322 (100), 295 (14), 294 (66), 293 (10), 279 (15), 253 (12), 237 (34); HRMS m/z (M^+) calcd for $C_{22}H_{24}O_5$: 368.1624. Found: 368.1621.

4.4.7. 1-(1-Hydroxy-6,6-dimethyl-6a,12b-dihydro-6H,7H-5,8-dioxabenzo[c]phenanthren-2-yl)propane-1-one (**21**)

A reaction of 2,4-dihydroxypropiophenone (**14**) (0.166 g, 1.0 mmol) with benzaldehyde **2** (0.380 g, 2.0 mmol) in refluxing xylene (10 mL) for 12 h and purification by column chromatography on silica gel (hexane/ethyl acetate, 20:1) afforded compound **21** (0.213 g, 63%) as a solid: mp 124–125 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.59 (1H, s), 7.64 (1H, d, J=8.9 Hz), 7.25 (1H, d, J=7.8 Hz), 7.07 (1H, d, J=7.8, 7.4 Hz), 6.80 (1H, dd, J=8.0, 7.4 Hz), 6.71 (1H, d, J=8.0 Hz), 6.38 (1H, d, J=8.9 Hz), 4.54–4.48 (3H, m), 2.99 (2H, q, 7.2 Hz), 2.25–2.20 (1H, m), 1.54 (3H, s), 1.27 (3H, t, J=7.5 Hz), 1.09 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.5, 163.6, 159.8, 154.0, 130.1, 129.2, 127.7, 122.4, 120.8, 115.9, 112.4, 110.8, 109.2, 78.6, 65.6, 38.6, 31.1, 29.1, 28.9, 23.8, 8.7; IR (KBr) 2980, 1620, 1489, 1416, 1323, 1258, 1123, 1071, 910, 891, 797, 754 cm^{-1}; m/z (EI) 338 (M^+, 100), 310 (13), 309 (64), 295 (33), 253 (45), 241 (25), 159 (9), 69 (10); HRMS m/z (M^+) calcd for $C_{21}H_{22}O_4$: 338.1518. Found: 338.1520.

*4.4.8. 1-(1-Hydroxy-6,6-dimethyl-6a,12b-dihydro-6H,7H-5,8-dioxabenzo[c]phenanthren-2-yl)phenylmethanone (**22**)*

A reaction of 2,4-dihydroxybenzophenone (**15**) (0.214 g, 1.0 mmol) with benzaldehyde **2** (0.380 g, 2.0 mmol) in refluxing xylene (10 mL) for 12 h and purification by column chromatography on silica gel (hexane/ethyl acetate, 15:1) afforded compound **22** (0.274 g, 71%) as a solid: mp 65–66 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.46 (1H, s), 7.65 (2H, d, J=8.9 Hz), 7.55–7.44 (4H, m), 7.33 (1H, d, J=7.8 Hz), 7.08 (1H, d, J=7.8, 7.4 Hz), 6.83 (1H, dd, J=8.0, 7.4 Hz), 6.72 (1H, d, J=8.0 Hz), 6.33 (1H, d, J=8.9 Hz), 4.63–4.49 (3H, m), 2.28–2.20 (1H, m), 1.54 (3H, s), 1.10 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.2, 164.8, 160.3, 154.0, 138.3, 133.9, 131.4, 129.3, 128.9, 128.3, 127.8, 122.3, 120.8, 115.9, 112.2, 111.0, 109.2, 78.8, 65.6, 38.6, 29.2, 28.9, 23.9; IR (KBr) 2980, 1615, 1487, 1348, 1269, 1138, 1071, 885, 756 cm^{-1}; HRMS m/z (M^+) calcd for $C_{25}H_{22}O_4$: 386.1518. Found: 386.1522.

*4.4.9. [1-Hydroxy-6-methyl-6-(4-methylpent-3-enyl)-6a,12b-dihydro-6H,7H-5,8-dioxabenzo[c]phenanthren-2-yl]-phenylmethanone (**23**)*

