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Article

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The CDC Reaction and Subsequent Cyclization for the Synthesis of 2-Hydroxy-3-alkyl-1,4-naphthoquinones and Pyranonaphthoquinones

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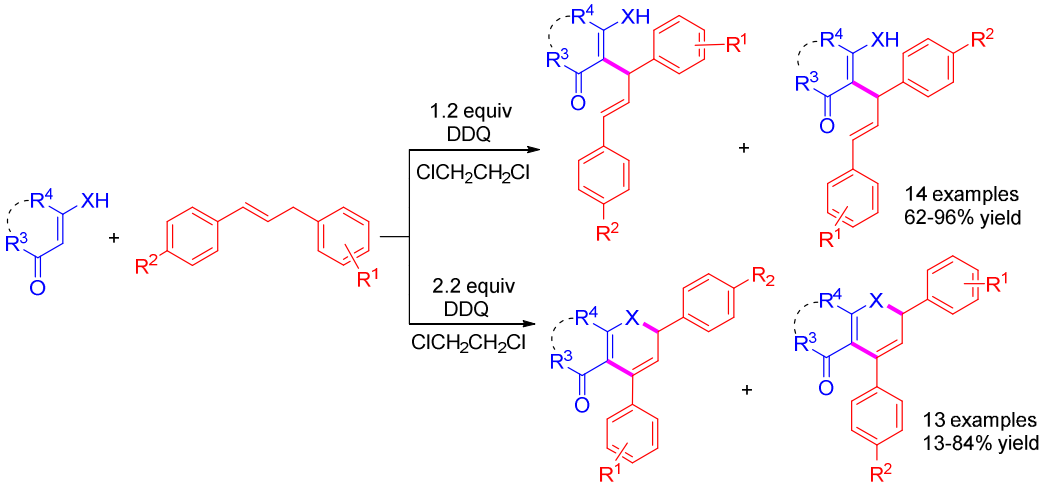


Abstract

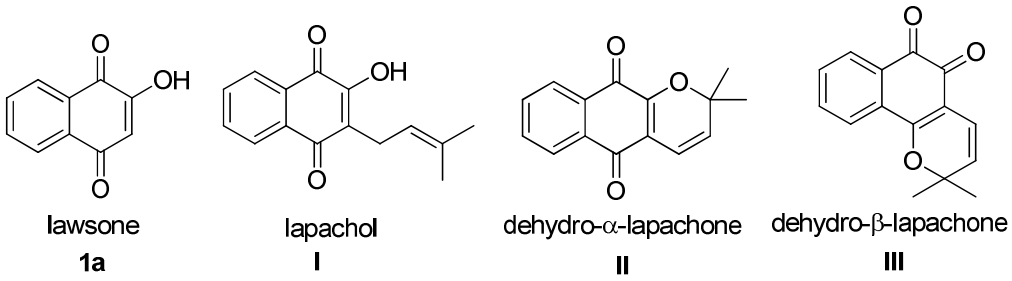
The metal-free cross-dehydrogenative coupling (CDC) reaction and subsequent cyclization of 2-hydroxy-1,4-naphthoquinone (lawsone) and 1,3-diarylpropene promoted by DDQ has been developed. 2-Hydroxy-3-alkyl-1,4-naphthoquinones and pyranonaphthoquinones with potential pharmaceutical applications are obtained in moderate to good yields. The reaction is also compatible for 4-hydroxycoumarins.

Keyword: Coupling reaction; DDQ; 2-Hydroxy-3-alkyl-1,4-naphthoquinone; Pyranonaphthoquinone

Introduction

CDC reaction has become a powerful tool to construct carbon-carbon bond, which possesses advantages of shorter synthetic step and higher atom economy due to avoiding prefunctionalization of the substrates.[1] To accomplish this transformation, transition metal is usually required in combination with an oxidant. However, use of transition metal brings the drawback of metal impurities which could be harmful in important pharmaceutical intermediates and final products.[2] Recently, metal-free approaches have been developed for the CDC reaction,[3] in which

2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) has proved to be an effective candidate.[1b] Among the CDC reaction promoted by DDQ, the couplings of Csp^3-H bonds with Csp^2-H bonds are few in comparison to the couplings of Csp^3-H bonds with Csp^3-H bonds.[4] Moreover, they are mainly limited to Csp^3-H bonds adjacent to heteroatoms. For example, Wang demonstrated an asymmetric oxidative coupling reaction of tertiary amines with α,β-unsaturated γ-butyrolactam promoted by DDQ and an chiral additive.[4e] Prabhu reported a CDC reaction of *N*-aryl tetrahydroisoquinolines and 4-hydroxycoumarins with a catalytic amount of DDQ and molecular oxygen as a terminal oxidant.[4g] A careful literature survey reveals that the DDQ-mediated CDC reaction of Csp^3-H bond not adjacent to heteroatoms with Csp^2-H bond is scare.[5]



Scheme 1. The structures of lawsone, lapachol, dehydro-α-lapachone, and dehydro-β-lapachone

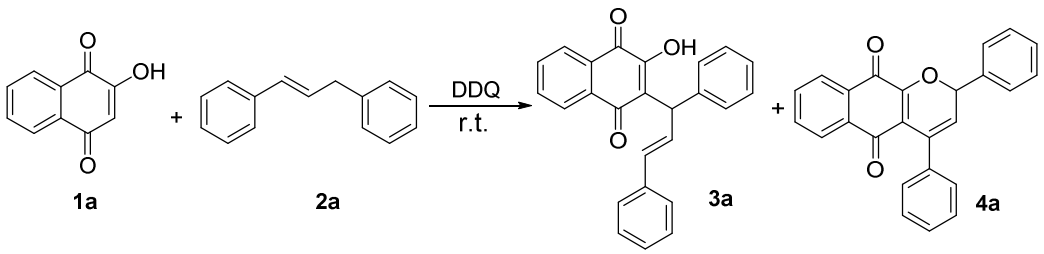
3-Alkyl-2-hydroxy-1,4-naphthoquinone is an important moiety in organic chemistry for its broad spectrum of pharmacological effects. The typical example is lapachol **I** (Scheme 1) which has the activities of antitumor, antimicrobial, antifungal, antiviral etc.[6] The common method for preparing 3-alkyl-2-hydroxy-1,4-naphthoquinone is the addition of lawsone **1a** (Scheme 1) with electrophilic reagents, such as the Mannich addition with intermediate of aldehyde and amine,[7] the Michael addition with α,β-unsaturated carbonyl compound,[8] the Knoevenagel condensation with aldehyde or ketone.[9] Another available way to synthesize 3-alkyl-2-hydroxy-1,4-naphthoquinone is the radical reaction of lawsone with carboxylic acid.[10] The naturally widely existing pyranonaphthoquinone plays important biological roles in animals and plants.[11] Synthesis of pyranonaphthoquinone could be achieved through acid or oxidative cyclization of lapachol,[12] or by the domino reaction like the Knoevenagel-electrocyclic reaction[13] from lawsone directly.

It was reported that both lapachol and isolapachol could be cyclized to give a mixture of dehydro-α-lapachone **II** and dehydro-β-lapachone **III** in the presence of DDQ (Scheme 1).[14] However, the alkylation and cyclization of lawsone with 1,3-diarylpropene through C-H bond oxidation has been not yet developed. In continuation of our interest in CDC reactions,[4a-4b] herein, we wish to report a metal-free DDQ mediated CDC reaction of Csp^2-H bond of lawsone and allylic Csp^3-H bond of 1,3-diarylpropene and subsequent cyclization to synthesize the corresponding products 3-alkyl-2-hydroxyl-1,4-naphthoquinones and pyranonaphthoquinones.

Results and Discussion

To obtain the optimized reaction conditions, the coupling reaction of lawsone **1a** with 1,3-diphenylpropene **2a** was chosen as a model reaction (Table 1). It was carried out under $MeNO_2$ in the presence of DDQ (1.2 equiv.). To our delight, the desired coupling product **3a** was obtained with 63% yield after 0.5 hr, accompanied by the formation of a small amount of cyclized product **4a** (entry 1). At first, several solvents were examined (entries 2-6). The coupling reaction could proceed in all examined solvents. The best result was given when 1,2-dichloroethane was used as the solvent (entry 2). Then the amount of DDQ was surveyed. With decreasing the amount of DDQ, the yield of coupling product was also decreased (entry 8). However, with increasing DDQ to a certain amount, the yield of coupling product was decreased and the yield of cyclized product could be promoted obviously (entries 9-10).

