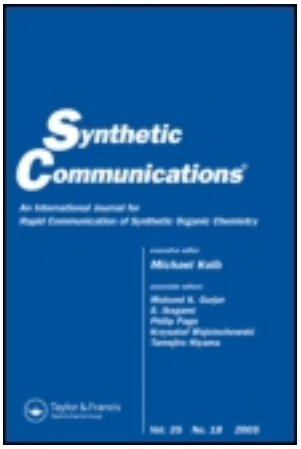

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Synthesis of Six-Membered Functionalized Carbocyclic Compounds by One-Pot Reaction of Hydroquinone Derivatives and Dienes

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SYNTHESIS OF SIX-MEMBERED FUNCTIONALIZED CARBOCYCLIC COMPOUNDS BY ONE-POT REACTION OF HYDROQUINONE DERIVATIVES AND DIENES

Guang-Rong Cai, Zhi Guan, and Yan-Hong He
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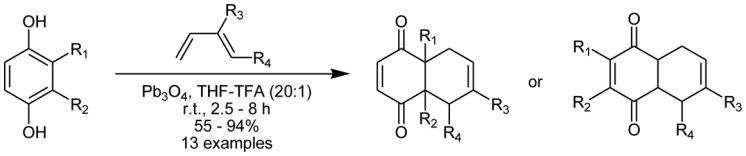
GRAPHICAL ABSTRACT



Abstract *A general method for one-pot reaction of hydroquinone derivatives and dienes has been developed. The system of Pb_3O_4 in tetrahydrofuran–trifluoroacetic acid was found to play dual roles as oxidant for the generation of quinones* in situ *and as catalyst for the Diels–Alder cycloaddition, which makes the one-pot reaction efficient and easy to carry out. Using this method, a variety of six-membered functionalized carbocyclic compounds can be easily prepared in medium to excellent yields at room temperature.*

Keywords Diels–Alder reaction; hydroquinone derivatives; lead tetroxide; one-pot reaction; oxidation

INTRODUCTION

Quinones are the most useful pericyclic materials for Diels–Alder reactions, especially for the construction of six-membered functionalized carbocyclic compounds,[1–3] and during the past several decades studying quinones as dienophiles in the reaction has produced dramatic results.[4–6] However, quinones possessing electron-withdrawing groups are difficult to isolate and decompose readily under air,[5] water,[5] and some Lewis acid catalysis.[7] Hence, it is favorable to take advantage of a suitable reagent and carry out the one-pot reaction of quinones generated *in situ*, followed by Diels–Alder reaction with dienes. In this field, some studies of limited scope concerning the use of Ag_2O,[8–14] $Pb(OAc)_4$,[2] MnO_2,[15,16] $PhI(OAc)_2$,[4,17] PbO_2,[18] and electrochemical oxidation[7] have been reported. However, in most methods the reagents were used only as oxidants to convert hydroquinone

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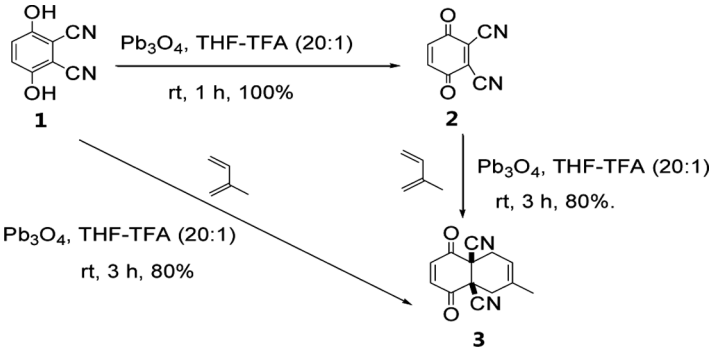
derivatives into corresponding quinones *in situ*. If a cheap and readily available reagent can play dual roles as oxidant for the generation of quinones and as catalyst for subsequent Diels–Alder cycloaddition in one pot, the result will be a nearly ideal process in terms of both efficiency and simplicity. In our study of the synthesis of functionalized carbocyclic compounds by a one-pot reaction of hydroquinone derivatives and dienes, we found that the system of Pb_3O_4 in tetrahydrofuran (THF) with a small amount of trifluoroacetic acid (TFA) not only can oxidize hydroquinone derivatives into the corresponding quinones *in situ* but also can catalyze the following Diels–Alder reaction in one pot. It has been known that Pb_3O_4 can oxidize hydroquinones into quinones,[19] but its catalytic activity for the Diels–Alder reaction to our knowledge has not been reported. Therefore, we now report the dual roles of Pb_3O_4 in one-pot reactions of hydroquinone derivatives and dienes.

