A New Synthetic Route to 2*H*-Benzo[*g*]chromene-5,10-diones Involving Ring Closing Metathesis

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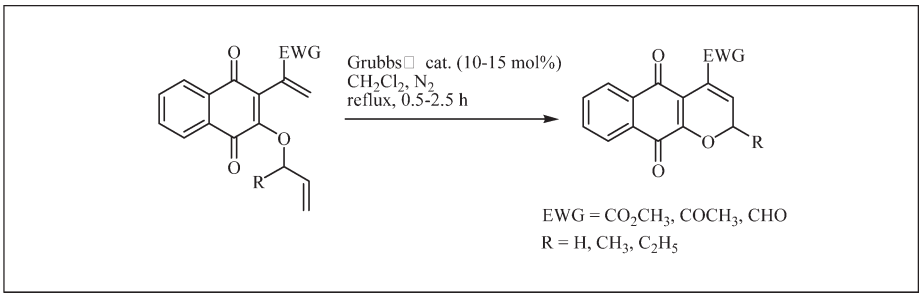

A simple synthesis of several 2*H*-benzo[*g*]chromene-5,10-diones *via* the ring closing metathesis reaction of prerequisite bisolefins, prepared from the α-vinylnaphthoquinones, is described.

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INTRODUCTION

Heterocyclic compounds sharing quinonoid constituents are wide spread in nature and exhibit a broad range of biological activities [1]. Among them, pyranonaphthoquinones with some famous examples such as α-lapachone [2], β-lapachone [3], pentalongin [4], and pyranokunthone A and B [5] have attracted considerable synthetic attention because of their interesting pharmacological actions (Fig. 1) [6]. Specifically, lapachone derivatives and lapachol-type naphthoquinone compounds obtained from the bark of the lapacho tree (*Tabebuia avellanedae*) from Central and South America [2a] are known to display antitumor [7], anti-inflammatory [8], antifungal [9], antimalarial [10], and antibacterial [11] properties. Owing to the remarkable biological activities of lapachones, there has been much interest in the development of easy and simple methodologies to synthesize lapachone derivatives. Pyranonaphthoquinones including lapachone derivatives are most typically produced through the alkylation of 2-hydroxy-1,4-naphthoquinone followed by cyclization [12]. Recently, Lee and coworkers reported one-pot synthesis of pyranonaphthoquinone derivatives starting from 2-hydroxy-1,4-naphthoquinone with a variety of α,β-unsaturated aldehydes by a tandem Knoevenagel-electrocyclic reaction [6b].

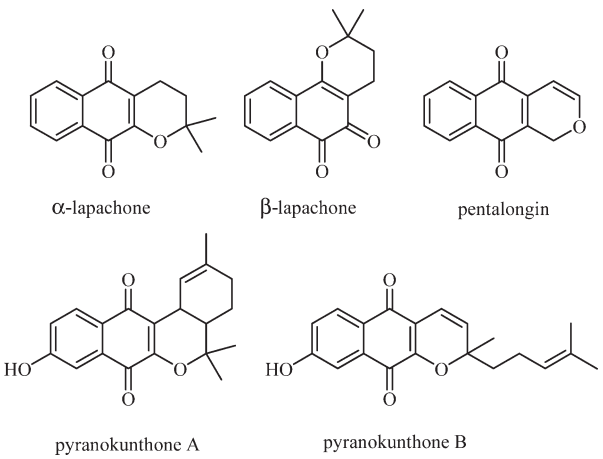
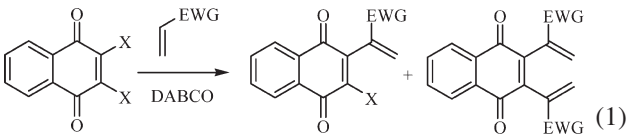


Figure 1. Naturally occuring pyranonaphthoquinones.

The Morita–Baylis–Hillman (MBH) reaction has been one of the most intensively studied carbon–carbon bond-forming reactions in organic synthesis [13]. Many efforts have been focused on the extension of useful electrophiles in the MBH reaction [14] besides aldehydes, which are the traditional source of electrophiles. In our earlier articles [15], we have demonstrated that 1,4-diazabicyclo[2,2,2]octane (DABCO)-assisted enolate anions of several activated olefins were useful in substitution reactions of 2,3-dihalo-1,4-naphthoquinones, leading to the formation of α-vinylnaphthoquinones and divinylnaphthoquinones under MBH reaction conditions [eq. (1)]. We also reported that these α-vinylated products were useful substrates for the synthesis of 4-chloro-5-hydroxy-1*H*-benzo[*g*]indoles in the presence of primary amines *via* the Nenitzescu indole synthetic route [15b].

As a continuation of our interest in the syntheses of heterocyclic compounds with possible biological

activities using MBH chemistry [16], we now report a new synthetic pathway to 2*H*-benzo[*g*]chromenes from α-vinylnaphthoquinones using Grubbs second generation catalyst for the ring closing step [4b,17]. Although various 2*H*-benzo[*g*]chromenes were prepared earlier [6], to our knowledge, no synthetic example of 4-acyl-2*H*-benzo[*g*]chromene derivatives has been previously reported.



