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Ru-Catalyzed δ-Arylation of *para*-Quninone Methides with Aryl Diazonium Salts to Synthesize Fuchsones

Lei Dai[†], Kaimin Mao[†], Ge Zhang[†], Chang Wang[†], Yun Liu[†], Liangce Rong*[,†], Jinpeng Zhang*[,‡]

[†]Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, School of Chemistry and Materials Science, Jiangsu Normal University, Xuzhou, 221116, Jiangsu, PR China

[‡]Key Lab of Environment and Health, School of Public Health, Xuzhou Medical University, Xuzhou, 221004, Jiangsu, PR China

E-mail. lcrong@jsnu.edu.cn; xiaopangpeng@126.com

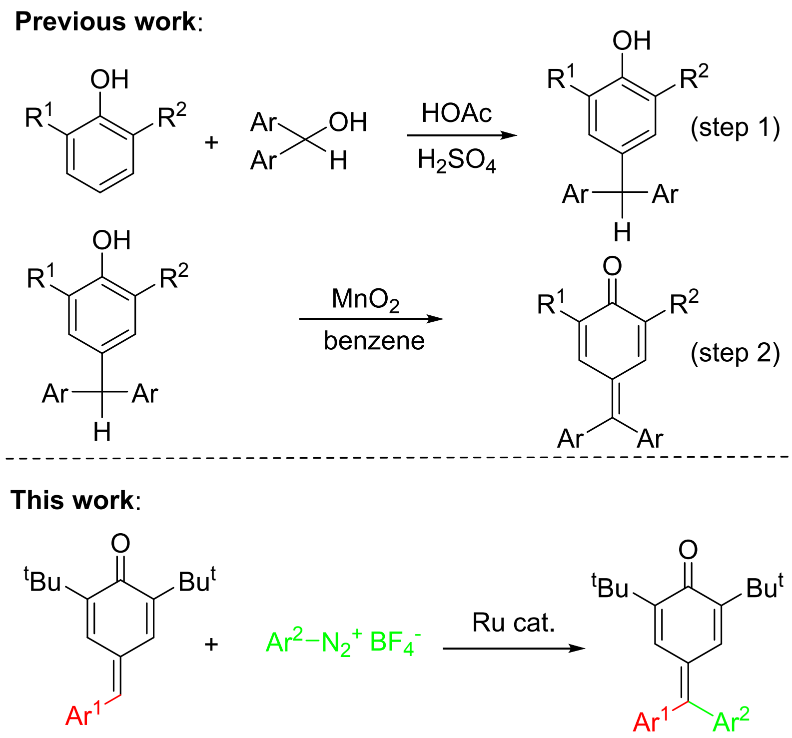
ABSTRACT: A novel reaction mode and efficient ruthenium-catalyzed Matsuda−Heck-type arylation of *para*-quinone methides (*p*-QMs) with aryl diazonium salts has been developed for the synthesis of symmetrical or unsymmetrical δ,δ'-diaryl quinone methides (fuchsones). Aryl groups are introduced at the δ-position of *p*-QMs via tandem olefin insertion reaction/β-H elimination processes. This reaction features advantages such as mild and green conditions, broad reactants scope and high yields.

INTRODUCTION

As a special structural system, fuchsones have been found to be able to rapidly interconvert chiral conformers in the liquid or solution state,[1] which were elicited interest from people because of their photochromic properties and utility in dyes, photographic printing, and to stabilize radicals,[2] etc. Recent study have shown that they can also be used as novel nonpeptide inhibitor of Caspase-3.[3] The traditional method for the synthesis of fuchsones was a two-step reaction. First, the substituted 4-hydroxytriphenylmethanes was obtained by the condensation reaction of substituted phenols and benzhydrol, and then fuchsones was formed by the oxidation of active manganese dioxide, nickel peroxide, or lead dioxide in benzene solution (Scheme 1, Previous work).[4] Other reported synthesis methods almost have been developed on the basis of this reaction.[1,5] Surprisingly, few new and effective methods for the synthesis of fuchsones have been reported so far.