RESULTS AND DISCUSSION

As previously reported,[19] Pb_3O_4 is an efficient oxidant for the conversion of hydroquinones into corresponding quinones. We observed that 2,3-dicyanhydroquinone (**1**) could be quickly oxidized into quinone **2** quantitatively by Pb_3O_4 in THF/TFA (20:1) at room temperature (Scheme 1). Therefore, we decided to use Pb_3O_4 in one-pot reactions of hydroquinones and dienes to generate quinones *in situ*. In our initial investigation to choose a suitable solvent for one-pot reaction of 2,3-dicyanhydroquinone (**1**) and isoprene in the presence of Pb_3O_4 (Scheme 1), we compared toluene, CH_2Cl_2, and acetone. They gave product **3** in disappointing yields, probably because 2,3-dicyanhydroquinone (**1**) has poor solubility and Pb_3O_4 has low dispersal in these solvents. However, when the solvent was THF, the formation of product **3** was observed at a dramatic rate and in satisfactory yield.

To prove whether Pb_3O_4 can catalyze the subsequent Diels–Alder reaction in one pot, the reaction of quinone **2** and isoprene was conducted at room temperature under different conditions (Scheme 1, Table 1). The Diels–Alder reaction in pure THF took a long time and gave the product **3** in tiny yield (entry 1, Table 1). When THF/TFA was used, the rate and yield of the reaction improved somewhat (entries 2 and 3, Table 1). However, when treatment involved Pb_3O_4 in THF, it provided the



Scheme 1. Oxidation of 2,3-dicyanhydroquinone (**1**) and one-pot reaction of **1** and isoprene.

Table 1. Diels–Alder reaction between quinone **2** and isoprene under different conditions at rt

Entry	Reaction condition	Time (h)	Yield of **3** (%)[a]
1	THF	24	5
2	THF-TFA (33:1)	16	35
3	THF-TFA (20:1)	16	37
4	Pb_3O_4 (0.2 eq), THF	16	58
5	Pb_3O_4 (0.4 eq), THF	16	62
6	Pb_3O_4 (0.8 eq), THF	16	65
7	Pb_3O_4 (0.2 eq), THF-TFA (33:1)	5	78
8	Pb_3O_4 (0.2 eq), THF-TFA (20:1)	3	80
9	Pb_3O_4 (0.2 eq), THF-TFA (10:1)	3	80

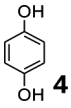
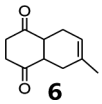
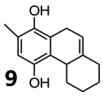
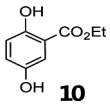
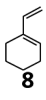
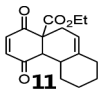
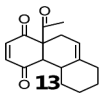
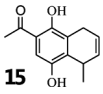
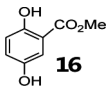
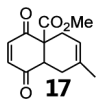
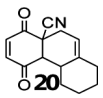
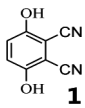
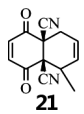
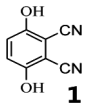
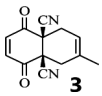
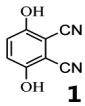
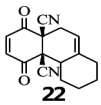
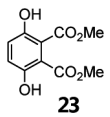
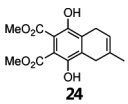
[a]Refers to yield of isolated product after chromatography.