1 **2**

X = Cl, Br

EWG = CO_2CH_3, $COCH_3$, CHO

RESULTS AND DISCUSSION

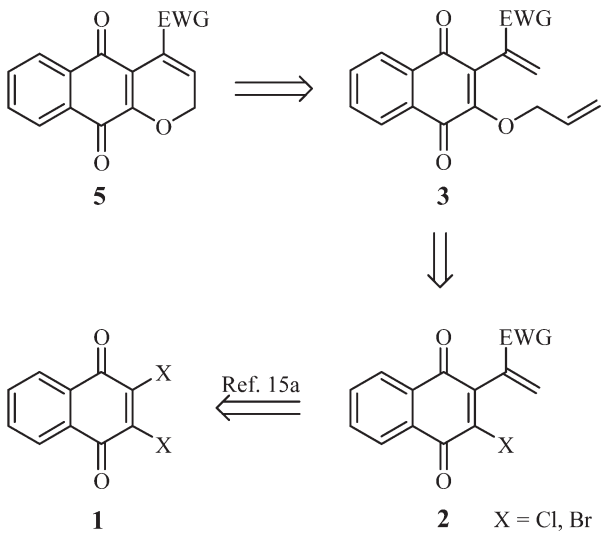
We hypothesized that a pyran ring might be obtained from the ring closing metathesis (RCM) reaction of an appropriate bisolefin precursor **3** as shown in Scheme 1. The bisolefin **3** would result from the nucleophilic substitution reaction of a halogen atom on the known α-vinylnaphthoquinone **2** into allyl alkoxide. Accordingly, the known α-vinylnaphthoquinone **2a** was first synthesized as the stating material under MBH reaction condition [15a]. Treatment of **2a** with a suspension of 1.2 equivalent of allyl alcohol and sodium hydride in *N*,*N*-dimethylformamide at room temperature afforded disubstituted naphthoquinone **3a** in a moderate yield (47%) (Scheme 2). With this precursor **3a** in hand, we undertook the RCM reaction using 1 mol % of Grubbs second generation catalyst in refluxing dichloromethane (0.01*M*) under nitrogen atmosphere. Unfortunately, the reaction did not proceed at all and no trace of ring closed product was detected on thin layer chromatography (TLC). However, to our delight, an increased amount of catalyst (5 mol %) allowed the formation of the desired RCM product **5a** in a moderate yield (56%) after 2 h, without dimerized compounds. Moreover, the yield improved to 74% and the reaction time was shortened to 30 min with increased amount of catalyst (10 mol %).

We then aimed to extend the utility of this RCM reaction; therefore, we investigated further reactions of other types of bisolefins with various allyl alcohols. At first, bisolefins **3b** and **3c**, which have more steric hinderance at the allylic position than **3a**, were prepared in 78 and 54% yields, respectively, and RCM reactions of **3b** and **3c** furnished cyclized products **5b** (63%) and **5c** (80%) in good yields after 2 h with 10 mol % of catalyst. In these cases, we observed that the steric effect of allyl alcohol moiety required greater loading of catalyst and more reaction time to complete the RCM reaction [18].