A reaction of 2,4-dihydroxybenzophenone (**15**) (0.214 g, 1.0 mmol) with benzaldehyde **3** (0.517 g, 2.0 mmol) in refluxing xylene (10 mL) for 24 h and purification by column chromatography on silica gel (hexane/ethyl acetate, 15:1) afforded compound **23** (0.291 g, 64%) as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.47 (1H, s), 7.66 (2H, d, J=8.9 Hz), 7.56–7.45 (4H, m), 7.35 (1H, d, J=7.8 Hz), 7.09 (1H, d, J=7.8, 7.4 Hz), 6.85 (1H, dd, J=8.0, 7.4 Hz), 6.74 (1H, d, J=8.0 Hz), 6.36 (1H, d, J=8.9 Hz), 5.16–5.12 (1H, m), 4.60 (1H, d, J=5.4 Hz), 4.52 (1H, dd, J=12.0, 3.9 Hz), 4.44 (1H, d, J=12.0 Hz), 2.40–2.32 (1H, m), 2.20–2.08 (2H, m), 1.86–1.80 (2H, m), 1.69 (3H, s), 1.61 (3H, s), 1.11 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.1, 164.8, 160.5, 154.1, 138.4, 133.9, 132.2, 131.4, 129.3, 129.9, 129.8, 128.3, 128.2, 127.7, 123.6, 122.7, 120.8, 115.9, 112.1, 110.9, 109.2, 80.2, 65.4, 40.6, 35.7, 29.1, 25.7, 22.7, 21.6, 17.7; IR (neat) 2924, 1613, 1487, 1449, 1412, 1381, 1346, 1269, 1155, 1111, 1069, 999, 909, 816, 733 cm^{-1}; m/z (EI) 454 (M^+, 7), 371 (11), 370 (26), 369 (100), 301 (21), 105 (22), 77 (9), 69 (14); HRMS m/z (M^+) calcd for $C_{30}H_{30}O_4$: 454.2144. Found: 454.2145.

*4.4.10. (E)-[6-(4,8-Dimethylnona-3,7-dienyl)-1-hydroxy-6-methyl-6a,12b-dihydro-6H,7H-5,8-dioxabenzo[c]phenanthren-2-yl]-phenylmethanone (**24**)*

A reaction of 2,4-dihydroxybenzophenone (**15**) (0.214 g, 1.0 mmol) with benzaldehyde **4** (0.653 g, 2.0 mmol) in refluxing xylene (10 mL) for 24 h and purification by column chromatography on silica gel (hexane/ethyl acetate, 15:1) afforded compound **24** (0.314 g, 60%) as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.51 (1H, s), 7.69 (2H, d, J=8.9 Hz), 7.59–7.47 (4H, m), 7.38 (1H, d, J=7.8 Hz), 7.11 (1H, d, J=7.8, 7.4 Hz), 6.86 (1H, dd, J=8.0, 7.4 Hz), 6.76 (1H, d, J=8.0 Hz), 6.40 (1H, d, J=8.9 Hz), 5.21–5.16 (1H, m), 5.14–5.09 (1H, m), 4.63 (1H, d, J=5.0 Hz), 4.53 (1H, dd, J=12.0, 4.0 Hz), 4.45 (1H, dd, J=12.0, 3.6 Hz), 2.42–2.34 (1H, m), 2.24–1.96 (6H, m), 1.90–1.84 (2H, m), 1.70 (3H, s), 1.64 (3H, s), 1.62 (3H, s), 1.14 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.1, 164.8, 160.5, 154.1, 138.3, 135.8, 133.8, 131.4, 131.3, 129.2, 128.8, 128.7, 128.2, 128.1, 127.7, 124.2, 123.4, 122.6, 120.7, 115.9, 112.1, 110.9, 109.2, 80.2, 65.4, 40.5, 39.6, 35.6, 29.1, 26.6, 25.7, 22.6, 21.5, 17.7, 16.0; IR (neat) 2922, 1613, 1487, 1449, 1412, 1381, 1346, 1269, 1154, 1109, 1067, 999, 903, 754 cm^{-1}; m/z (EI) 522 (M^+, 7), 371 (12), 370 (26), 369 (100), 301 (18), 105 (19), 81 (16), 69 (41); HRMS m/z (M^+) calcd for $C_{35}H_{38}O_4$: 522.2770. Found: 522.2774.

*4.4.11. 6,6-Dimethyl-6a,7-dihydro-6H,12bH-5,8-dioxabenzo[c]-chrysene (**30**)*

A reaction of 1-naphthol (**27**) (0.144 g, 1.0 mmol) with benzaldehyde **2** (0.380 g, 2.0 mmol) in refluxing xylene (10 mL) for 12 h and purification by column chromatography on silica gel (hexane/ethyl acetate, 30:1) afforded compound **30** (0.297 g, 94%) as a solid: mp 108–109 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30–8.28 (1H, m), 7.78–7.73 (1H, m), 7.54–7.45 (4H, m), 7.35 (1H, d, J=8.6 Hz), 7.26 (1H, dd, J=8.0, 7.4 Hz), 7.07 (1H, dd, J=7.6, 7.4 Hz), 6.90 (1H, d, J=8.0 Hz), 4.53 (1H, d, J=11.8 Hz), 4.33 (1H, d, J=4.6 Hz), 3.96 (1H, dd, J=11.8, 11.1 Hz), 2.37–2.30 (1H, m), 1.69 (3H, s), 1.52 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.0, 146.4, 133.4, 132.4, 128.4, 127.3, 126.3, 126.0, 125.4, 125.1, 122.4, 122.0, 119.7, 119.6, 116.8, 114.8, 74.7, 63.5, 37.1, 33.5, 26.4, 26.2; IR (KBr) 3057, 2980, 2926, 1583, 1491, 1454, 1387, 1329, 1302, 1238, 1148, 1093, 1057, 1042, 1026, 965, 939, 909, 870, 814, 791, 758 cm^{-1}; HRMS m/z (M^+) calcd for $C_{22}H_{20}O_2$: 316.1463. Found: 316.1465.