product in medium yields (entries 4–6, Table 1). Interestingly, when the combined system of Pb_3O_4 and THF/TFA was employed, the product was obtained in good yields (entries 7–9, Table 1). The experiments clearly showed that both Pb_3O_4 and TFA can catalyze the Diels–Alder reaction of quinone **2** and isoprene, but Pb_3O_4 is more efficient than TFA. The best chemical yield and rate were obtained when both Pb_3O_4 and TFA were present in the system. Thus, taking into account the consumption of an equimole of Pb_3O_4 as oxidant for the generation of quinones and 0.2 equimoles of Pb_3O_4 as catalyst for the following Diels–Alder reaction, we decided to use 1.2 equimoles of Pb_3O_4 in a one-pot reaction in the presence of THF/TFA (20:1).

In the present procedure, the reaction was easy to carry out under the system of Pb_3O_4 (1.2 eq) in THF-TFA (20:1) at room temperature. A variety of hydroquinone derivatives and different dienes underwent the one pot reaction smoothly to afford corresponding functionalized carbocyclic compounds in medium to good yields (55%–80%) (Table 2). This one-pot method was also applicable to catechol derivative **25**, which directly gave the isomerized adduct **26** in excellent yield of 94% in 2.5 h (entry 12 in Table 2, Scheme 2). Some unstable resultant adducts were involved because of easy aromatization (entries 2, 5, and 11, Table 2). In these cases, steady-going aromatized products could be obtained directly after the one-pot reaction, followed by routine workup and purification on silica gel. However, the one-pot reaction of hydroquinone **4** and isoprene **5** gave the unstable adduct **27,** which was reduced without purification using Zn and HOAc[8] to give stable diketone **6** (entry 1 in Table 2, Scheme 3).

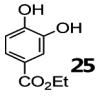
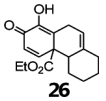
To our surprise, the one-pot reaction of 1-(2,5-dihydroxyphenyl) ethanone (**12**) and 1,3-pentadiene (**14**) gave product **15** (entry 5, Table 2). In comparison with the reaction of **12** and **8**, which gave product **13** (entry 4, Table 2), it is reasonable to assume that the cycloaddition had initially taken place at the acetyl-substituted double bond to give adduct **28** because of the extra-activation by acetyl group (Scheme 4). The formation of **15** may be through the 1,5-migration of the acetyl group[20] and aromatization of **30**. The mechanism of the 1,5-shift of acetyl has been described by Cooper and Sammes.[21] They proposed that acetyl was rearranged by a pathway involving prior enolization of one carbonyl group, followed by the 1,5-acetyl migration and next enolization of the remaining carbonyl group to

Table 2. One-pot reaction of hydroquinones and dienes under the system of Pb_3O_4 (1.2 eq) in THF-TFA (20:1) at rt

Entry	Hydroquinone	Diene	Product	Time (h)	Yield (%)[a]
1	 **4**	 **5**	 **6**	6	80
2	 **7**	 **8**	 **9**	7.5	64
3	 **10**	 **8**	 **11**	3	57
4	 **12**	 **8**	 **13**	3	65
5	 **12**	 **14**	 **15**	6	55
6	 **16**	 **5**	 **17**	3	61
7	 **18**	 **8**	 **20**	3	75
8	 **1**	 **14**	 **21**	3	75
9	 **1**	 **5**	 **3**	3	80
10	 **1**	 **8**	 **22**	3	80
11	 **23**	 **5**	 **24**	4	75

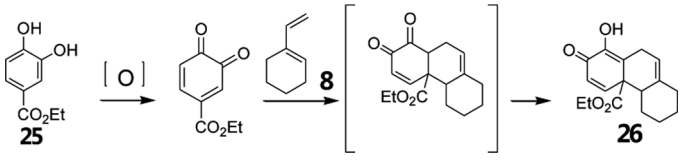
(*Continued*)

Table 2. Continued

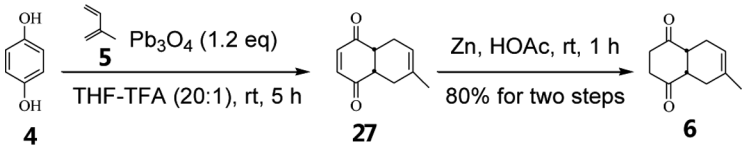
Entry	Hydroquinone	Diene	Product	Time (h)	Yield (%)[a]
12	 **25**	 **8**	 **26**	2.5	94

[a]Refers to yield of isolated product.