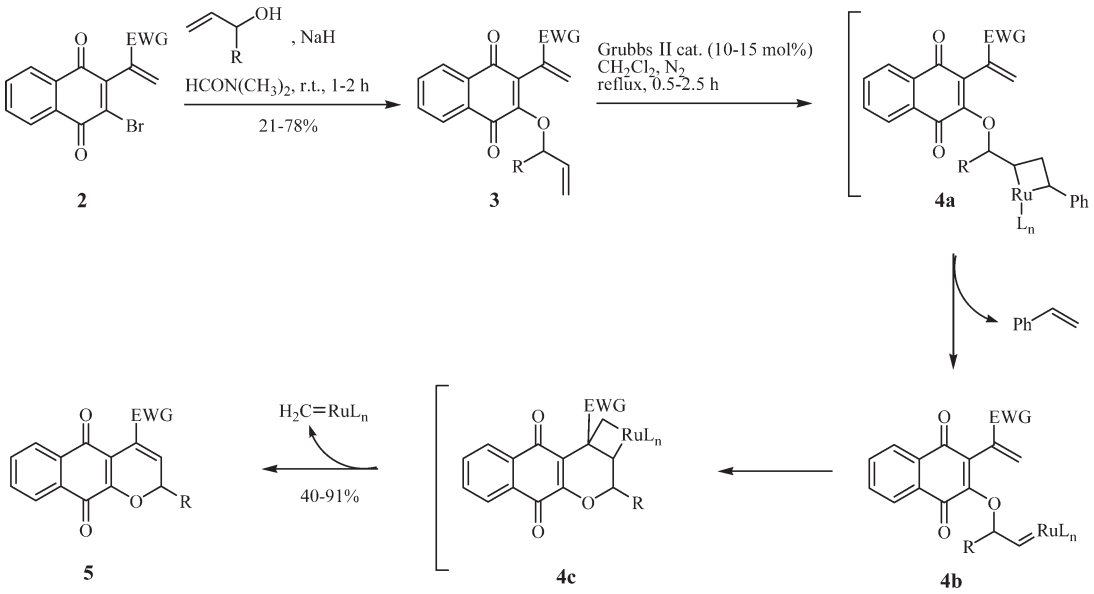
We next examined the reactivity of other electron-deficient olefin systems such as acetyl and formyl groups. The bisolefins **3d-f** were prepared under similar reaction conditions from **2b** [15a] in 56–69% yields. Generally, the RCM reactions of **3d-f** required more catalyst and longer reaction times as shown in Table 1. In the case of **3d**, 5 mol % loading of catalyst was not sufficient to obtain the desired product **5d**. The bisolefin **3d** was transformed into the desired 2*H*-benzo[*g*]chromene **5d** in an excellent yield (91%) using 10 mol % of catalyst in refluxing dichloromethane (0.01*M*) after 40 min. Also, addition of 15 mol % catalyst led to successful formation of **5e** and **5f** in acceptable yields (41 and 66%) from the bisolefin **3e** and **3f**, respectively [19]. Additionally, the reactions of **2c** [15a] with 3-buten-2-ol and 1-penten-3-ol afforded the corresponding bisolefin **3g** and **3h** in low yields (21 and 31%), respectively. These relatively poor yields may arise from the high reactivity of *O*-nucleophiles toward the aldehyde group. On exposure of these bisolefins to RCM reaction conditions (15 mol % of catalyst), the RCM products **5g** [20] and **5h** were obtained in 40 and 42% yields, respectively. Efforts to obtain more steric secondary and tertiary alcohols such as α-vinylbenzyl alcohol, 1,4-pentadien-3-ol, and 2-methyl-3-buten-2-ol from the substitution reaction of **2a** were unsuccessful under various reaction conditions.

The mechanism for the formation of **5** is proposed in Scheme 2. The ruthenium carbene complex adds to one of the olefins as a [2 + 2] cycloaddition to give a four-membered ring **4a** with the metal atom in the ring. In this instance, the same reaction happens in reverse, either to give the starting materials or, by cleavage of the other two bonds, a new carbene complex **4b** and

Scheme 1



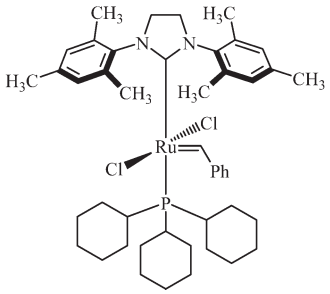
Scheme 2



2 **3** **4a** **4b** **4c** **5**

2	EWG	**3, 5**	R	EWG
a	CO_2CH_3	**a**	H	CO_2CH_3
		b	CH_3	CO_2CH_3
		c	C_2H_5	CO_2CH_3
b	$COCH_3$	**d**	H	$COCH_3$
		e	CH_3	$COCH_3$
		f	C_2H_5	$COCH_3$
c	CHO	**g**	CH_3	CHO
		h	C_2H_5	CHO

Grubbs II catalyst



styrene. Next, an intramolecular [2 + 2] cycloaddition joins up the six-member ring and produces a second metalla cyclobutane **4c**, which decomposes in the same way as the first one to give a third carbene complex and the product **5**.

The structure of **5** was established on the basis of spectroscopic data. The ^{1}H NMR spectra of both **5a** and **5d** showed disappearance of terminal alkenic protons. In the ^{1}H NMR of **5a**, the signal from the two C2 methylene protons appeared at δ 5.03 as a doublet (J = 4.1 Hz), and C3 vinylic proton appeared at δ 6.34 as a triplet (J = 4.1 Hz). In the case of **5d**, the signal corresponding to the two C2 methylene protons was observed at δ 5.05 as a doublet (J = 4.0 Hz), and C3 vinylic proton appeared at δ 6.10 as a triplet (J = 4.0 Hz). The ^{13}C NMR spectra of **5a** and **5d** each exhibited fifteen absorption peaks, including a signal at δ 166.3 for the ester carbonyl group of **5a** and a signal at δ 199.2 for the acetyl carbonyl group of **5d**.

CONCLUSION

In summary, we have synthesized several 2*H*-benzo[*g*]chromene derivatives with electron-withdrawing substituents at C4 position *via* RCM reaction from the easily accessible α-vinylnaphthoquinones. However, couplings

Table 1

4-Acyl-2*H*-benzo[*g*]chromene-5,10-diones **5**.