para-Quinone methides (*p*-QMs) have been recognized for more than one century.[6] This motif exists in a variety of biologically active compounds[7] and is a key intermediates of versatile medicinal and biological processes.[8] Consequently, there are great demands to explore new reaction of *p*-QMs. Up to now, many reactions have been accomplished by employing *p*-QMs as the substrates and the main reaction modes involve reduction,[9] cyclization[10-13] and 1,6-conjugate addition.[14-22] Although great progress has been made, there are still some limitations needing to be overcome. i) The reported reactions of *p*-QMs generally led to aromatic products, whereas dearomatized products were rarely obtained. ii) The new reaction mode has not broken through. iii) To the best of our knowledge, there is no report of aryl diazonium salts to react with *p*-QMs so far. Hence, there are great demands to synthesize dearomatic products via olefin insertion reaction/ β-H elimination processes of *p*-QMs as well as to introduce aryl groups at the δ-position of *p*-QMs.

In the past decades, aryl diazonium salts have been widely used in organic synthesis.[23,24] Among these, transition-metal catalyzed Matsuda−Heck reaction is a typical application which reacted arenediazonium salts with alkenes in the aid of palladium catalyst.[25] Compared with traditional electrophiles as aryl halides and aryl triflates, aryl diazonium salts generate nitrogen as the only byproduct and are more eco-friendly. Although some alkenes were applied as the coupling partners in Matsuda−Heck reaction, *p*-QMs had never being investigated yet. Herein, we reported a novel reaction mode and highly regioselective ruthenium-catalyzed δ-arylation of *p*-QMs with aryldiazonium salts to synthesize fuchsone derivatives (Scheme 1, This work). This reaction proceeds under mild conditions and give the symmetrical or unsymmetrical fuchsones in high yields.

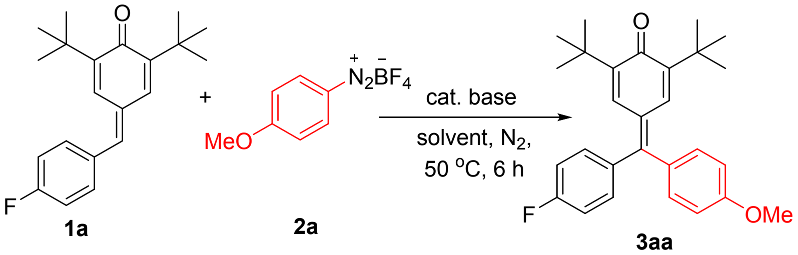


Scheme 1. Synthesis of fuchsone derivatives (Previous work and This work)

RESULTS AND DISCUSSION

For the optimization of reaction conditions, we chose 2,6-di-tert-butyl-4-(4-fluorobenzylidene)cyclohexa-2,5-dien-1-one **1a** and 4-methoxyphenyl diazonium salt **2a** as the model reactants, and the results were listed in Table 1. Initially, by heating the mixture of **1a** (0.3 mmol), **2a** (0.6 mmol), palladium acetate (10 mol%), potassium carbonate (0.3 mmol) in acetonitrile (2 mL) under nitrogen atmosphere for 6 hours in a Schlenk tube, we isolated target product **3a** in 42% yields (Table 1, entry 1). Different metal catalysts were then examined, and ruthenium chloride performed the best and afforded product **3a** in 79 % yield (Table1, entries 2-7). With $RuCl_3$ as the catalyst, we tried other base instead of K_2CO_3, but did not get better result (Table 1, entries 8-13). On the basis of this, we further investigated the effect of different solvents. The results showed acetonitrile was the best choice (Table1, entries 14-18). For the loading of catalyst and base, it showed that 10 mol% ruthenium catalyst and 1 equiv of K_2CO_3 was enough to ensure the high yield of **3a** (Table 1, entries 19-23). In addition, the reaction yield decreased obviously with decreasing the reaction temperature, but the yield of the reaction did not increase significantly with the increase of reaction temperature (Table1, entries 24, 25). Finally, we carried out this reaction in the air, and isolated **3a** only in 30% yield (Table1, entry 26). It is probably due to diazonium salt **2a** is reactive in the air and tends to decompose. Therefore, the optimized conditions were set to heating the mixture of **1a** (0.3 mmol), **2a** (0.6 mmol) in acetonitrile at 60 ºC for 6 h in a sealed tube with 10 mol% $RuCl_3$ as the catalyst and 1 equiv. of K_2CO_3 as the base.