Table 1: Screening of the coupling reaction conditions[a]



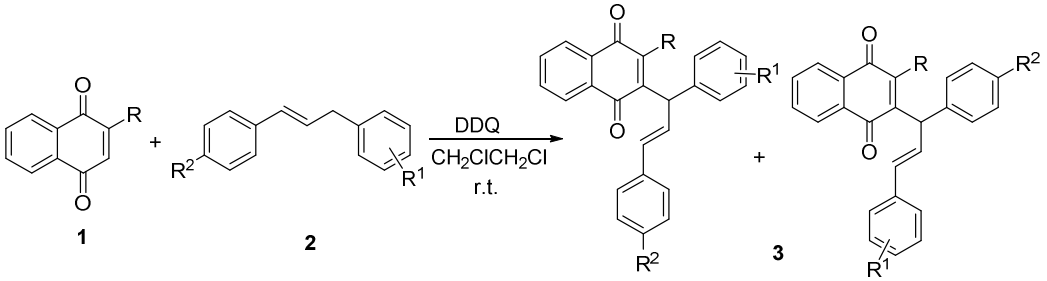
Entry	Time (hr)	Solvent	DDQ (equiv.)	Yield of **3a** (%)[b]
1	0.5	$MeNO_2$	1.2	63
2	0.5	CH_2ClCH_2Cl	1.2	87
3	0.5	CH_2Cl_2	1.2	65

4	0.5	1,4-dioxane	1.2	11
5	0.5	$CH_3COOC_2H_5$	1.2	74
6	0.5	$CHCl_3$	1.2	62
7	1	CH_2ClCH_2Cl	1.2	86
8	0.5	CH_2ClCH_2Cl	1.1	78
9	0.5	CH_2ClCH_2Cl	1.5	70
10	1	CH_2ClCH_2Cl	2.0	21

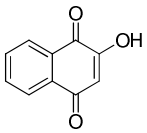
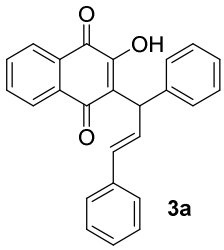
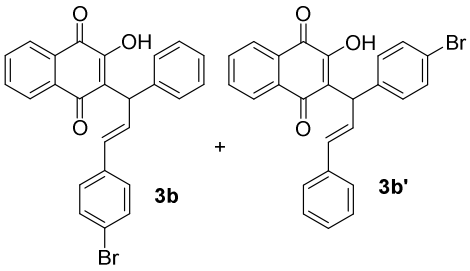
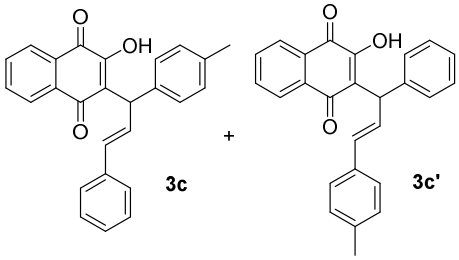
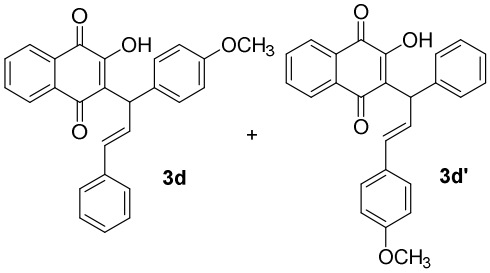
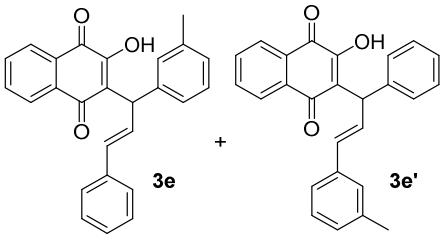
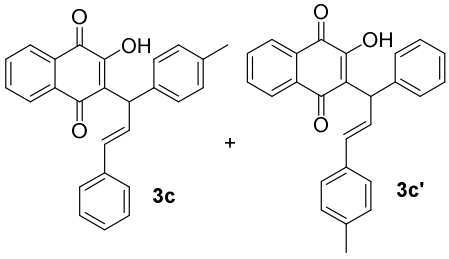
[a] 0.2 mmol of **1a**, 0.24 mmol of **2a**, 2 mL of solvent, r.t. [b] Isolated yield of **3a**.

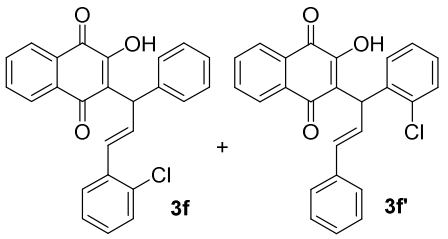
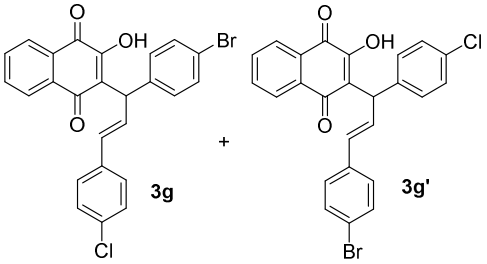
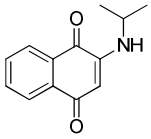
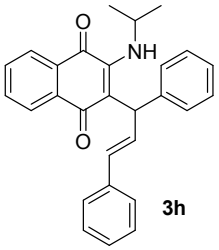
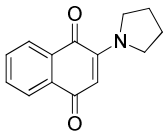
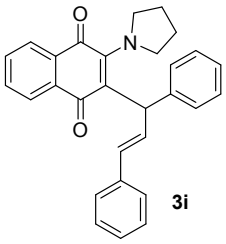
With the optimized reaction conditions in hand, various 1,3-diarylpropenes **2** were subjected to the coupling reaction (Table 2). Compound **2b** possessing bromo group on the para-position of benzene ring gave the coupling product **3b** with 96% yield (entry 2). The corresponding products were obtained with 62-82% yields when compounds **2** bearing electron-donating group in benzene ring reacted with lawsone **1a** (entries 3-6). It should be pointed out that a mixture of α- and γ- isomers were given when the unsymmetric 1,3-diarylpropenes **2b**-**2h** were used as the substrates, which indicated that the allylic free radical or allylic cation from 1,3-diarylpropenes could exist in the procedure. 2-Isopropylamino-naphthoquinone **1b** was also adapted to the reaction. The coupling product **3h** was obtained in 70% yield when the reaction time was prolonged to 1 hr at 40 ^oC (entry 9). However, the reaction system became complex when 2-pyrrolidine-naphthoquinone **1c** reacted with 1,3-diphenylpropene **2a**. The desired product was obtained with only 16% yield. According to the literature,[15] the addition sequence of substrate was changed and the yield could be promoted to 64% (Table 2, entry 10).

Table 2: The coupling reaction of naphthoquinones and 1,3-diarylpropenes[a]



Entry	**1**	R^1, R^2, **2**	**3**	Yield (%)[b]

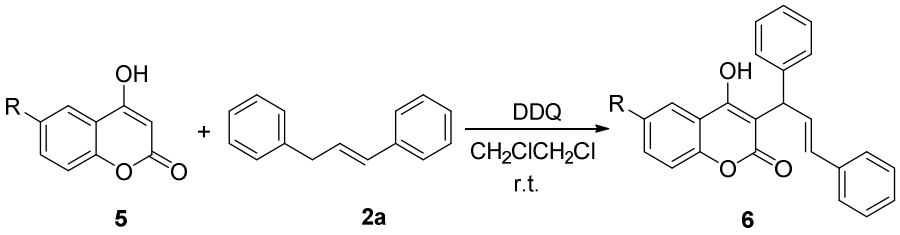
1	 **1a**	H, H, **2a**	 **3a**	87
2	**1a**	4-Br, H, **2b**	 **3b** + **3b'**	96
3	**1a**	4-CH_3, H, **2c**	 **3c** + **3c'**	77
4	**1a**	4-CH_3O, H, **2d**	 **3d** + **3d'**	62
5	**1a**	3-CH_3, H, **2e**	 **3e** + **3e'**	78
6	**1a**	H, 4-CH_3, **2f**	 **3c** + **3c'**	82

7	**1a**	2-Cl, H, **2g**	 **3f** + **3f'**	75
8	**1a**	4-Br, 4-Cl, **2h**	 **3g** + **3g'**	76
9[c]	 **1b**	**2a**	 **3h**	70
10[d]	 **1c**	**2a**	 **3i**	64

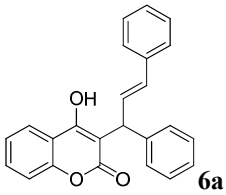
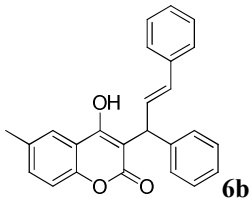
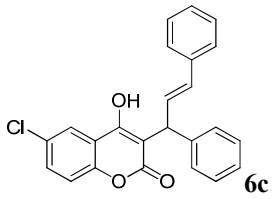
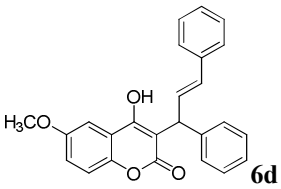
[a] 0.2 mmol of **1**, 0.24 mmol of **2**, 0.24 mmol of DDQ, 2 mL of CH_2ClCH_2Cl, 0.5 hr. [b] Isolated yield. [c] 40 °C, 1 hr. [d] 0.24 mmol of **2a**, 0.24 mmol of DDQ, 2 mL of CH_2ClCH_2Cl, stir for 5 min, then 0.2 mmol of **1c**, 1 hr.