Bisolefin	Catalyst (mol %)	Time[a]	Product	Yield (%)
3a	5/10	2 h/30 min	**5a**	56/74
3b	10	2 h	**5b**	63
3c	10	2 h	**5c**	80
3d	10	40 min	**5d**	91
3e	15	2 h 30 min	**5e**	41
3f	15	2 h 30 min	**5f**	66
3g	15	1 h	**5g**	40
3h	15	1 h 30 min	**5h**	42

[a] Reflux temperature.

between α-vinylnaphthoquinones and some steric allyl alcohols to produce bisolefin precursors remain limited.

EXPERIMENTAL

Silica gel 60 (70-230 mesh ASTM) used for column chromatography was supplied by E. Merck. Analytical TLC was performed on Merck silica gel 60 F_{254} TLC plates. Melting points were measured by an Electrothermal melting point apparatus and were uncorrected. Microanalysis was obtained using a Thermo Electron Corporation Flash EA 1112 element analyzer. Infrared spectra were recorded with a Nicolet Magna 550 FTIR spectrometer. Electron impact (EI) mass and high resolution mass spectra were obtained using a Jeol SX 102 mass spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were measured on a Gemini 300 spectrometer using deuteriochloroform. All chemical shifts are reported in parts per million relative to tetramethylsilane. The coupling constants (*J*) are expressed in Hertz.

Allyl alcohol, 3-buten-2-ol, 1-penten-3-ol, 1,4-pentadien-3-ol, 2-methyl-3-buten-2-ol, α-vinylbenzyl alcohol, and Grubbs second-generation catalyst were obtained from Aldrich and used without further purification. The known α-vinylnaphthoquinones **2a**, **2b**, and **2c** were prepared according to the published procedures [15a].

Methyl 2-[3-(allyloxy)-1,4-dihydro-1,4-dioxonaphthalen-2-yl]acrylate (3a). To a stirred suspension of ally alcohol (0.16 mL, 2.4 mmol) and sodium hydride (58 mg, 2.4 mmol) in *N*,*N*-dimethylformamide (5 mL) was added **2a** (642 mg, 2 mmol) at room temperature. After stirring for 2 h, the reaction mixture was diluted with water (40 mL) and extracted with dichloromethane (3 × 30 mL). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was evaporated *in vacuo*. The resulting mixture was chromatographed on silica gel eluting with hexane/ethyl acetate (6:1) to produce **3a** (280 mg, 47%) as an oil; IR (neat): 1727, 1673, 1657, 1595, 1576, 1335 cm^{-1}; ^{1}H NMR (deuteriochloroform): δ 3.77 (s, 3H), 4.91 (d, *J* = 5.5 Hz, 1H), 5.24 (d, *J* = 10.4 Hz, 1H), 5.35 (d, *J* = 17.1 Hz, 1H), 5.88 (s, 1H), 5.97 (ddd, *J* = 17.1, 10.4 and 5.5 Hz, 1H), 6.69 (s, 1H), 7.72–7.75 (m, 2H), 8.08–8.11 (m, 2H). ^{13}C NMR (deuteriochloroform): δ 52.3, 74.3, 118.7, 126.3, 126.5, 129.2, 131.3, 131.5, 131.6, 131.7, 132.9, 133.5, 134.2, 156.6, 166.1, 181.6, 183.7; *Anal*. Calcd. for $C_{17}H_{14}O_5$: C, 68.45; H, 4.73. Found: C, 68.27; H, 4.82.

Methyl 2-[3-(but-3-en-2-yloxy)-1,4-dihydro-1,4-dioxonaphthalen-2-yl]acrylate (3b). A mixture of 3-buten-2-ol (0.21 mL, 2.4 mmol), sodium hydride (58 mg, 2.4 mmol), and **2a** (642 mg, 2 mmol) in *N*,*N*-dimethylformamide (5 mL) was stirred at room temperature for 2 h. The work-up procedure was the same as described earlier to produce **3b** (487 mg, 78%) as an oil; IR (neat): 1728, 1673, 1657, 1596, 1576, 1437 cm^{-1}; ^{1}H NMR (deuteriochloroform): δ 1.41 (d, *J* = 6.4 Hz, 3H), 3.76 (s, 3H), 5.10 (d, *J* = 10.1 Hz, 1H), 5.19 (d, *J* = 17.4 Hz, 1H), 5.48 (qd, *J* = 7.0 and 6.4 Hz, 1H), 5.82 (ddd, *J* = 17.4, 10.1, and 7.0 Hz, 1H), 5.87 (s, 1H), 6.67 (s, 1H), 7.71–7.74 (m, 2H), 8.06–8.10 (m, 2H); ^{13}C NMR (deuteriochloroform): δ 21.4, 52.2, 80.8, 117.5, 126.3, 126.5, 128.9, 130.9, 131.5, 131.7, 131.8, 133.4, 134.1, 138.3, 156.3, 166.2, 181.9, 183.8; *Anal*. Calcd. for $C_{18}H_{16}O_5$: C, 69.22; H, 5.16. Found: C, 69.44; H, 5.23.