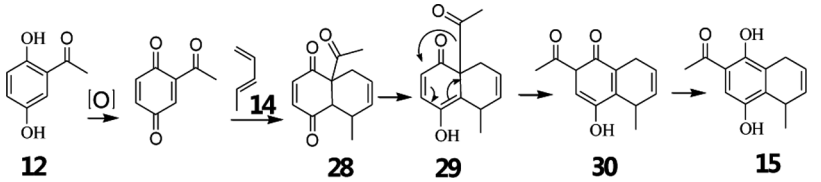
produce quinol **15** (Scheme 4). An alternative explanation for the formation of **15** was proposed as sequential reactions of retro-Diels–Alder/Diels–Alder/aromatization (Scheme 5). Although cycloaddition of 2-acetyl-1,4-benzoquinone with diene is known to favor addition across the 2,3 π-π bond to initially form adduct **28,** with the acetyl group occupying one of the angular positions, the reversibility of the Diels–Alder reaction and aromatization of less favorable adduct **31** can shift the equilibrium toward the formation of **15**. However, in comparison with the formation of adduct **13** (entry 4, Table 2), diene **8** is more sterically hindered than diene **14**, and it should be preferable to attack 2-acetyl-1,4-benzoquinone on the non substituted double bond than **14**, but only adduct **13** was obtained as an acetyl-substituted double-bond addition product. We therefore prefer the mechanism of 1,5-shift of acetyl to sequential reactions. No rearrangement of adduct **13** could be explained



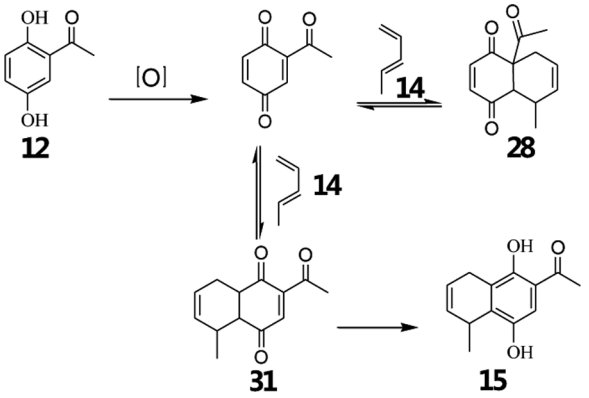
Scheme 2. One-pot reaction of catechol **25** and diene **8**.



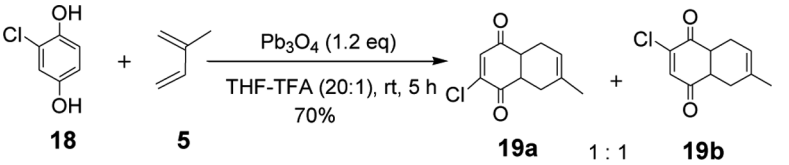
Scheme 3. One-pot reaction of **4** and **5** and reduction of adduct **27**.



Scheme 4. Proposed 1,5-acetyl shift pathway.



Scheme 5. Proposed mechanism of sequential reactions.



Scheme 6. One-pot reaction of **18** and **5**.

because the acetyl group migration depends on the substituents of diene.[21,22] Besides, the tricyclic compound **13** might be more stable than the bicyclical compound **28**. We tried to recognize some intermediates for the proposed mechanisms but failed.