4-Hydroxycoumarin derivatives possess a broad range of pharmacological and physiological activities.[16] A considerable number of methods about C_3-alkylation of 4-hydroxycoumarin were reported. To provide an alternative for C_3-allylation of 4-hydroxycoumarin through C-H bonds oxidation, the reaction of 4-hydroxycoumarin **5** and 1,3-diphenylpropene **2a** promoted by DDQ was examined. Under the previous optimized reaction conditions, the desired coupling products were also obtained in satisfactory yields (Table 3, entries 1-4).

Table 3 The coupling reaction with 1,3-diphenylpropene and 4-hydroxycoumarins[a]



5 **2a** **6**

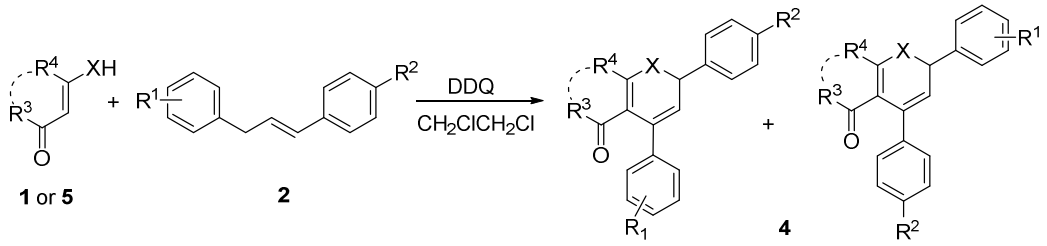
Entry	R, **5**	Product, **6**	Yield (%)[b]
1	H, **5a**	 **6a**	74
2	CH_3, **5b**	 **6b**	76
3	Cl, **5c**	 **6c**	64
4	OCH_3, **5d**	 **6d**	67

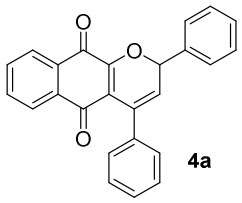
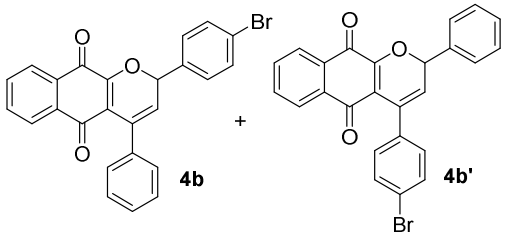
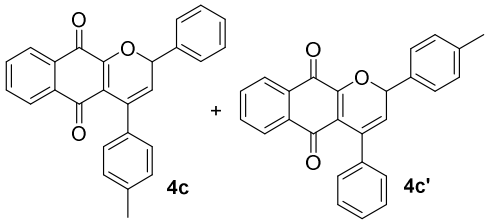
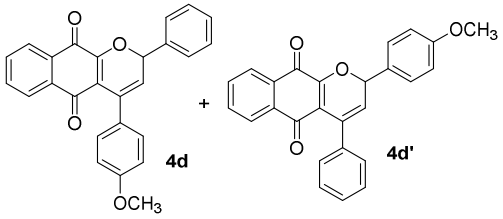
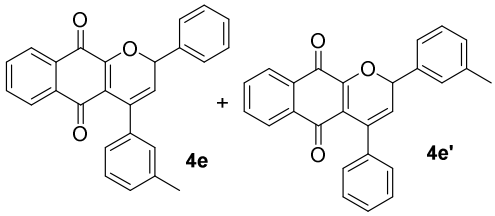
[a] 0.2 mmol of **5**, 0.24 mmol of **2a**, 0.24 mmol of DDQ, 2 mL of CH_2ClCH_2Cl, 0.5 hr. [b] Isolated yield.

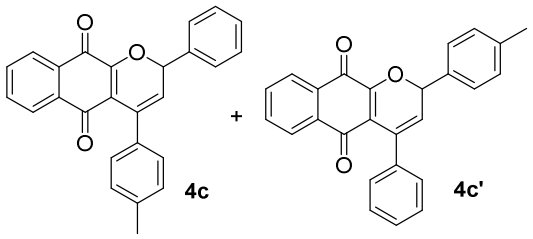
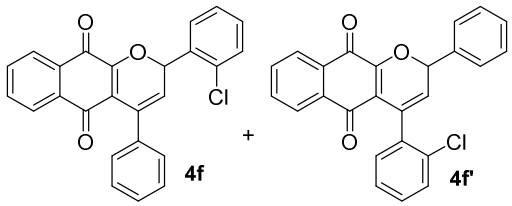
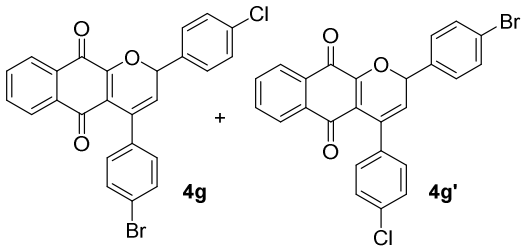
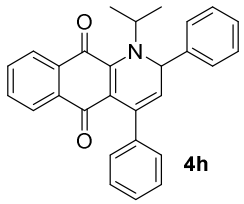
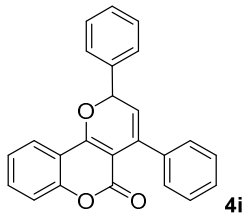
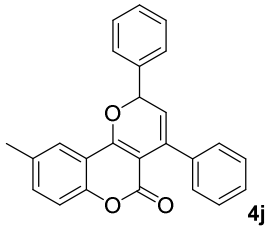
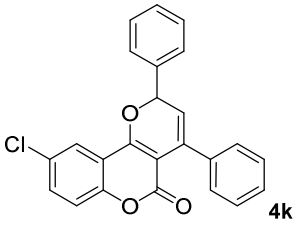
In optimization of the coupling reaction conditions, the cyclization product **4a** was isolated in low yield when lawsone **1a** reacted with 1,3-diphenylpropene **2a**. In the continuation of our research, the cyclization reaction was further investigated. Extra DDQ (1.0 equiv.) was added to the reaction mixture after the coupling reaction of lawsone **1a** with 1,3-diphenylpropene **2a**. It continued to be stirred for 1 hr at room temperature and the cyclization product was obtained with 84% yield. Similarly, various substrates were subjected to the cyclization reaction. The corresponding pyranonaphthoquinones and pyranocoumarins were given in moderate to good yields

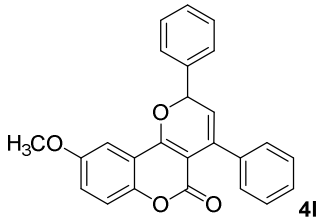
(Table 4, entries 1-13).

Table 4: Scope of the cyclization reaction[a]



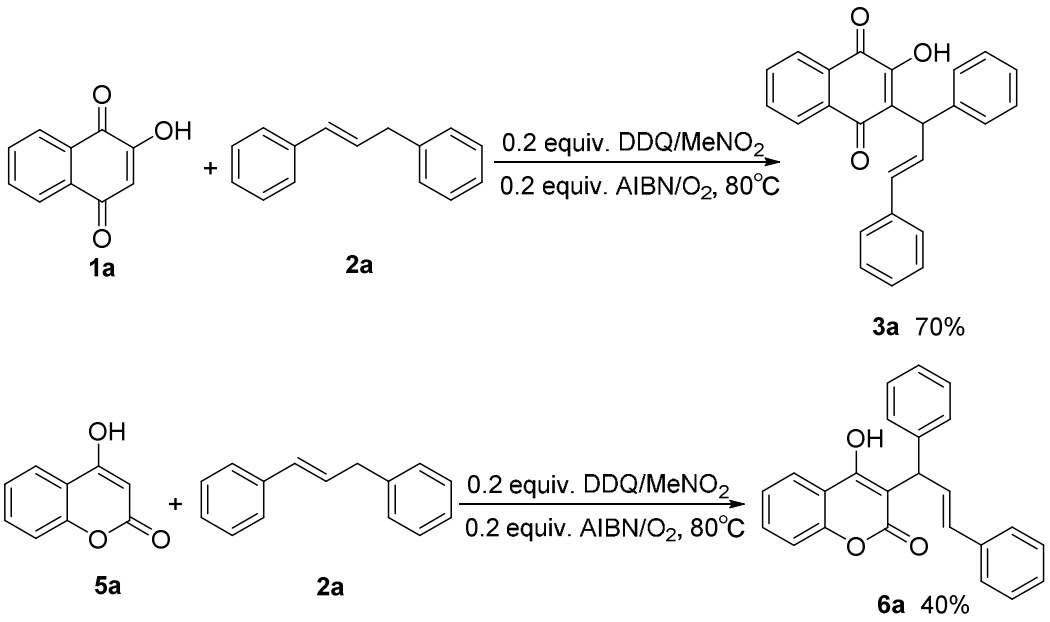
Entry	**1** or **5**	**2**	Product **4**	Yield (%)[b]
1	**1a**	**2a**	 **4a**	84
2	**1a**	**2b**	 **4b** + **4b'** (Br)	64
3	**1a**	**2c**	 **4c** + **4c'**	78
4	**1a**	**2d**	 **4d** (OCH3) + **4d'** (OCH3)	65
5	**1a**	**2e**	 **4e** + **4e'**	60

6	**1a**	**2f**	 **4c** + **4c'**	62
7	**1a**	**2g**	 **4f** + **4f'**	51
8	**1a**	**2h**	 **4g** + **4g'**	69
9[c]	**1b**	**2a**	 **4h**	13
10[c]	**5a**	**2a**	 **4i**	68
11[c]	**5b**	**2a**	 **4j**	52
12[c]	**5c**	**2a**	 **4k**	66

13[c]	**5d**	**2a**	 **4l**	54

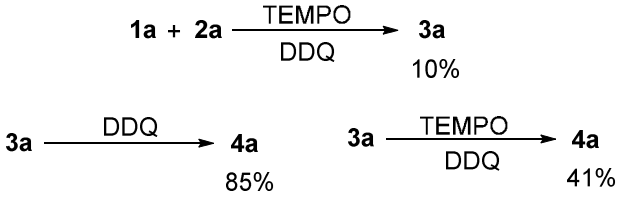
[a] 0.2 mmol of **1** or **5**, 0.24 mmol of **2**, 3 mL of CH_2ClCH_2Cl, 0.24 mmol of DDQ, 0.5 hr; then 0.2 mmol of DDQ, 1 hr, r.t. [b] Isolated yield. [c] 40 °C.