Table 1. Optimization of reaction conditions[a]



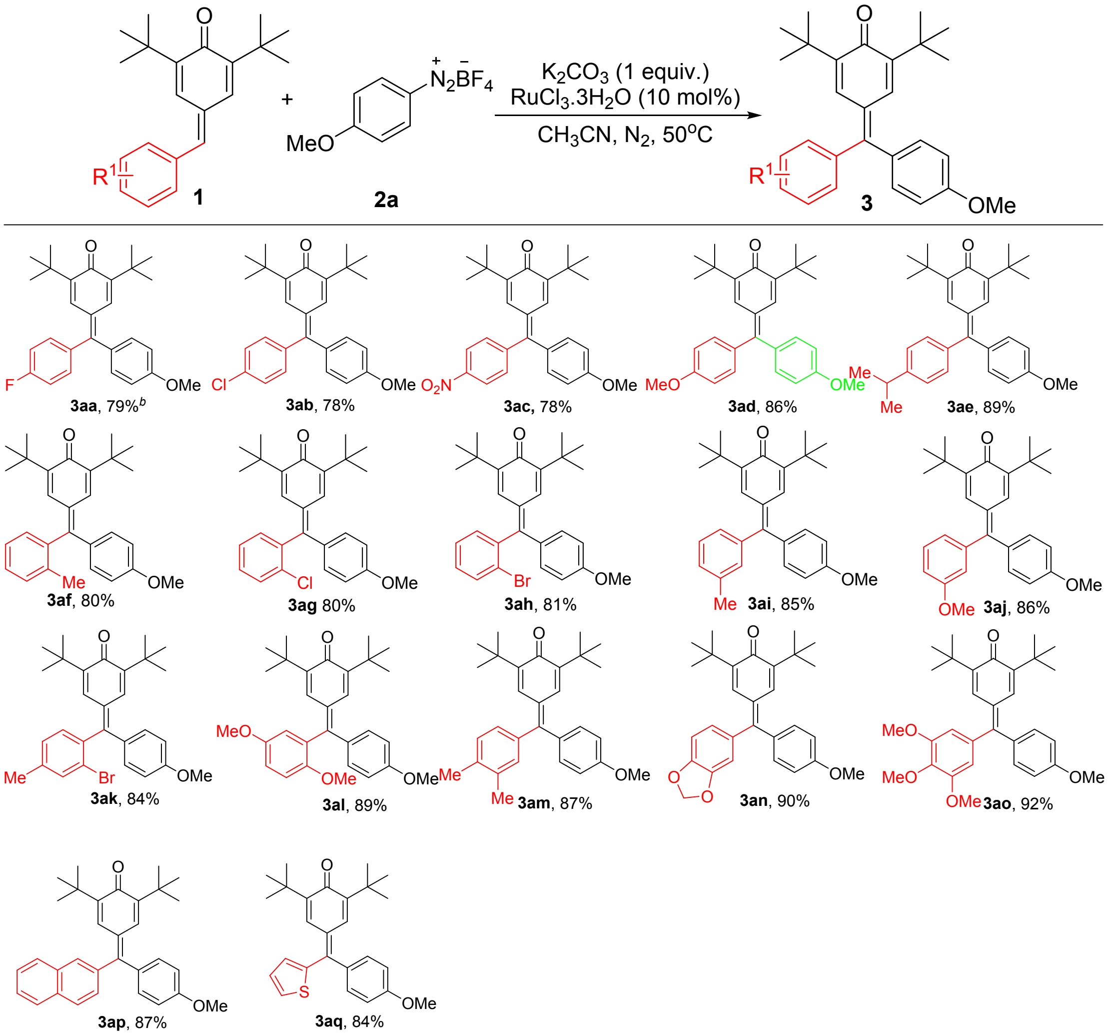
Entry	Cat. (mol%)	Base	Solvent	Yield (%)[b]
1	$Pd(OAc)_2$ (10)	K_2CO_3	CH_3CN	42
2	$Pd(pph_3)_4$ (10)	K_2CO_3	CH_3CN	40
3	$FeCl_2$ (10)	K_2CO_3	CH_3CN	30
4	CuI (10)	K_2CO_3	CH_3CN	35
5	$Cu(OAc)_2$ (10)	K_2CO_3	CH_3CN	37
6	$RuCl_3{\cdot}3H_2O$ (10)	K_2CO_3	CH_3CN	79
7	$Ru(bpy)_3Cl_2$ (10)	K_2CO_3	CH_3CN	32
8	$RuCl_3{\cdot}3H_2O$ (10)	Et_3N	CH_3CN	49
9	$RuCl_3{\cdot}3H_2O$ (10)	^{t}BuOK	CH_3CN	60
10	$RuCl_3{\cdot}3H_2O$ (10)	Cs_2CO_3	CH_3CN	51
11	$RuCl_3{\cdot}3H_2O$ (10)	DBU	CH_3CN	23
12	$RuCl_3{\cdot}3H_2O$ (10)	KOH	CH_3CN	30
13	$RuCl_3{\cdot}3H_2O$ (10)	DABCO	CH_3CN	32
14	$RuCl_3{\cdot}3H_2O$ (10)	K_2CO_3	DCE	30
15	$RuCl_3{\cdot}3H_2O$ (10)	K_2CO_3	DMF	18
16	$RuCl_3{\cdot}3H_2O$ (10)	K_2CO_3	DMSO	24
17	$RuCl_3{\cdot}3H_2O$ (10)	K_2CO_3	1,4-dioxane	34
18	$RuCl_3{\cdot}3H_2O$ (10)	K_2CO_3	THF	trace