In addition, it is notable that the complete regioselectivity was observed in adducts from one-pot reactions of electron-withdrawing group substituted hydroquinones and dienes. All the electron-withdrawing groups including carboxylate, acetyl, and nitrile activated the connected double bonds of corresponding quinones, and different dienes were added to these electron-deficient double bonds except for 2,3-dicarboxylate hydroquinone **23** (entry 11, Table 2) because of steric hinderance. Each reaction gave a single adduct from NMR. However, electron-donating groups such as methyl and chlorine caused the connected double bonds of corresponding quinones to be inactive, and the addition exclusively took place on the nonsubstituted double bonds. The one-pot reaction of 2-methylbenzene-1,4-diol **7** and vinylcyclohexene **8** gave the single aromatized product **9** (entry 2, Table 2). The regioselectivity is in agreement with the previous report by Stojanac and coworkers.[23] Nevertheless, hydroquinone **18** and isoprene **5** gave a 1:1 mixture of **19a** and **19b** from NMR, and these compounds were not able to be separated by flash chromatography (Scheme 6).

CONCLUSION

In summary, we have developed a synthetic application of one-pot reactions of hydroquinone derivatives and dienes in the presence of Pb_3O_4 and THF-TFA. In this transformation, cheap and readily available reagent Pb_3O_4 plays important roles not

only as an efficient oxidant for the generation of quinone derivatives *in situ*, but also as an excellent catalyst for the following Diels–Alder reaction. The dual roles of Pb_3O_4 in one pot make the reaction efficient and easy to carry out. Using this method, different hydroquinone derivatives and dienes can be efficiently converted into six-membered functionalized carbocyclic compounds in medium to excellent yields in a short reaction time at room temperature.

EXPERIMENTAL

General Methods

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker AV-300 spectrometer with tetramethysilane (TMS) as an internal standard. The chemical shifts (δ) are given in parts per million (ppm), and the coupling constants (*J*) are in hertz (Hz). Electospray ionization–high-resolution mass spectoscopic (ESI-HRMS) spectra were recorded on a BioTOF Q spectrometer. Melting points were determined on a X-4 digital display micromelting-point apparatus and were uncorrected. Unless otherwise noted, all reagents were obtained from commercial suppliers and were used without further purification. Organic solvents used were dried by standard methods when necessary. All reactions were monitored by thin-layer chromatography (TLC) with Haiyang GF254 silica-gel plates. Flash column chromatography was carried out using 200 to 300-mesh silica gel at increased pressure.

Typical Procedure for One-Pot Reaction of Hydroquinones and Dienes: 1,4,4a,5,8,8a-Hexahydro-6-methyl-1,4-dioxonaphthalene-4a,8a-dicarbonitrile (3)

Pb_3O_4 (605 mg, 0.88 mmol), F_3CCO_2H (0.25 mL), and isoprene (3.0 mmol) were added to a solution of 2,3-dicyanhydroquinone **1** (100 mg, 0.63 mmol) in THF (5 mL). The reaction mixture was stirred at rt for 3 h and then filtered. The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography (petroleum ether/ethylacetate 5:1) to provide compound **3** (106 mg, 80%) as white crystals. mp. 140–142 °C; ^{1}H NMR (CD_3COCD_3) δ 7.19 (s, 2H), 5.54 (brs, 1H), 2.94–3.04 (m, 2H), 2.65–2.77 (m, 2H), 1.78 (s, 3H); ^{13}C NMR (CD_3COCD_3) δ 187.5, 187.1, 139.1, 139.0, 130.9, 116.8, 116.5 (×2), 52.7, 52.2, 33.4, 30.1, 30.0; HRMS (ESI) calcd. for $[M + Na]^+$ $C_{13}H_{10}N_2O_2Na$: 249.0634; found: 249.0652.