*4.4.12. 6-Methyl-6-(4-methylpent-3-enyl)-6a,7-dihydro-6H,12bH-5,8-dioxabenzo[c]chrysene (**31**)*

A reaction of 1-naphthol (**27**) (0.144 g, 1.0 mmol) with benzaldehyde **3** (0.517 g, 2.0 mmol) in refluxing xylene (10 mL) for 24 h and purification by column chromatography on silica gel (hexane/ethyl acetate, 30:1) afforded compound **31** (0.319 g, 83%) as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59–8.47 (1H, m), 7.99–7.97 (1H, m), 7.76–7.69 (4H, m), 7.57 (1H, d, J=9.0 Hz), 7.48 (1H, dd, J=8.0, 7.4 Hz), 7.29 (1H, dd, J=7.6, 7.4 Hz), 7.13 (1H, d, J=8.0 Hz), 5.34–5.30 (1H, m), 4.53 (1H, dd, J=11.8, 1.8 Hz), 4.55 (1H, d, J=4.0 Hz), 4.23 (1H, dd, J=11.8, 11.4 Hz), 2.72–2.63 (1H, m), 2.48–2.36 (2H, m), 2.13–2.02 (2H, m), 1.88 (6H, s), 1.80 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1, 146.3, 133.4, 132.4, 132.0, 128.4, 127.3, 126.2, 126.0, 125.4, 125.1, 123.5, 122.4, 122.0, 119.7, 119.6, 116.8, 115.1, 76.9, 63.7, 38.2, 35.4, 33.3, 25.6, 22.8, 22.7, 22.1, 17.5; IR (neat) 2918, 1584, 1491, 1454, 1386, 1327, 1262, 1240, 1099, 1057, 964, 812, 758 cm^{-1}; m/z (EI) 384 (M^+, 23), 300 (22), 299 (94), 248 (18), 247 (15), 232 (19), 231 (100), 69 (22); HRMS m/z (M^+) calcd for $C_{27}H_{28}O_2$: 384.2089. Found: 384.2086.

*4.4.13. (E)-6-(4,8-Dimethylnona-3,7-dienyl)-6-methyl-6a,7-dihydro-6H,12bH-5,8-dioxabenzo[c]chrysene (**32**)*

A reaction of 1-naphthol (**27**) (0.144 g, 1.0 mmol) with benzaldehyde **4** (0.653 g, 2.0 mmol) in refluxing xylene (10 mL) for 24 h and purification by column chromatography on silica gel (hexane/ethyl acetate, 30:1) afforded compound **32** (0.317 g, 70%) as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23–8.19 (1H, m), 7.72–7.68 (1H, m), 7.49–7.39 (4H, m), 7.28 (1H, d, J=8.9 Hz), 7.20 (1H, dd, J=8.0, 7.4 Hz), 7.00 (1H, dd, J=7.6, 7.4 Hz), 6.83 (1H, d, J=8.0 Hz), 5.06–5.00 (2H, m), 4.53–4.48 (1H, m), 4.27 (1H, d, J=4.0 Hz), 3.95 (1H, dd, J=11.8, 11.1 Hz), 2.45–2.39 (1H, m), 2.22–2.09 (2H, m), 2.00–195 (2H, m), 1.91–1.77 (4H, m), 1.63 (3H, s), 1.61 (3H, s), 1.53 (3H, s), 1.51 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1, 146.3, 135.7, 133.4, 132.3, 131.3, 128.4, 127.2, 126.2, 126.0, 125.4, 125.1, 124.2, 123.3, 122.4, 122.0, 119.7, 119.6, 116.8, 115.0, 76.9, 63.6, 39.6, 38.2, 35.4, 33.3, 26.6, 25.6, 22.8, 22.0, 17.6, 15.9; IR (neat) 2922, 1584, 1491, 1454, 1385, 1240, 1101, 1055, 965, 812, 758 cm^{-1}; HRMS m/z (M^+) calcd for $C_{32}H_{36}O_2$: 452.2715. Found: 452.2713.