19	$RuCl_3{\cdot}3H_2O$ (5)	K_2CO_3	CH_3CN	28
20	$RuCl_3{\cdot}3H_2O$ (15)	K_2CO_3	CH_3CN	78
21	$RuCl_3{\cdot}3H_2O$ (20)	K_2CO_3	CH_3CN	79
22	$RuCl_3{\cdot}3H_2O$ (10)	K_2CO_3	CH_3CN	78[c]
23	$RuCl_3{\cdot}3H_2O$ (10)	K_2CO_3	CH_3CN	43[d]
24	$RuCl_3{\cdot}3H_2O$ (10)	K_2CO_3	CH_3CN	52[e]
25	$RuCl_3{\cdot}3H_2O$ (10)	K_2CO_3	CH_3CN	78[f]
26	$RuCl_3{\cdot}3H_2O$ (10)	K_2CO_3	CH_3CN	30[g]

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.6 mol), catalyst (5%-20%), base (1 eq), solvent (2.0 ml), N_2, 50 °C, 6h; [b] Isolated yield; [c] 2 equiv of K_2CO_3. [d] 0.5 equiv of K_2CO_3. [e] Under 40 °C. [f] Under 70 °C. [g] In the air.

With the optimal conditions in hand, we then screened the scope of reactants **1** and **2**. By employing 4-methoxy arenediazonium salt **2a** as the coupling partner, we firstly investigated the generality of *p*-QMs **1** (Table 2). It is found that electronic and steric factors of *p*-QMs have little effect to this reaction. For *para*-substituted *p*-QMs with electron-donating groups (OMe, *i*-Pr) or with electron-withdrawing groups (F, Cl, NO_2), the target products **3aa-3ae** were afforded in high yields. However, it seems that the yield of *p*-QMs with electron-donating groups is better than that of with withdrawing groups (**3aa-3ac** vs **3ad** and **3ae**). Similarly, *ortho*-substituted *p*-QMs attached with different groups underwent this reaction smoothly as well, giving products **3af-3ah** in 80% to 81% yields. Besides, *meta*-substituted *p*-QMs also gived corresponding products with good yields (**3ai**, **3aj**). It should be noted that the position of substituents has no effect on the yield of the reaction, which can be seen from the yields of **3ab** & **3ag** and **3ad** & **3aj**. In addition, the multi-substituted and annulated *p*-QMs were all proven to be good reactant substrates, generating **3ak-3ap** in 84% to 92% yields. Moreover, the heterocyclic *p*-QMs was also be applied to this synthesis, generating **3aq** in 84% yield. In Table 2, we could see compound **3ad** is a absolutely symmetrical structure.