Spectroscopic Data for Compounds 11, 13, 15, 20, 21, 22, and 26

Ethyl 1,2,3,4,4a,4b,5,8,8a,9-decahydro-5,8dioxophenanthrene-8a-carboxylate (11). Yellow oil; ^{1}H NMR ($CDCl_3$) δ 6.75 (dd, 2H, $J = 10.5$ Hz, $J = 10.2$ Hz), 5.32 (brs, 1H), 4.29–4.22 (m, 2H), 3.76–3.74 (m, 1H), 2.98 (d, 1H, $J = 12.9$ Hz), 2.72 (m, 1H), 2.19 (m, 1H), 2.02–1.97 (m, 2H), 1.75 (d, 2H, $J = 11.7$ Hz), 1.43–1.36 (m, 2H), 1.29–1.27 (m, 2H), 1.24 (m, 3H); ^{13}C NMR ($CDCl_3$)

δ 197.9, 197.3, 169.8, 141.2, 139.7, 139.0, 114.7, 63.5, 62.3, 47.1, 42.1, 36.5, 33.4, 28.4, 27.2, 20.5, 14.1. HRMS (ESI) calcd. for $[M]^+$ $C_{17}H_{20}O_4^+$: 289.1395; found: 289.1364.

10a-Acetyl-5,6,7,8,10,10a-hexahydrophenanthrene-1,4(4aH,4bH)-dione (13). Yellow oil; ^{1}H NMR ($CDCl_3$) δ 6.83 (d, 1H, $J = 9.9$ Hz), 6.60 (d, 1H, $J = 10.2$ Hz), 5.29 (brs, 1H), 3.72 (d, 1H, $J = 6.7$ Hz), 2.87–2.71 (m, 2H), 2.32 (s, 3H), 2.23–2.18 (m, 1H), 2.03–1.98 (m, 2H), 1.83–1.73 (m, 3H), 1.44–1.35 (m, 2H), 1.24–1.20 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 204.5, 200.0, 198.1, 141.4, 139.3, 137.7, 115.5, 67.9, 45.7, 42.6, 38.7, 36.3, 28.6, 27.4, 19.7; HRMS m/z (ESI) calcd. for $[M]^+$ $C_{16}H_{18}O_3^+$: 259.1289; found: 259.1275.

1-(1,4-Dihydro-5,8-dihydroxy-1-methylnaphthalen-6-yl)ethanone (15). Yellow crystals, mp 162–164 °C; ^{1}H NMR ($CDCl_3$) δ 7.00 (s, 1H), 5.97–5.86 (m, 2H), 3.71 (m, 1H), 3.40–3.14 (m, 2H), 2.57 (s, 3H), 1.26 (d, 3H, $J = 6.6$ Hz); ^{13}C NMR ($CDCl_3$) δ 203.8, 155.0, 144.7, 132.3, 131.6, 130.8, 120.9, 116.6, 111.8, 29.0, 26.7, 25.0, 21.6; HRMS (ESI) calcd. for $[M - H]^+$ $C_{13}H_{13}O_3$: 217.0859; found: 217.0867.

1,2,3,4,4a,4b,5,8,8a,9-Decahydro-5,8-dioxophenanthrene-8a-carbonitrile (20). White crystals; mp 215–217 °C. ^{1}H NMR ($CDCl_3$) δ 6.98 (s, 2H), 5.45 (brs, 1H), 3.01 (m, 1H), 2.85–2.67 (m, 2H), 2.37–2.32 (m, 1H), 1.87–1.77 (m, 2H), 1.59 (d, 2H, $J = 10.1$ Hz), 1.36–1.23 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 187.6, 185.2, 140.2, 138.9, 136.6, 115.9, 113.6, 44.5, 34.5, 31.6, 27.5, 27.2, 26.8, 26.5, 26.0.

1,4,4a,5,8,8a-Hexahydro-5-methyl-1,4-dioxonaphthalene-4a,8a-dicarbonitrile (21). White crystals; mp 140-142 °C. ^{1}H NMR (CD_3COCD_3) δ 7.15 (s, 2H), 5.73–5.85 (m, 2H), 2.79–3.12 (m, 3H), 1.42 (d, 3H, $J = 7.4$ Hz); ^{13}C NMR (CD_3COCD_3) δ 188.3, 187.2, 140.6, 138.4, 129.5, 121.4, 117.0, 116.4, 55.1, 54.9, 36.5, 30.8, 17.1; HRMS m/z (ESI) calcd. for $[M + Na]^+$ $C_{13}H_{10}N_2O_2Na^+$: 249.0634; found: 249.0631.