Besides, the reaction of lawsone **1a** or 4-hydroxycoumarin **5a** with 1,3-diphenylpropene **2a** promoted by a catalytic amount of DDQ was examined (Scheme 2). It was performed under AIBN at 80 °C in the presence of oxygen atmosphere (oxygen balloon). The coupling product **3a** or **6a** was given within 6 hrs.



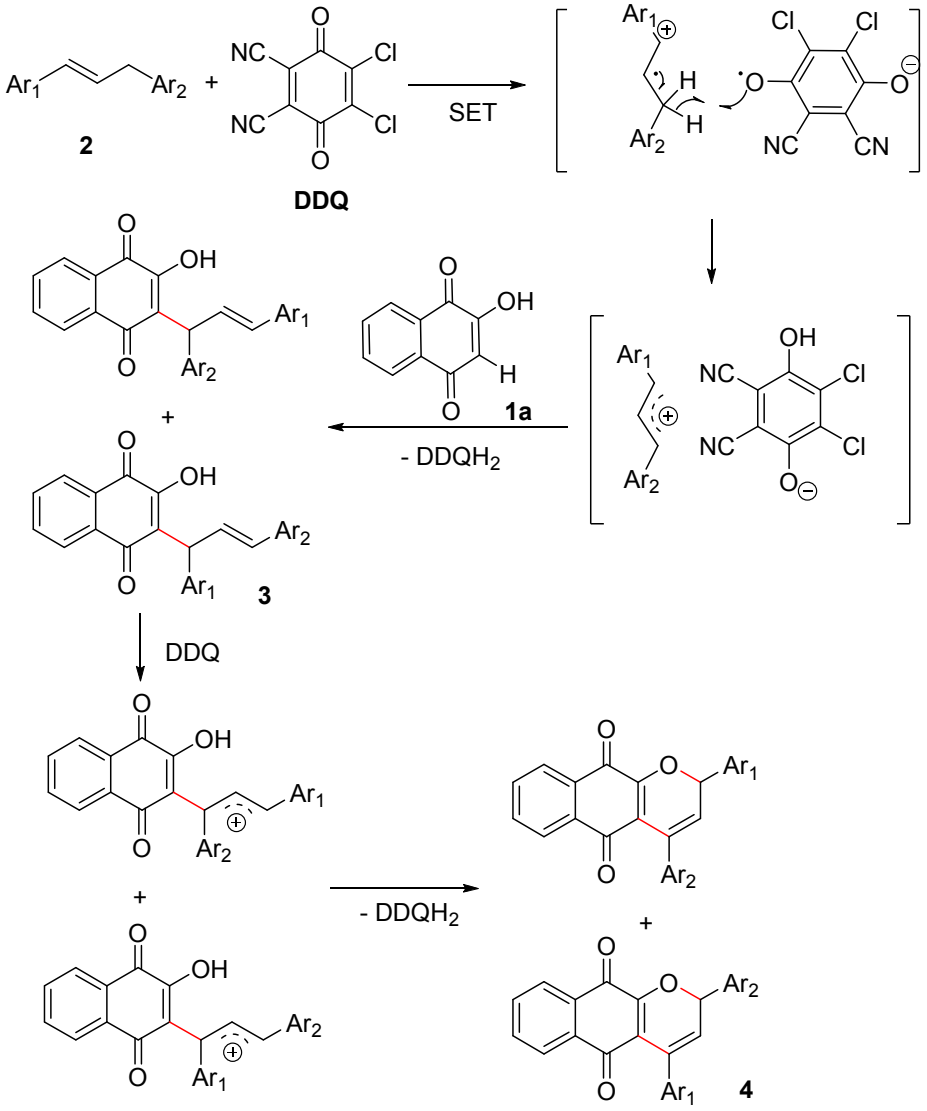
Scheme 2. The coupling reaction promoted by DDQ/AIBN/O_2 system.

Mechanism



Scheme 3. Some control experiments.

To explore the reaction mechanism, some control experiments were performed (Scheme 3). The yield of coupling product **3a** was decreased from 86% to 10% when



Scheme 4. Possible reaction mechanism

a radical scavenger TEMPO was added to the reaction mixture, which obviously indicated that the reaction was a single-electron transfer in the process. The cyclization of coupling product **3a** was examined under CH_2ClCH_2Cl in the presence of DDQ (1.2 equiv.). The cyclization product **4a** was obtained in 85% yield within 1 hr. The yield was decreased to 41% when TEMPO was added to the system. On the base of the literatures[4d] and our experiments, a possible mechanism was proposed as Scheme 4. In the presence of DDQ, 1,3-diarylpropene generated an allylic cation which was attacked by the nucleophilic reagent lawsone to give the coupling product **3**. The allylic cation was rearranged between α- and γ- positions. In our experiment, a mixture of α- and γ- isomers was obtained when unsymmetric 1,3-diarylpropene was

used as the substrate. Similarly, compound **3** could react with DDQ to give the allylic cation, followed by the intramolecular nucleophilic attack of hydroxyl group to produce the cyclization product **4**.

Conclusion

In conclusion, we have developed a novel Csp^3-H and Csp^2-H CDC reaction and subsequent cyclization of lawsones or 4-hydroxycoumarins and 1,3-diarylpropenes promoted by DDQ. Various 2-hydroxy-3-alkyl-1,4-naphthoquinones and pyranonaphthoquinones were obtained in good yields under mild conditions.

Experimental Section

General information. Column chromatography was carried out on silica gel (200-300 mesh). ^{1}H NMR spectra were recorded on a 500 MHz spectrometer. ^{13}C NMR spectra were recorded on a 125 MHz spectrometer. Chemical shifts were reported in parts per million (δ) relative to the internal standard TMS (0 ppm) for $CDCl_3$. The coupling constants, *J*, were reported in Hertz (Hz). High-resolution mass spectra (HRMS) were recorded on ESI-TOF. The reagents were purchased from commercial chemical reagent companies and used without further purification unless otherwise stated.

1. **General procedure for the synthesis of 3 or 6**: To a solution of lawsone **1** or 4-hydroxycoumarin **5** (0.2 mmol) and 1,3-diarylpropene **2** (0.24 mmol) in CH_2ClCH_2Cl (2 mL), DDQ (0.24 mmol, 0.055 g) was added. The resulting mixture was stirred for 0.5 hr at room temperature. After the completion of the reaction, the solvent was concentrated under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether and ethyl acetate (3:1) as the eluent to give the pure product **3** or **6**.

*(E)-2-(1,3-Diphenylallyl)-3-hydroxynaphthoquinone (**3a**).* Purification by flash chromatography afforded **3a** (0.064 g, 87% yield) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$/TMS): δ 8.16-8.14 (m, 1H), 8.11-8.09 (m, 1H), 7.79-7.76 (m, 1H), 7.72-7.68 (m, 1H), 7.57 (s, 1H), 7.45-7.44 (m, 4H), 7.34-7.31 (m, 4H), 7.25- 7.22 (m, 2H), 7.05, 7.02 (dd, *J* = 8.9, 15.7 Hz, 1H), 6.64 (d, *J* = 15.8 Hz, 1H), 5.41 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$/TMS): δ 183.8, 181.8, 152.8, 141.7, 137.3, 135.2, 133.0, 132.9, 132.5, 129.3, 128.6, 128.5, 128.4, 127.8, 127.5, 127.2, 126.5, 126.4, 126.2, 124.8, 44.1. HRMS (ESI): calcd. for $C_{25}H_{18}O_3$ [M+H$^+$] 367.1329; found 367.1335.