Methyl 2-[1,4-dihydro-1,4-dioxo-3-(pent-1-en-3-yloxy)-naphthalene-2-yl]acrylate (3c). A mixture of 1-penten-3-ol (0.25 mL, 2.4 mmol), sodium hydride (58 mg, 2.4 mmol) and **2a** (642 mg, 2 mmol) in *N*,*N*-dimethylformamide (5 mL) was stirred at room temperature for 2 h. The work-up procedure was the same as described earlier to produce **3c** (352 mg, 54%) as an oil; IR (neat): 1728, 1672, 1656, 1595, 1575, 1436 cm^{-1}; ^{1}H NMR (deuteriochloroform): δ 0.94 (t, *J* = 7.6 Hz, 3H), 1.59–1.73 (m, 1H), 1.76–1.87 (m, 1H), 3.76 (s, 3H), 5.15 (d, *J* = 10.1 Hz, 1H), 5.17 (d, *J* = 17.1 Hz, 1H), 5.31 (td, *J* = 7.9 and 7.3 Hz, 1H), 5.72 (ddd, *J* = 17.1, 10.1, and 7.9 Hz, 1H), 5.87 (s, 1H), 6.68 (s, 1H), 7.69–7.76 (m, 2H), 8.05–8.09 (m, 2H); ^{13}C NMR (deuteriochloroform): δ 9.3, 28.4, 52.2, 85.8, 119.0, 126.3, 126.5, 127.8, 130.7, 131.5, 131.7, 131.8, 133.4, 134.0, 136.8, 156.5, 166.2, 181.9, 183.8; *Anal*. Calcd. for $C_{19}H_{18}O_5$: C, 69.93; H, 5.56. Found: C, 69.69; H, 5.44.

3-(Allyloxy)-2-(but-3-en-2-one-3-yl)naphthalene-1,4-dione (3d). A mixture of allyl alcohol (0.16 mL, 2.4 mmol), sodium hydride (58 mg, 2.4 mmol), and **2b** (610 mg, 2 mmol) in *N*,*N*-dimethylformamide (5 mL) was stirred at room temperature for 2 h. The work-up procedure was the same as described earlier to produce **3d** (288 mg, 51%) as an oil; IR (neat): 1673, 1654, 1594, 1576, 1364, 1333 cm^{-1}; ^{1}H NMR (deuteriochloroform): δ 2.45 (s, 3H), 4.86 (d, *J* = 5.8 Hz, 1H), 5.23 (d, *J* = 10.4 Hz, 1H), 5.33 (d, *J* = 17.1 Hz, 1H), 5.94 (ddd, *J* = 17.1, 10.4 and 5.8 Hz, 1H), 6.00 (s, 1H), 6.48 (s, 1H), 7.70–7.76 (m, 2H), 8.05–8.09 (m, 2H); ^{13}C NMR (deuteriochloroform): δ 26.1, 74.3, 118.8, 126.3, 126.5, 129.7, 130.3, 131.4, 131.7, 132.9, 133.5, 134.1, 140.5, 156.9, 181.5, 183.8, 197.8; *Anal*. Calcd. for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00. Found: C, 72.48; H, 5.23.

3-(But-3-en-2-yloxy)-2-(but-3-en-2-one-3-yl)naphthalene-1,4-dione (3e). A mixture of 3-buten-2-ol (0.21 mL, 2.4 mmol), sodium hydride (58 mg, 2.4 mmol) and **2b** (610 mg, 2 mmol) in *N*,*N*-dimethylformamide (5 mL) was stirred at room temperature for 2 h. The work-up procedure was the same as described earlier to produce **3e** (397 mg, 67%) as an oil; IR (neat): 1673, 1652, 1595, 1334, 1254 cm^{-1}; ^{1}H NMR (deuteriochloroform): δ 1.39 (d, *J* = 6.4 Hz, 3H), 2.44 (s, 1H), 5.11 (d, *J* = 10.4 Hz, 1H), 5.18 (d, *J* = 17.4 Hz, 1H), 5.45 (qd, *J* = 7.0 and 6.4 Hz, 1H), 5.80 (ddd, *J* = 17.4, 10.4, and 7.0 Hz, 1H), 5.97 (s, 1H), 6.45 (s, 1H), 7.69–7.75 (m, 2H), 8.04–8.08 (m, 2H); ^{13}C NMR (deuteriochloroform): δ 21.3, 26.3, 80.8, 117.6, 126.3, 126.5, 129.5, 131.4, 131.7, 132.1, 133.4, 134.0, 138.3, 140.6, 156.5, 181.8, 183.9, 197.9; *Anal*. Calcd. for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.72; H, 5.28.