1,4,4a,4b,5,6,7,8,10,10a-Decahydro-1,4-dioxophenanthrene-4a,10a-dicarbonitrile (22). White crystals; mp 173–175 °C. ^{1}H NMR (CD_3COCD_3) δ 7.30 (s, 2H), 5.52 (brs, 1H), 2.71–2.14 (m, 3H), 1.82–1.83 (m, 2H), 1.25–1.65 (m, 6H); ^{13}C NMR (CD_3COCD_3) δ 188.8, 186.6, 141.5, 140.1, 137.4, 117.4, 116.9, 114.5, 56.8, 44.7, 36.0, 32.6, 29.8, 28.5, 28.0, 27.2; HRMS (ESI) calcd. for $[M + Na]^+$ $C_{16}H_{14}N_2O_2Na$: 289.0947; found: 298.0954.

Ethyl 2,4a,4b,5,6,7,8,10-octahydro-1-hydroxy-2-oxophenanthrene-4a-carboxylate (26). Yellow oil; ^{1}H NMR ($CDCl_3$) δ 6.89 (d, 1H, $J = 9$ Hz), 6.52 (d, 1H, $J = 9$ Hz), 5.34 (brs, 1H), 4.15 (q, 2H, $J = 10.15$), 3.39–3.14 (m, 2H), 2.97–2.90 (m, 1H), 2.25–2.06 (m, 2H), 1.84–1.73 (m, 4H), 1.50–1.25 (m, 2H), 1.20 (t, 3H); ^{13}C NMR ($CDCl_3$) 180.6, 170.6, 149.9, 144.4, 140.8, 128.2, 125.6, 114.4, 62.4, 56.3, 48.7, 36.5, 30.2, 29.7, 26.7, 25.5, 14.1; HRMS (ESI) calcd. for $[M + Na]^+$ $C_{17}H_{20}O_4Na$: 311.1253; found: 311.1262.