*Mixture of (E)-2-(3-(4-bromophenyl)-1-phenylallyl)-3-hydroxynaphthoquinone (**3b**) and (E)-2-(1-(4-bromophenyl)-3-phenylallyl)-3-hydroxynaphthoquinone (**3b'**) as 3:2.* Purification by flash chromatography afforded **3b** and **3b'**(0.085 g, 96% yield) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$/TMS): δ 8.15-8.13 (m, 1H), 8.11-8.09 (m, 1H), 7.80-7.76 (m, 1H), 7.72-7.68 (m, 1H), 7.60 (s, 1H), 7.44-7.42 (m, 4H), 7.33-7.29 (m, 4H), 7.26-7.22 (m, 1H), 7.05-6.93 (m, 1H), 6.63, 6.56 (dd, *J* = 15.8, 15.8 Hz, 1H), 5.39 (d, *J* = 8.9 Hz, 3/5×1H), 5.34 (d, *J* = 9.0 Hz, 2/5×1H). ^{13}C NMR (125 MHz, $CDCl_3$/TMS): δ 183.8, 183.7, 181.8, 181.7, 152.87, 152.86, 141.4, 140.8, 137.0, 136.2, 135.3, 135.2, 133.2, 133.1, 132.9, 132.8, 131.6, 131.4, 131.2, 129.7, 129.6, 129.24, 129.22, 128.6, 128.5, 128.0, 127.9, 127.8, 127.6, 127.2, 126.6, 126.4, 126.24, 126.19, 124.6, 124.3, 121.2, 120.4, 44.1, 43.6. HRMS (ESI): calcd. for $C_{25}H_{16}BrO_3$[M-H]$^-$ 443.0288; found 443.0298.

*Mixture of (E)-2-hydroxy-3-(3-phenyl-1-(p-tolyl)allyl)naphthoquinone (**3c**) and*

*(E)-2-hydroxy-3-(1-phenyl-3-(p-tolyl)allyl)naphthoquinone (**3c'**) as 3:2*. Purification by flash chromatography afforded **3c** and **3c'** (0.059 g, 77% yield) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$/TMS): δ 8.16 (d, *J* = 7.7 Hz, 1H), 8.10-8.09 (m, 1H), 7.79-7.75 (m, 1H), 7.71-7.67 (m, 1H), 7.62 (s, 1H), 7.47-7.45 (m, 2H), 7.37-7.32 (m, 4H), 7.26-7.23 (m, 1H), 7.16-7.13 (m, 2H), 7.08-6.98 (m, 1H), 6.65, 6.64 (dd, *J* = 15.8, 15.7 Hz, 1H), 5.43-5.39 (m, 1H), 2.36 (s, 2/5×3H), 2.35 (s, 3/5×3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 183.83, 183.81, 181.8, 152.8, 152.7, 141.8, 138.6, 137.3, 137.2, 136.0, 135.1, 134.5, 133.0, 132.8, 132.3, 132.2, 129.2, 129.1, 128.9, 128.5, 128.3, 127.8, 127.7, 127.5, 127.4, 127.1, 126.43, 126.39, 126.30, 126.1, 125.0, 124.9, 44.1, 43.7, 21.2, 21.0. HRMS (ESI): calcd. for $C_{26}H_{19}O_3$ $[M-H]^-$ 379.1340; found 379.1322.

*Mixture of (E)-2-hydroxy-3-(1-(4-methoxyphenyl)-3-phenylallyl)naphthoquinone (**3d**) and (E)-2-hydroxy-3-(3-(4-methoxyphenyl)-1-phenylallyl)naphthoquinone (**3d'**) as 7:3*. Purification by flash chromatography afforded **3d** and **3d'** (0.049 g, 62% yield) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$/TMS): δ 8.15-8.13 (m, 1H), 8.10-8.08 (m, 1H), 7.79-7.76 (m, 1H), 7.71-7.68 (m, 1H), 7.58 (s, 7/10×1H), 7.56 (s, 3/10×1H), 7.45-7.43 (m, 2H), 7.39-7.35 (m, 2H), 7.33-7.30 (m, 2H), 7.25-7.20 (m, 1H), 7.03, 7.00 (dd, *J* = 8.8, 15.8 Hz, 7/10×1H), 6.91-6.85 (m, 2H+3/10×1H), 6.61, 6.59 (dd, *J* = 15.8, 15.7 Hz, 1H), 5.38 (d, *J* = 9.1 Hz, 3/10×1H), 5.35 (d, *J* = 8.8 Hz, 7/10×1H), 3.82 (s, 3/10×3H), 3.79 (s, 7/10×3H). ^{13}C NMR (125 MHz, $CDCl_3$/TMS): δ 183.9, 181.9, 159.1, 158.2, 152.8, 152.7, 137.3, 135.1, 133.8, 133.0, 132.9, 132.1, 131.9, 129.2, 129.0, 128.9, 128.5, 128.4, 127.8, 127.6, 127.4, 127.1, 126.4, 126.3, 126.1, 125.0, 114.0, 113.8, 55.3, 55.2, 44.1, 43.4. HRMS (ESI): calcd. for $C_{26}H_{19}O_4$ $[M-H]^-$ 395.1289; found 395.1294.

*Mixture of (E)-2-hydroxy-3-(3-phenyl-1-(m-tolyl)allyl)naphthoquinone (**3e**) and (E)-2-hydroxy-3-(1-phenyl-3-(m-tolyl)allyl)naphthoquinone (**3e'**) as 3:2*. Purification by flash chromatography afforded **3e** and **3e'** (0.059 g, 78% yield) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$/TMS): δ 8.16-8.14 (m, 1H), 8.10 (d, *J* = 7.6 Hz, 1H), 7.80-7.76 (m, 1H), 7.72-7.68 (m, 1H), 7.57 (s, 1H), 7.46-7.43 (m, 2H), 7.34-7.31 (m, 2H), 7.25-7.20 (m, 4H), 7.06-6.99 (m, 2H), 6.63, 6.61 (dd, *J* = 15.8, 15.8 Hz, 1H), 5.41 (d, *J* = 9.1 Hz, 2/5×1H), 5.38 (d, *J* = 10.0 Hz, 3/5×1H), 2.36 (s, 2/5×3H), 2.34 (s, 3/5×3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 183.8, 183.7, 181.70, 181.67, 152.83, 152.80, 141.71, 141.65, 141.58, 138.0, 137.9, 137.23, 137.18, 137.11, 135.0, 132.9, 132.73, 132.72, 132.5, 132.3, 132.2, 129.1, 128.8, 128.6, 128.5, 128.4, 128.3, 128.22, 128.17, 127.8, 127.4, 127.3, 127.2, 126.99, 126.96, 126.42, 126.39, 126.35, 126.0, 124.81, 124.76, 124.71, 123.6, 44.1, 44.0, 21.5, 21.3. HRMS (ESI): calcd. for $C_{26}H_{19}O_3$ $[M-H]^-$ 379.1340; found 379.1331.

*Mixture of (E)-2-hydroxy-3-(3-phenyl-1-(p-tolyl)allyl)naphthoquinone (**3c**) and (E)-2-hydroxy-3-(1-phenyl-3-(p-tolyl)allyl)naphthoquinone (**3c'**) as 3:2*. Purification by flash chromatography afforded **3c** and **3c'** (0.062 g, 82% yield) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$/TMS): δ 8.15 (d, *J* = 7.3 Hz, 1H), 8.09 (d, *J* = 7.7 Hz, 1H), 7.79-7.75 (m, 1H), 7.71-7.67 (m, 1H), 7.60 (s, 1H), 7.46-7.44 (m, 2H), 7.36-7.31 (m, 4H), 7.25-7.22 (m, 1H), 7.15-7.13 (m, 2H), 7.06-6.96 (m, 1H), 6.64, 6.63 (dd, *J* = 15.8, 15.8 Hz, 1H), 5.42-5.38 (m, 1H), 2.35 (s, 2/5×3H), 2.34 (s, 3/5×3H). ^{13}C NMR (125 MHz, $CDCl_3$/TMS): δ 183.84, 183.82, 181.8, 152.79, 152.75, 141.8, 138.7, 137.3, 137.2, 136.0, 135.1, 134.5, 133.0, 132.9, 132.3, 132.2, 129.2, 129.1, 128.9, 128.5, 128.4, 127.8, 127.7, 127.5, 127.4, 127.1, 126.43, 126.39, 126.31, 126.1, 125.0, 124.9, 44.1, 43.7, 21.2, 21.0. HRMS (ESI): calcd. for $C_{26}H_{19}O_3$ $[M-H]^-$ 379.1340; found 379.1326.