2-(But-3-en-2-one-3-yl)-3-(pent-1-en-3-yloxy)naphthalene-1,4-dione (3f). A mixture of 1-penten-3-ol (0.25 mL, 2.4 mmol), sodium hydride (58 mg, 2.4 mmol), and **2b** (610 mg, 2 mmol) in *N*,*N*-dimethylformamide (5 mL) was stirred at room temperature for 2 h. The work-up procedure was the same as described earlier to produce **3f** (428 mg, 69%) as an oil; IR (neat): 1673, 1656, 1595, 1573, 1334, 1293 cm^{-1}; ^{1}H NMR (deuteriochloroform): δ 0.93 (t, *J* = 7.3 Hz, 3H), 1.40–1.71 (m, 1H), 1.73–1.85 (m, 1H), 2.43 (s, 3H), 5.15 (d, *J* = 10.4 Hz, 1H), 5.17 (d, *J* = 17.1 Hz, 1H), 5.31 (td, *J* = 7.9 and 7.0 Hz, 1H), 5.7 (ddd, *J* = 17.1, 10.4, and 7.9 Hz, 1H), 5.96 (s, 1H), 6.45 (s, 1H), 7.68–7.74 (m, 2H), 8.03–8.07 (m, 2H); ^{13}C NMR (deuteriochloroform): δ 9.3, 26.3, 28.4, 85.8, 119.1, 126.3, 126.4, 129.4, 131.5, 131.7, 131.8, 133.4, 134.0, 136.8, 140.7, 156.7, 181.8, 183.9, 197.9; *Anal*. Calcd. for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.40; H, 5.66.

2-[3-(But-3-en-2-yloxy)-1,4-dihydro-1,4-dioxonaphthalen-2-yl]acrylaldehyde (3g). A mixture of 3-buten-2-ol (0.21 mL, 2.4 mmol), sodium hydride (58 mg, 2.4 mmol), and **2c** (582 mg, 2 mmol) in *N*,*N*-dimethylformamide (5 mL) was stirred at room temperature for 1 h. The work-up procedure was the same as described earlier to produce **3g** (119 mg, 21%) as an oil; IR (neat): 1697, 1673, 1654, 1595, 1575, 1331 cm^{-1}; ^1H NMR (deuteriochloroform): δ 1.38 (d, J = 6.1 Hz, 3H), 5.11 (d, J = 10.4 Hz, 1H), 5.17 (d, J = 17.4 Hz, 1H), 5.53 (qd, J = 7.3 and 6.1 Hz, 1H), 5.80 (ddd, J = 17.4, 10.4, and 7.3 Hz, 1H), 6.48 (s, 1H), 6.58 (s, 1H), 7.69–7.77 (m, 2H), 8.05–8.09 (m, 2H), 9.64 (s, 1H); ^{13}C NMR (deuteriochloroform): δ 21.4, 80.8, 117.7, 126.4, 126.5, 128.7, 131.4, 131.7, 133.5, 134.1, 138.1, 138.2, 140.9, 157.0, 181.6, 183.3, 191.1; *Anal*. Calcd. for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00. Found: C, 72.08; H, 5.29.

2-[1,4-Dihydro-1,4-dioxo-3-(pent-1-en-3-yloxy)-naphthalene-2-yl]acrylaldehyde (3h). A mixture of 1-penten-3-ol (0.25 mL, 2.4 mmol), sodium hydride (58 mg, 2.4 mmol), and **2c** (582 mg, 2 mmol) in *N*,*N*-dimethylformamide (5 mL) was stirred at room temperature for 1 h. The work-up procedure was the same as described earlier to produce **3h** (184 mg, 31%) as an oil; IR (neat): 1697, 1674, 1655, 1595, 1575, 1331 cm^{-1}; ^1H NMR (deuteriochloroform): δ 0.92 (t, J = 7.3 Hz, 3H), 1.56–1.70 (m, 1H), 1.72–1.86 (m, 1H), 5.15 (d, J = 9.8 Hz, 1H), 5.18 (d, J = 17.7 Hz, 1H), 5.35 (td, J = 7.9 and 7.0 Hz, 1H), 5.70 (ddd, J = 17.7, 9.8, and 7.9 Hz, 1H), 6.48 (s, 1H), 6.60 (s, 1H), 7.67–7.75 (m, 2H), 8.04–8.08 (m, 2H), 9.64 (s, 1H); ^{13}C NMR (deuteriochloroform): δ 9.3, 28.4, 85.9, 119.3, 126.4, 126.5, 127.9, 131.5, 131.7, 133.5, 134.1, 136.7, 138.1, 140.9, 157.3, 181.7, 183.3, 191.1; *Anal*. Calcd. for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.63; H, 5.28.

Preparation of 2*H*-benzo[*g*]chromenes 5a-h: General Procedure. Bisolefin **3a-h** (0.5 mmol) was dissolved in 50 mL (0.01*M*) of dichloromethane. Then Grubbs II catalyst was added (10–15 mol %) and the solution was refluxed for 0.5–2.5 h under nitrogen atmosphere. The mixture was concentrated *in vacuo*. Purification on silica gel (hexane/ethyl acetate, 2:1) afforded **5a-h** as a solid.