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REFERENCES

1. Takao, K. I.; Munakata, R.; Tadano, K. I. Recent advances in natural product synthesis by using intramolecular Diels–Alder reactions. *Chem. Rev.* **2005**, *105*, 4779–4807.
2. Johnson, T. W.; Corey, E. J. Enantiospecific synthesis of the proposed structure of the antitubercular marine diterpenoid pseudopteroxazole: Revision of stereochemistry. *J. Am. Chem. Soc.* **2001**, *123*, 4475–4479.
3. Kumar, A. Salt effects on Diels–Alder reaction kinetics. *Chem. Rev.* **2001**, *101*, 1–20.
4. García Ruano, J. L.; Almparte, C. Synthesis and dienophilic behavior of (*S*)-2-cyano-3-(*p*-tolylsulfinyl)-1,4-benzoquinone. *J. Org. Chem.* **2004**, *69*, 1405–1408.
5. Finley, K. T. *Kirk–Othmer Encyclopedia of Chemical Technology*; Wiley-Interscience: New York, 1982; vol. 19, p. 572.
6. Naruta, Y.; Maruyama, K. *The Chemistry of Quinonoid Compounds*; Wiley-Interscience: New York, 1988; vol 2, p. 241.
7. Chiba, K.; Tada, M. Diels–Alder reaction of quinones generated in situ by electrochemical oxidation in lithium perchlorate–nitromethane. *J. Chem. Soc., Chem. Commun.* **1994**, 2485–2486.
8. Kraus, G. A.; Taschner, M. J. Model studies for the synthesis of quassinoids, 1: Construction of the BCE ring system. *J. Org. Chem.* **1980**, *45*, 1175–1176.
9. White, J. D.; Cutshall, N. S.; Kim, T. S.; Shin, H. Total synthesis of (±)-euonyminol, the sesquiterpenoid nucleus of cathedulin K-19, via an epoxide cascade cyclization. *J. Am. Chem. Soc.* **1995**, *117*, 9780–9781.
10. Rani, A.; Kumar, B.; Suryawanshi, S. N.; Bhakuni, D. S. Diels–Alder reaction of in-situ generated *p*-benzoquinones with isoprenoidal dienol acetate: Novel synthesis of 2-isoprenoidal naphthalene-5,8-quinols. *Tetrahedron Lett.* **1996**, *37*, 8037–8040.
11. Sasaki, M.; Noguchi, T.; Tachibana, K. Intramolecular radical cyclization ring-closing metathesis approach to fused polycyclic ethers: Convergent synthesis and conformational analysis of the (E)FGH ring system of ciguatoxin. *J. Org. Chem.* **2002**, *17*, 3301–3310.
12. Yoshida, N.; Konno, H.; Kamikubo, T.; Takahashi, M.; Ogasawara, K. Preparation of a synthetic equivalent of chiral methyl 2,5-dihydroxycyclohexane-1,4-dienecarboxylate. *Tetrahedron: Asymmetry* **1999**, *10*, 3849–3857.
13. White, J. D. The chemistry of khat: An approach to the synthesis of euonyminol. *Pure Appl. Chem.* **1994**, *66*, 2183–2188.
14. Mukopadhyay, A.; Ali, S. M.; Husain, M.; Suryawanshi, S. N.; Bhakuni, D. S. Diels–Alder reaction of in-situ generated 2-methoxycarbonyl-p-quinone with D-glucose based dienes: A new approach to forskolin. *Tetrahedron Lett.* **1989**, *30*, 1853–1856.
15. Valderrama, J. A.; Fariab, F.; Paredesb, M. C. Studies on quinones, XVIII: Synthesis of Diels–Alder adducts of activated quinones with (E)-1-trimethylsilyloxybuta-1,3-diene. *Synth Commun.* **1989**, *19*, 3301–3312.
16. Kurosu, M.; Marcin, L. R.; Grinsteniner, T. J.; Kishi, Y. Total synthesis of (±)-batrachotoxinin A. *J. Am. Chem. Soc.* **1998**, *120*, 6627–6628.
17. Hsu, D.-S.; Liao, C.-C. Total syntheses of sesterpenic acids: Refuted (±)-bilosespenes A and B. *Org. Lett.* **2003**, *5*, 4741–4743.
18. DesMarteau, D. D.; Donadelli, A.; Montanari, V.; Petrov, V. A.; Resnati, G. Mild and selective oxyfunctionalization of hydrocarbons by perfluorodialkyloxaziridines. *J. Am. Chem. Soc.* **1993**, *115*, 4897–4898.
19. Adams, R.; Eilar, K. R. Quinone imides, V: Aluminum chloride–catalyzed arylations of *p*-quinone dibenzenesulfonimides. *J. Am. Chem. Soc.* **1951**, *73*, 1149–1152.

20. Robins, P. A.; Walker, J. Studies of the Diels–Alder reaction, part I: The reaction between 1-vinylcyclohex-1-ene and benzoquinone, and the reduction of 2,9(14)-decahydro-1,4-diketophenanthrene. *J. Chem. Soc.* **1952**, 642–649.
21. Cooper, S. C.; Sammes, P. G. (1,5)-Acetyl shifts in cycloadducts derived from 2-acetyl-1,4-benzoquinones. *J. Chem. Soc., Chem. Commun.* **1980**, 633–634.
22. Cooper, S. C.; Sammes, P. G. Acyl rearrangements in acylbenzoquinone cycloadducts. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2407–2413.
23. Stojanac, Z.; Dickinson, R. A.; Stojanac, N.; Woznow, R. J.; Valenta, Z. Catalyzed orientation reversals in Diels–Alder reactions. *Can. J. Chem.* **1975**, *53*, 616–618.