*Mixture of (E)-2-(3-(2-chlorophenyl)-1-phenylallyl)-3-hydroxynaphthoquinone (**3f**) and (E)-2-(1-(2-chlorophenyl)-3-phenylallyl)-3-hydroxynaphthoquinone (**3f'**) as 13:12*. Purification by flash chromatography afforded **3f** and **3f'** (0.060 g, 75% yield) as yellow oil. ^{1}H NMR (500 MHz,

$CDCl_3$/TMS): δ 8.16-8.15 (m, 1H), 8.10-8.08 (m, 1H), 7.79-7.75 (m, 1H), 7.71-7.65 (m, 2H), 7.64 (s, 12/25×1H), 7.54 (s, 13/25×1H), 7.48-7.44 (m, 2H), 7.36-7.17 (m, 6H), 7.10-7.01 (m, 12/25×1+12/25×1H), 6.86, 6.83 (dd, *J* = 8.4, 15.8 Hz, 13/25×1H), 6.64 (d, *J* = 15.8 Hz, 13/25×1H), 5.64 (d, *J* = 8.4 Hz, 13/25×1H), 5.47 (d, *J* = 7.4 Hz, 12/25×1H). ^{13}C NMR (125 MHz, $CDCl_3$/TMS): δ 183.8, 183.4, 181.8, 181.6, 153.0, 152.9, 141.4, 139.2, 137.1, 135.3, 135.2, 133.7, 133.03, 132.97, 132.95, 132.84, 132.4, 131.7, 130.6, 129.6, 129.4, 129.3, 129.2, 128.53, 128.46, 128.43, 127.9, 127.8, 127.6, 127.2, 127.14, 127.07, 127.04, 126.8, 126.6, 126.5, 126.4, 126.2, 124.6, 123.3, 44.4, 41.9. HRMS (ESI): calcd. for $C_{25}H_{16}ClO_3$ $[M-H]^-$ 399.0793; found 399.0798.

*Mixture of (E)-2-(1-(4-bromophenyl)-3-(4-chlorophenyl)allyl)-3-hydroxynaphthoquinone (**3g**) and (E)-2-(3-(4-bromophenyl)-1-(4-chlorophenyl)allyl)-3-hydroxynaphthoquinone (**3g'**)*. Purification by flash chromatography afforded **3g** and **3g'** (0.073 g, 76% yield) as yellow oil. H NMR (500 MHz, $CDCl_3$/TMS): δ 8.13 (d, *J* = 7.7 Hz, 1H), 8.10 (d, *J* = 7.6 Hz, 1H), 7.80-7.77 (m, 1H), 7.72-7.69 (m, 1H), 7.63 (s, 1H), 7.44-7.42 (m, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.30-7.27 (m, 4H), 6.97-6.90 (m, 1H), 6.58, 6.54 (dd, *J* = 15.8, 15.8 Hz, 1H), 5.34, 5.32 (dd, *J* = 8.1, 8.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$/TMS): δ 183.7, 181.6, 152.9, 140.5, 139.9, 136.0, 135.5, 135.3, 133.2, 132.7, 132.4, 131.7, 131.6, 131.5, 129.6, 129.2, 129.0, 128.7, 128.5, 128.0, 127.6, 127.2, 126.3, 124.1, 124.0, 121.3, 120.5, 43.6, 43.5. HRMS (ESI): calcd. for $C_{25}H_{15}BrClO_3$ $[M-H]^-$ 476.9899; found 476.9907.

*(E)-2-(1,3-Diphenylallyl)-3-(isopropylamino)naphthoquinone (**3h**)*. Purification by flash chromatography afforded **3h** (0.057 g, 70% yield) as orange oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11-8.09 (m, 1H), 8.01-7.99 (m, 1H), 7.70-7.67 (m, 1H), 7.61-7.58 (m, 1H), 7.42 (d, *J* = 7.4 Hz, 2H), 7.37-7.29 (m, 7H), 7.27-7.21 (m, 1H), 6.80, 6.76 (dd, *J* = 7.2, 15.9 Hz, 1H), 6.57 (d, *J* = 15.8 Hz, 1H), 5.69 (d, *J* = 7.2 Hz, 1H), 5.12 (d, *J* = 8.6 Hz, 1H), 4.32-4.29 (m, 1H), 1.06 (d, *J* = 6.3 Hz, 3H), 0.90 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 183.6, 181.8, 146.5, 141.9, 137.1, 134.2, 133.0, 132.6, 131.9, 131.2, 128.7, 128.6, 127.8, 127.5, 127.4, 126.6, 126.4, 126.3, 125.9, 118.1, 47.2, 43.3, 24.24, 24.18. HRMS (ESI): calcd. For $C_{28}H_{26}NO_2$ $[M+H^+]$ 408.1958; found 408.1955.

*(E)-2-(1,3-Diphenylallyl)-3-(pyrrolidin-1-yl)naphthoquinone (**3i**)*. Purification by flash chromatography afforded **3i** (0.054 g, 64% yield) as red oil. ^{1}H NMR (500 MHz, $CDCl_3$/TMS): δ 7.99-7.98 (m, 1H), 7.91-7.89 (m, 1H), 7.66-7.63 (m, 1H), 7.59-7.56 (m, 1H), 7.46 (d, *J* = 7.3 Hz, 2H), 7.39 (d, *J* = 7.6 Hz, 2H), 7.34-7.29 (m, 4H), 7.25-7.18 (m, 2H), 7.12, 7.09 (dd, *J* = 8.4, 16.0 Hz, 1H), 6.56 (d, *J* = 16.0 Hz, 1H), 4.98 (d, *J* = 8.3 Hz, 1H), 3.77 (t, *J* = 6.4 Hz, 4H), 1.91-1.87 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 185.5, 182.1, 154.5, 143.6, 137.5, 133.6, 133.3, 132.1, 132.0, 131.6, 128.5, 128.0, 127.6, 127.2, 126.4, 125.8, 125.6, 125.3, 120.1, 54.2, 48.5, 25.8. HRMS (ESI): calcd. for $C_{29}H_{26}NO_2$ $[M+H^+]$ 420.1958; found 420.1955.

*(E)-3-(1,3-Diphenylallyl)-4-hydroxy-2H-chromen-2-one (**6a**)*.[17] Purification by flash chromatography afforded **6a** (0.052 g, 74% yield) as white solid, mp 155-157 °C. ^{1}H NMR (500 MHz, $CDCl_3$/TMS): δ 7.83-7.81 (m, 1H), 7.58-7.55 (m, 1H), 7.45-7.39 (m, 6H), 7.35-7.26 (m, 6H), 7.13 (s, 1H), 6.81, 6.77 (dd, *J* = 6.3, 16.1 Hz, 1H), 5.57-6.53 (m, 1H), 5.50 (d, *J* = 5.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.1, 160.9, 152.7, 139.5, 136.1, 134.0, 132.2, 129.4, 128.7, 128.14, 128.09, 127.7, 126.6, 124.0, 123.1, 116.5, 115.9, 106.4, 44.0.

*(E)-3-(1,3-Diphenylallyl)-4-hydroxy-6-methyl-2H-chromen-2-one (**6b**)*. Purification by flash chromatography afforded **6b** (0.056 g, 76% yield) as white solid, mp 87-89 °C. ^{1}H NMR (500 MHz, $CDCl_3$/TMS): δ 7.63 (d, *J* = 1.2 Hz, 1H), 7.45-7.37 (m, 7H), 7.35-7.31 (m, 3H), 7.29-7.27

(m, 2H), 7.22 (d, J = 8.5 Hz, 1H), 6.83, 6.80 (dd, J = 6.4, 16.0 Hz, 1H), 6.57-6.53 (m, 1H), 5.50 (d, J = 6.1 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.4, 161.0, 150.9, 139.7, 136.2, 133.74, 133.71, 133.2, 129.2, 128.6, 128.3, 128.03, 127.99, 127.6, 126.5, 122.8, 116.3, 115.5, 106.3, 44.0, 20.9. HRMS (ESI): calcd. for $C_{25}H_{19}O_3$ $[M-H]^-$ 367.1340; found 367.1341.

*(E)-6-Chloro-3-(1,3-diphenylallyl)-4-hydroxy-2H-chromen-2-one (**6c**).*[17] Purification by flash chromatography afforded **6c** (0.050 g, 64% yield) as white solid, mp 87-89 °C. ^{1}H NMR (500 MHz, $CDCl_3$/TMS): δ 7.81 (d, J = 2.5 Hz, 1H), 7.50-7.48 (m, 1H), 7.43-7.38 (m, 6H), 7.35-7.32 (m, 3H), 7.29-7.25 (m, 3H), 6.80, 6.77 (dd, J = 6.5, 16.1 Hz, 1H), 6.57-6.54 (m, 1H), 5.47 (d, J = 6.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.7, 159.8, 151.0, 139.3, 136.0, 134.1, 132.1, 129.6, 129.4, 128.7, 128.1, 128.0, 127.8, 127.7, 126.5, 122.8, 118.0, 117.1, 107.4, 44.1.

*(E)-3-(1,3-Diphenylallyl)-4-hydroxy-6-methoxy-2H-chromen-2-one (**6d**).* Purification by flash chromatography afforded **6d** (0.051 g, 67% yield) as white solid, mp 148-150 °C. ^{1}H NMR (500 MHz, $CDCl_3$/TMS): δ 7.44-7.38 (m, 6H), 7.34-7.31 (m, 3H), 7.29-7.25 (m, 4H), 7.15-7.12 (m, 1H), 6.81, 6.78 (dd, J = 6.3, 16.1 Hz, 1H), 6.56-6.52 (m, 1H), 5.50 (d, J = 6.2 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.4, 160.7, 155.9, 147.2, 139.6, 136.2, 133.9, 129.3, 128.7, 128.2, 128.1, 127.7, 126.6, 120.5, 117.7, 116.2, 106.6, 104.7, 55.8, 44.0. HRMS (ESI): calcd. for $C_{25}H_{20}NaO_4$ $[M+Na]^+$ 407.1254; found 407.1238.