The physical and spectral data of **5a-h** prepared by this general method are listed in the following paragraphs.

Methyl 5,10-dihydro-5,10-dioxo-2H-benzo[g]chromene-4-carboxylate (5a). Yellow solid; yield 74%; mp 182–183°C; IR (potassium bromide): 1724, 1676, 1650, 1631, 1591, 1571, 1455 cm^{-1}; ^1H NMR (deuteriochloroform): δ 3.86 (s, 3H), 5.03 (d, J = 4.1 Hz, 2H), 6.34 (t, J = 4.1 Hz, 1H), 7.70–7.79 (m, 2H), 8.08–8.13 (m, 2H); ^{13}C NMR (deuteriochloroform): δ 52.6, 66.3, 119.8, 126.0, 126.4, 126.6, 127.2, 130.8, 131.5, 133.5, 134.5, 154.9, 166.3, 178.8, 180.3; ms: m/z (%) = 270 (28) [M^+], 238 (15), 210 (16), 183 (42), 127 (64), 115 (26), 104 (100); hrms (EI): m/z Calcd. for $C_{15}H_{10}O_5$: 270.0528; Found: 270.0518; *Anal*. Calcd. for $C_{15}H_{10}O_5$: C, 66.67; H, 3.73. Found: C, 66.52; H, 3.59.

Methyl 5,10-dihydro-2-methyl-5,10-dioxo-2H-beno[g]chromene-4-carboxylate (5b). Yellow solid; yield 63%; mp 148–149°C; IR (potassium bromide): 1732, 1677, 1651, 1632, 1591, 1571, 1438 cm^{-1}; ^1H NMR (deuteriochloroform): δ 1.61 (d, J = 6.7 Hz, 3H), 3.86 (s, 3H), 5.24 (qd, J = 6.7 and 3.7 Hz, 1H), 6.21 (d, J = 3.7 Hz, 1H), 7.69–7.77 (m, 2H), 8.08–8.13 (m, 2H); ^{13}C NMR (deuteriochloroform): δ 19.9, 52.6, 73.7, 118.9, 126.3, 126.4, 126.6, 130.2, 131.0, 131.6, 133.4, 134.4, 154.1, 166.6, 179.0, 180.4; ms: m/z (%) = 284 (73) [M^+], 269 (100), 252 (99), 241 (66), 224 (64), 197 (80), 196 (72), 163 (30), 139 (34), 115 (39), 104 (37). hrms (EI): m/z Calcd. for $C_{16}H_{12}O_5$: 284.0685; Found: 284.0683; *Anal*. Calcd. for $C_{16}H_{12}O_5$: C, 67.60; H, 4.25. Found: C, 61.45; H, 4.43.

Methyl 2-ethyl-5,10-dihydro-5,10-dioxo-2H-benzo[g]-chromene-4-carboxylate (5c). Yellow solid; yield 80%; mp 94–95°C; IR (potassium bromide): 1729, 1676, 1652, 1634, 1590, 1570, 1456, 1435 cm^{-1}; ^1H NMR (deuteriochloroform): δ 1.09 (t, J = 7.4 Hz, 3H), 1.86–2.03 (m, 2H), 3.86 (s, 1H), 5.05 (td, J = 6.3 and 3.9 Hz, 1H), 6.23 (d, J = 3.9 Hz, 1H), 7.68–7.78 (m, 2H), 8.07–8.13 (m, 2H); ^{13}C NMR (deuteriochloroform): δ 8.8, 27.0, 52.5, 78.4, 119.0, 126.3, 126.5, 126.7, 129.2, 131.0, 131.6, 133.4, 134.3, 154.3, 166.7, 178.9, 180.4; ms: m/z (%) = 298 (31) [M^+], 270 (96), 269 (100), 241 (100), 239 (47), 210 (31), 181 (29), 153 (30), 104 (52); hrms (EI): m/z Calcd. for $C_{17}H_{14}O_5$: 298.0841; Found: 298.0839; *Anal*. Calcd. for $C_{17}H_{14}O_5$: C, 68.45; H, 4.73. Found: C, 68.20; H, 4.55.

4-Acetyl-2H-benzo[g]chromene-5,10-dione (5d). Red solid; yield 91%; mp 173–174°C; IR (potassium bromide): 1702, 1678, 1650, 1591, 1571, 1404 cm^{-1}; ^1H NMR (deuteriochloroform): δ 2.37 (s, 3H), 5.05 (d, J = 4.0 Hz, 2H), 6.10 (t, J = 4.0 Hz, 1H), 7.71–7.79 (m, 2H), 8.07–8.13 (m, 2H); ^{13}C NMR (deuteriochloroform): δ 29.0, 66.4, 120.3, 122.8, 126.4, 126.6, 130.8, 131.3, 133.7, 134.5, 135.6, 155.2, 178.8, 180.9, 199.2; ms: m/z (%) = 254 (45) [M^+], 212 (19), 183 (77), 155 (28), 139 (12), 128 (100), 127 (100), 104 (66); hrms (EI): m/z Calcd. for $C_{15}H_{10}O_4$: 254.0579; Found: 254.0580; *Anal*. Calcd. for $C_{15}H_{10}O_4$: C, 70.86; H, 3.96. Found: C, 70.59; H, 4.21.