*4.4.14. 14-Methoxy-6,6-dimethyl-6a,7-dihydro-6H,12bH-5,8-dioxabenzo[c]chrysene (**33**)*

A reaction of 4-methoxy-1-naphthol (**28**) (0.174 g, 1.0 mmol) with benzaldehyde **2** (0.380 g, 2.0 mmol) in refluxing xylene (10 mL) for 18 h and purification by column chromatography on silica gel (hexane/ethyl acetate, 10:1) afforded compound **33** (0.236 g, 68%) as a solid: mp 154–155 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22–8.12 (2H, m), 7.55–7.43 (3H, m), 7.22 (1H, dd, J=8.0, 7.6 Hz), 7.03 (1H, dd, J=7.6, 7.4 Hz), 6.87 (1H, d, J=8.0 Hz), 6.83 (1H, s), 4.54–4.48 (1H, m), 4.26 (1H, d, J=3.8 Hz), 3.95 (1H, dd, J=11.2, 8.2 Hz), 3.84 (3H, s), 2.33–2.26 (1H, m), 1.62 (3H, s), 1.47 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 154.1, 148.9, 140.0, 131.9, 128.3, 126.2, 125.7, 125.4, 122.5, 121.7, 121.5, 119.6, 116.8, 113.9, 103.8, 74.2, 63.7, 55.3, 37.2, 33.8, 26.2, 26.0; IR (KBr) 3067, 2976, 1632, 1586, 1491, 1460, 1383, 1329, 1308, 1267, 1236, 1152, 1126, 1099, 1042, 1026, 962, 932,

756 cm^{-1}; HRMS *m*/*z* (M^+) calcd for $C_{23}H_{22}O_3$: 346.1569. Found: 346.1568.

*4.4.15. 14-Chloro-6,6-dimethyl-6a,7-dihydro-6H,12bH-5,8-dioxabenzo[c]chrysene (**34**)*

A reaction of 4-chloro-1-naphthol (**29**) (0.179 g, 1.0 mmol) with benzaldehyde **2** (0.380 g, 2.0 mmol) in refluxing xylene (10 mL) for 18 h and purification by column chromatography on silica gel (hexane/ethyl acetate, 40:1) afforded compound **34** (0.256 g, 73%) as a solid: mp 155–156 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (1H, d, *J*=8.0 Hz), 8.11 (1H, d, *J*=7.6 Hz), 7.60–7.44 (4H, m), 7.23 (1H, dd, *J*=8.0, 7.6 Hz), 7.04 (1H, dd, *J*=7.6, 7.4 Hz), 6.85 (1H, d, *J*=8.0 Hz), 4.52–4.46 (1H, m), 4.25 (1H, d, *J*=4.5 Hz), 3.87 (1H, dd, *J*=11.4, 11.3 Hz), 2.34–2.25 (1H, m), 1.68 (3H, s), 1.47 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.9, 145.6, 132.1, 130.3, 128.6, 127.1, 126.5, 126.1, 125.8, 124.0, 122.8, 122.4, 121.7, 120.0, 116.9, 115.4, 77.2, 75.1, 63.3, 36.8, 33.3, 26.2, 26.0; IR (KBr) 3073, 2982, 1586, 1493, 1454, 1375, 1327, 1300, 1263, 1229, 1146, 1107, 1042, 914, 760, 737 cm^{-1}; HRMS *m*/*z* (M^+) calcd for $C_{22}H_{19}ClO_2$: 350.1074. Found: 350.1073.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.10.101.

References and notes

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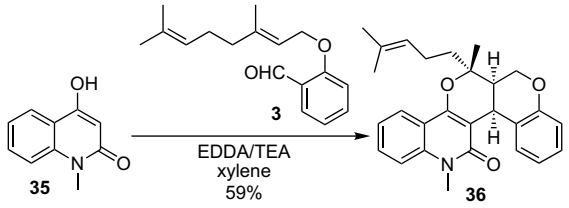
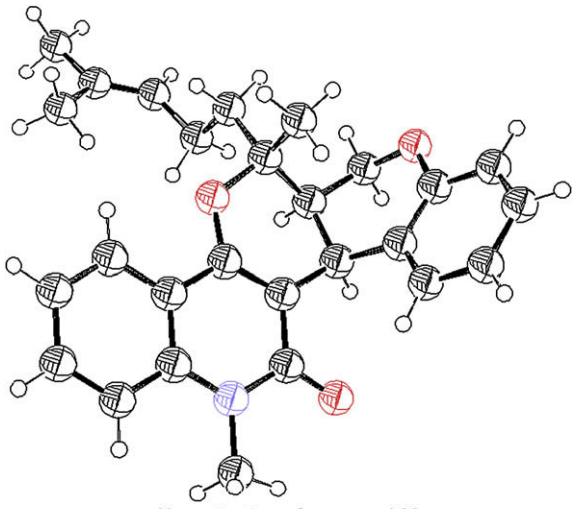
21. Reaction of 4-hydroxy-1-methyl-2-quinolone (**35**) with **3** in the presence of EDDA/TEA gave product **36** (59%) as a sole compound.





X-ray structure of compound **36**