2. **General procedure for the synthesis of 4**: To a solution of lawsone **1** or 4-hydroxycoumarin **5** (0.2 mmol), 1,3-diarylpropene **2** (0.24 mmol) in CH_2ClCH_2Cl (3 mL), DDQ (0.24 mmol, 0.055 g) was added. The resulting mixture was stirred for 0.5 hr at room temperature. Then extra DDQ (0.2 mmol, 0.045 g) was added. The mixture was stirred for another 1 hr at room temperature. After the completion of the reaction, the solvent was concentrated under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether and ethyl acetate (5:1) as the eluent to give the pure product **4**.

*2,4-Diphenyl-2H-benzo[g]chromene-5,10-dione (**4a**).* Purification by flash chromatography afforded **4a** (0.061 g, 84% yield) as yellow solid, mp 174-176 °C. ^{1}H NMR (500 MHz, $CDCl_3$/TMS): δ 8.12-8.10 (m, 1H), 8.01-7.99 (m, 1H), 7.71-7.69 (m, 2H), 7.58 (d, J = 6.5 Hz, 2H), 7.44-7.39 (m, 6H), 7.30-7.28 (m, 2H), 6.16 (d, J = 4.5 Hz, 1H), 5.98 (d, J = 4.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 181.3, 179.4, 154.8, 138.6, 137.5, 135.2, 134.3, 133.2, 132.2, 131.1, 129.4, 128.9, 128.1, 127.8, 127.7, 127.4, 126.7, 126.1, 124.2, 121.0, 78.1. HRMS (ESI): calcd. for $C_{25}H_{17}O_3$ $[M+H^+]$ 365.1172; found 365.1175.

*Mixture of 2-(4-bromophenyl)-4-phenyl-2H-benzo[g]chromene-5,10-dione (**4b**) and 4-(4-bromophenyl)-2-phenyl-2H-benzo[g]chromene-5,10-dione (**4b'**) as 13:12.* Purification by flash chromatography afforded **4b** and **4b'** (0.057 g, 64% yield) as yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$/TMS): δ 8.11-8.09 (m, 1H), 8.00-7.99 (m, 1H), 7.73-7.68 (m, 2H), 7.56-7.51 (m, 3H), 7.46-7.39 (m, 4H), 7.28-7.26 (m, 1H), 7.17-7.14 (m, 1H), 6.15 (d, J = 4.5 Hz, 12/25×1H), 6.11 (d, J = 4.6 Hz, 13/25×1H), 5.96 (d, J = 4.6 Hz, 12/25×1H), 5.94 (d, J = 4.6 Hz, 13/25×1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 181.3, 181.2, 179.33, 179.28, 155.0, 154.6, 138.4, 137.6, 137.4, 136.6, 135.7, 134.4, 133.4, 133.3, 132.2, 132.1, 131.33, 131.28, 131.0, 129.5, 129.3, 129.1, 129.0, 128.2, 128.0, 127.7, 127.4, 126.8, 126.7, 126.2, 126.1, 124.5, 123.7, 123.5, 121.9, 121.1, 120.5, 78.2. HRMS (ESI): calcd. for $C_{25}H_{16}BrO_3$ $[M+H^+]$ 443.0277; found 443.0287.

*Mixture of 2-phenyl-4-(p-tolyl)-2H-benzo[g]chromene-5,10-dione (**4c**) and 4-phenyl-2-(p-tolyl)-2H-benzo[g]chromene-5,10-dione (**4c'**) as 13:12.* Purification by flash chromatography afforded **4c** and **4c'** (0.059 g, 78% yield) as yellow solid. ^{1}H NMR (500 MHz,

$CDCl_3$): δ 8.11-8.08 (m, 1H), 8.02-7.99 (m, 1H), 7.71-7.67 (m, 2H), 7.59-7.57 (m, 1H), 7.48-7.46 (m, 1H), 7.42-7.39 (m, 3H), 7.30-7.28 (m, 1H), 7.23-7.17 (m, 3H), 6.15-6.13 (m, 1H), 5.97-5.94 (m, 1H), 2.41 (s, 13/25×3H), 2.37 (s, 12/25×3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 181.4, 181.3, 179.5, 179.4, 154.81, 154.78, 139.5, 138.7, 137.6, 135.7, 135.1, 135.0, 134.4, 134.3, 134.2, 133.2, 133.1, 132.26, 132.23, 131.1, 129.5, 129.3, 128.9, 128.8, 128.1, 127.83, 127.76, 127.7, 127.4, 127.2, 126.7, 126.6, 126.0, 124.2, 123.7, 121.2, 121.0, 78.1, 78.0, 21.3, 21.2. HRMS (ESI): calcd. for $C_{26}H_{19}O_3$ [M+H$^+$] 379.1329; found 379.1326.

*Mixture of 4-(4-methoxyphenyl)-2-phenyl-2H-benzo[g]chromene-5,10-dione **(4d)** and 2-(4-methoxyphenyl)-4-phenyl-2H-benzo[g]chromene-5,10-dione **(4d')** as 2:1.* Purification by flash chromatography afforded **4d** and **4d'** (0.051 g, 65% yield) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10-8.07 (m, 1H), 8.02-7.99 (m, 1H), 7.71-7.68 (m, 2H), 7.58 (d, *J* = 6.9 Hz, 2/3×2H), 7.52 (d, *J* = 8.5 Hz, 1/3×2H), 7.43-7.39 (m, 3H), 7.31-7.29 (m, 2/3×1H), 7.22-7.21 (m, 1+1/3×1H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.12 (d, *J* = 4.2 Hz, 1H), 5.95, 5.93 (dd, *J* = 4.6, 4.4 Hz, 1H), 3.85 (s, 2/3×3H), 3.81 (s, 1/3×3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 181.3, 181.2, 179.4, 179.3, 160.5, 159.3, 154.8, 154.7, 138.7, 137.6, 135.0, 134.7, 134.18, 134.15, 133.09, 133.06, 132.3, 132.2, 131.05, 131.02, 130.9, 129.5, 129.3, 129.2, 128.8, 128.5, 128.0, 127.7, 127.6, 127.3, 126.6, 126.5, 125.9, 124.1, 123.3, 121.1, 120.9, 114.2, 113.5, 78.1, 77.9, 55.3, 55.2. HRMS (ESI): calcd. for $C_{26}H_{19}O_4$ [M+H$^+$] 395.1278; found 395.1294.

*Mixture of 2-phenyl-4-(m-tolyl)-2H-benzo[g]chromene-5,10-dione **(4e)** and 4-phenyl-2-(m-tolyl)-2H-benzo[g]chromene-5,10-dione **(4e')** as 27:23.* Purification by flash chromatography afforded **4e** and **4e'** (0.045 g, 60% yield) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12-8.10 (m, 1H), 8.01-7.99 (m, 1H), 7.71-7.69 (m, 2H), 7.59-7.57 (m, 1H), 7.42-7.37 (m, 4H), 7.30-7.27 (m, 2H), 7.21-7.20 (m, 23/50×1+23/50×1H), 7.12 (s, 27/50×1H), 7.06 (d, *J* = 7.7 Hz, 27/50×1H), 6.15 (d, *J* = 4.6 Hz, 27/50×1H), 6.12 (d, *J* = 4.5 Hz, 23/50×1H), 5.97-5.95 (m, 1H), 2.40 (s, 27/50×3H), 2.39 (s, 23/50×3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 181.30, 181.26, 179.4, 154.9, 154.7, 138.69, 138.67, 138.61, 137.7, 137.6, 137.5, 135.2, 135.0, 134.3, 133.2, 132.3, 131.1, 130.1, 129.3, 128.9, 128.7, 128.6, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 127.4, 126.7, 126.0, 124.8, 124.5, 124.3, 124.0, 121.2, 121.0, 78.3, 78.1, 21.50, 21.45. HRMS (ESI): calcd. for $C_{26}H_{19}O_3$ [M+H$^+$] 379.1329; found 379.1342.

*Mixture of 2-phenyl-4-(p-tolyl)-2H-benzo[g]chromene-5,10-dione **(4c)** and 4-phenyl-2-(p-tolyl)-2H-benzo[g]chromene-5,10-dione **(4c')** as 1:1.* Purification by flash chromatography afforded **4c** and **4c'** (0.047 g, 62% yield) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11-8.08 (m, 1H), 8.02-7.99 (m, 1H), 7.71-7.68 (m, 2H), 7.59-7.57 (m, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.43-7.39 (m, 3H), 7.30-7.28 (m, 1H), 7.23-7.17 (m, 3H), 6.15-6.13 (m, 1H), 5.97-5.95 (m, 1H), 2.42 (s, 1/2×3H), 2.37 (s, 1/2×3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 181.4, 181.3, 179.4, 154.81, 154.78, 139.4, 138.7, 137.58, 137.55, 135.7, 135.1, 135.0, 134.4, 134.24, 134.22, 133.15, 133.13, 132.25, 132.23, 131.0, 129.5, 129.3, 128.84, 128.80, 128.0, 127.8, 127.74, 127.68, 127.4, 127.2, 126.64, 126.61, 126.0, 124.2, 123.7, 121.2, 121.0, 78.1, 78.0, 21.3, 21.2. HRMS (ESI): calcd. for $C_{26}H_{19}O_3$ [M+H$^+$] 379.1329; found 379.1338.