4-Acetyl-2-methyl-2H-benzo[g]chromene-5,10-dione (5e). Red solid; yield 41%; mp 137–138°C; IR (potassium bromide): 1695, 1675, 1646, 1592, 1569, 1394 cm^{-1}; ^1H NMR (deuteriochloroform): δ 1.61 (d, J = 6.7 Hz, 3H), 2.36 (s, 3H), 5.25 (qd, J = 6.7 and 3.7 Hz, 1H), 5.95 (d, J = 3.7 Hz, 1H), 7.71–7.78 (m, 2H), 8.07–8.13 (m, 2H); ^{13}C NMR (deuteriochloroform): δ 20.2, 29.2, 73.8, 119.4, 126.4, 126.6, 127.0, 131.0, 131.3, 133.6, 134.4, 134.7, 154.4, 179.1, 181.0, 199.6; ms: m/z (%) = 268 (100) [M^+], 253 (27), 225 (47), 197 (56), 183 (30), 141 (22), 115 (28), 105 (18); hrms (EI): m/z Calcd. for $C_{16}H_{12}O_4$: 268.0736; Found: 268.0733; *Anal*. Calcd. for $C_{16}H_{12}O_4$: C, 71.64; H, 4.51. Found: C, 71.51; H, 4.42.

4-Acetyl-2-ethyl-2H-benzo[g]chromene-5,10-dione (5f). Yellow solid; yield 66%; mp 85–86°C; IR (potassium bromide): 1700, 1676, 1652, 1593, 1569, 1394 cm^{-1}; ^1H NMR (deuteriochloroform): δ 1.09 (t, J = 7.3 Hz, 3H), 1.86–2.05 (m, 2H), 2.36 (s, 3H), 5.07 (td, J = 6.1 and 3.7 Hz, 1H), 5.97 (d, J = 3.7 Hz, 1H), 7.70–7.78 (m, 2H), 8.06–8.13 (m, 2H); ^{13}C NMR (deuteriochloroform): δ 8.8, 27.4, 29.2, 78.6, 119.4, 125.9, 126.4, 126.6, 131.0, 131.4, 133.6, 134.4, 135.1, 154.6, 179.0, 181.0, 199.8; ms: m/z (%) = 282 (57) [M^+], 253 (100), 239 (28), 225 (100), 211 (29), 197 (39), 183 (33), 165 (31), 105 (33); hrms (EI): m/z Calcd. for $C_{17}H_{14}O_4$: 282.0892; Found: 282.0892; *Anal*. Calcd. for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00. Found: C, 72.11; H, 4.85.

5,10-Dihydro-2-methyl-5,10-dioxo-2H-benzo[g]chromene-4-carbaldehyde (5g). Orange solid; yield 40% [20]; ^1H NMR (deuteriochloroform): δ 1.62 (d, J = 7.0 Hz, 3H), 5.35 (qd, J = 4.0 and 7.0 Hz, 1H), 6.49 (d, J = 4.0 Hz, 1H), 7.74–7.81 (m, 2H), 8.12–8.14 (m, 2H), 10.16 (s, 1H).

2-Ethyl-5,10-dihydro-5,10-dioxo-2H-benzo[g]chromene-4-carbaldehyde (5h). Orange solid; yield 42%; mp 109–110°C; IR (potassium bromide): 1719, 1676, 1647, 1612, 1592, 1561, 1458, 1346 cm^{-1}; ^1H NMR (deuteriochloroform): δ 1.10 (t, J = 7.4 Hz, 3H), 1.93–1.99 (m, 2H), 5.17 (td, J = 6.1 and 4.1 Hz, 1H), 6.52 (d, J = 4.1 Hz, 1H), 7.72–7.80 (m, 2H), 8.11–8.13 (m, 2H), 10.16 (s, 1H); ^{13}C NMR (deuteriochloroform): δ

8.7, 27.4, 78.8, 118.0, 126.4, 126.6, 131.0, 131.4, 131.6, 131.7, 133.7, 134.5, 154.7, 178.9, 182.0, 189.0; ms: *m/z* (%) = 268 (69) [M^+], 240 (100), 222 (56), 197 (37), 165 (36), 135 (21), 105 (14); *Anal*. Calcd. for $C_{16}H_{12}O_4$: C, 71.64; H, 4.51. Found: C, 71.90; H, 4.38.

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[18] No RCM product was observed using 5 mol % of Grubbs second-generation catalyst during expanded reaction time.

[19] 10 mol % loading of catalyst was ineffective in these cases.

[20] The RCM product 5 g decomposed during vacuum drying. This unstableness resulted in only ^{1}H NMR spectroscopic data.