*2-(2-Chlorophenyl)-4-phenyl-2H-benzo[g]chromene-5,10-dione **(4f)**.* Purification by flash chromatography afforded **4f** (0.025 g, 31% yield) as yellow solid, mp 158-160 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15-8.13 (m, 1H), 8.03-8.02 (m, 1H), 7.74-7.70 (m, 2H), 7.67-7.65 (m, 1H), 7.48-7.45 (m, 1H), 7.39-7.32 (m, 5H), 7.28-7.25 (m, 2H), 6.51 (d, *J* = 4.0 Hz, 1H), 5.87 (d, *J* = 3.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 181.3, 179.1, 155.2, 138.4, 135.3, 135.2, 134.4, 133.3,

132.7, 132.2, 131.1, 130.2, 130.1, 128.8, 128.1, 127.9, 127.4, 127.3, 126.7, 126.1, 123.8, 121.0, 75.6. HRMS (ESI): calcd. for $C_{25}H_{16}ClO_3$ $[M+H^+]$ 399.0782; found 399.0779.

4-(2-Chlorophenyl)-2-phenyl-2H-benzo[g]chromene-5,10-dione (***4f'***). Purification by flash chromatography afforded **4f'** (0.016 g, 20% yield) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10-8.08 (m, 1H), 7.99-7.97 (m, 1H), 7.69-7.60 (m, 4H), 7.46-7.32 (m, 7H), 6.27-6.16 (m, 1H), 6.00-5.85 (m, 1H). ^{13}C NMR (125 MHz, DMSO): δ 181.1, 179.2, 138.5, 135.1, 134.2, 131.6, 131.1, 130.6, 129.7, 129.33, 129.25, 128.1, 127.7, 126.4, 126.1, 120.4, 75.1. HRMS (ESI): calcd. for $C_{25}H_{16}ClO_3$ $[M+H^+]$ 399.0782; found 399.0800.

Mixture of 4-(4-bromophenyl)-2-(4-chlorophenyl)-2H-benzo[g]chromene-5,10-dione ***(4g)*** *and 2-(4-bromophenyl)-4-(4-chlorophenyl)-2H-benzo[g]chromene-5,10-dione* ***(4g')***. Purification by flash chromatography afforded **4g** and **4g'** (0.066 g, 69% yield) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11-8.09 (m, 1H), 8.00-7.98 (m, 1H), 7.72-7.70 (m, 2H), 7.55-7.49 (m, 3H), 7.44-7.35 (m, 3H), 7.21-7.19 (m, 1H), 7.15-7.13 (m, 1H), 6.11, 6.10 (dd, J = 4.6, 4.7 Hz, 1H), 5.921, 5.917 (dd, J = 4.5, 4.5 Hz, 1H). ^{13}C NMR (125 MHz, DMSO): δ 180.8, 178.7, 154.6, 137.7, 137.32, 137.26, 136.8, 134.5, 133.7, 133.6, 133.0, 132.9, 132.1, 131.75, 131.72, 130.8, 130.7, 129.6, 129.5, 129.3, 129.2, 128.8, 127.7, 126.0, 125.5, 125.08, 125.07, 122.4, 120.6, 120.44, 120.38, 76.32, 76.29. HRMS (ESI): calcd. for $C_{25}H_{15}BrClO_3$ $[M+H^+]$ 476.9888; found 476.9866.

1-Isopropyl-2,4-diphenyl-1,10a-dihydrobenzo[g]quinoline-5,10(2H,4aH)-dione ***(4h)***. Purification by flash chromatography afforded **4h** (0.011 g, 13% yield) as purple oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06-8.04 (m, 1H), 7.93-7.91 (m, 1H), 7.64-7.62 (m, 2H), 7.37 (d, J = 7.7 Hz, 2H), 7.34-7.30 (m, 3H), 7.27-7.18 (m, 5H), 5.93 (d, J = 7.4 Hz, 1H), 5.35 (d, J = 7.4 Hz, 1H), 4.92-4.89 (m, 1H), 1.49 (d, J = 6.6 Hz, 3H), 1.30 (d, J = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 182.9, 180.2, 146.4, 141.7, 140.8, 136.9, 133.8, 133.1, 132.6, 132.4, 128.4, 127.9, 127.7, 127.4, 127.1, 126.3, 126.1, 125.9, 122.7, 122.4, 53.8, 52.7, 24.3, 21.7. HRMS (ESI): calcd. For $C_{28}H_{23}NO_2$ $[M+H^+]$ 406.1802; found 406.1809.

2,4-Diphenylpyrano[3,2-c]chromen-5(2H)-one ***(4i)***. Purification by flash chromatography afforded **4i** (0.048 g, 68% yield) as yellow solid, mp 149-151 ^{o}C . ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89-7.87 (m, 1H), 7.60-7.54 (m, 3H), 7.46-7.41 (m, 3H), 7.40-7.35 (m, 5H), 7.32 (d, J = 8.2 Hz, 1H), 7.30-7.27 (m,1H), 6.17 (d, J = 4.2 Hz, 1H), 5.79 (d, J = 4.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.4, 158.7, 153.7, 138.3, 137.9, 135.3, 132.6, 129.3, 129.0, 128.0, 127.9, 127.55, 127.47, 124.0, 123.3, 120.3, 116.7, 115.3, 102.9, 78.8. HRMS (ESI): calcd. for $C_{24}H_{17}O_3$ $[M+H^+]$ 353.1172; found 353.1180.

9-Methyl-2,4-diphenylpyrano[3,2-c]chromen-5(2H)-one ***(4j)***. Purification by flash chromatography afforded **4j** (0.038 g, 52% yield) as yellow solid, mp 202-204 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (s, 1H), 7.60 (d, J = 6.9 Hz, 2H), 7.48-7.36 (m, 9H), 7.23 (d, J = 8.4 Hz, 1H), 6.15 (d, J = 4.1 Hz, 1H), 5.78 (d, J = 4.1 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.4, 158.9, 151.8, 138.3, 137.9, 135.3, 133.69, 133.66, 129.2, 128.9, 127.9, 127.8, 127.5, 127.4, 122.8, 120.1, 116.4, 114.8, 102.7, 78.8, 20.9. HRMS (ESI): calcd. For $C_{25}H_{19}O_3$ $[M+H^+]$ 367.1329; found 367.1317.

9-Chloro-2,4-diphenylpyrano[3,2-c]chromen-5(2H)-one ***(4k)***. Purification by flash chromatography afforded **4k** (0.051 g, 66% yield) as yellow solid, mp 203-205 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, J = 2.5 Hz, 1H), 7.59-7.57 (m, 2H), 7.50-7.44 (m, 4H), 7.40-7.33 (m, 5H), 7.26 (d, J = 8.8 Hz, 1H), 6.17 (d, J = 4.2 Hz, 1H), 5.80 (d, J = 4.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.1, 158.1, 151.9, 137.9, 137.6, 135.0, 132.5, 129.53, 129.50, 129.0, 128.00, 127.98,

127.6, 127.4, 122.7, 120.8, 118.1, 116.4, 103.4, 79.1. HRMS (ESI): calcd. For $C_{24}H_{16}ClO_3$ [M+H$^+$] 387.0782; found 387.0794.

*9-Methoxy-2,4-diphenyl-4a,10b-dihydropyrano[3,2-c]chromen-5(2H)-one (**4l**).* Purification by flash chromatography afforded **4l** (0.042 g, 54% yield) as yellow solid, mp 148-149 ^oC. ^1H NMR (500 MHz, $CDCl_3$): δ 7.61-7.59 (m, 2H), 7.48-7.43 (m, 3H), 7.42-7.35 (m, 5H), 7.27-7.25 (m, 2H), 7.16-7.13 (m, 1H), 6.16 (d, J = 4.2 Hz, 1H), 5.79 (d, J = 4.2 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.1, 158.8, 155.9, 148.2, 138.2, 137.9, 135.3, 129.2, 128.9, 127.9, 127.8, 127.5, 127.4, 120.9, 120.3, 117.8, 115.4, 104.8, 103.0, 78.8, 55.9. HRMS (ESI): calcd. For $C_{25}H_{19}O_4$ [M+H$^+$] 383.1278; found 383.1272.

3. **General procedure for the coupling reaction catalyzed by DDQ**: To a solution of lawsone **1a** or 4-hydroxycoumarin **5a** (0.2 mmol) and 1,3-diphenylpropene **2a** (0.24 mmol, 0.047 g) in $MeNO_2$ (1 mL), DDQ (0.04 mmol, 0.009 g) and AIBN (0.04 mmol, 0.007 g) was added. The resulting mixture was stirred for 6 hrs at 80 ^oC in the presence of oxygen atmosphere (oxygen balloon). After the completion of the reaction, the solvent was concentrated under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether and ethyl acetate (3:1) as the eluent to give the pure product **3a** or **6a**.

Supporting information

Copies of ^1H and ^{13}C NMR spectra for all isolated compounds.

Acknowledgements

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