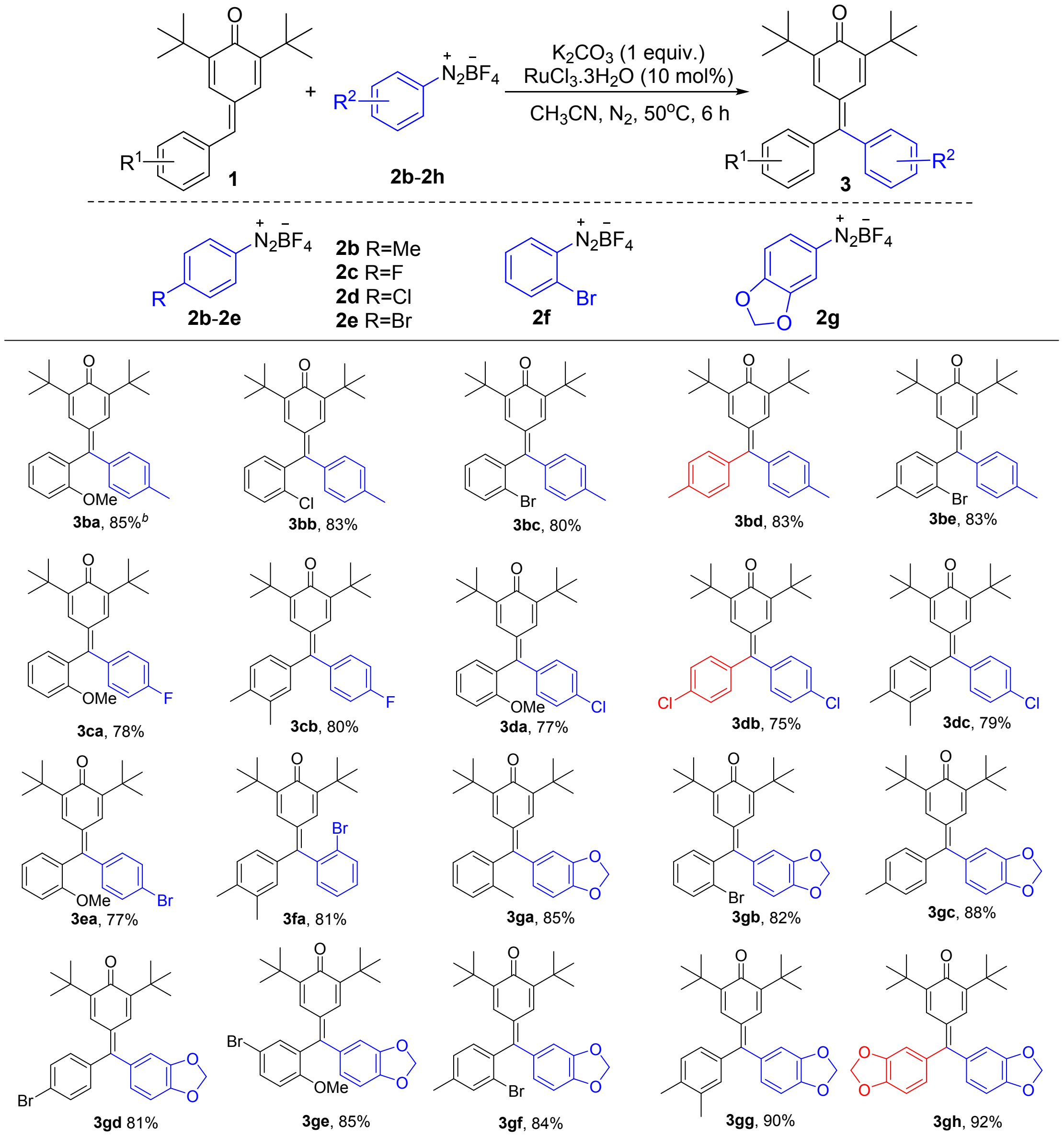
Table 2. Scope of reactant **1**[a]



[a]Conditions: **1** (0.3 mmol), **2a** (0.6 mol), $RuCl_3{\cdot}3H_2O$ (10 mol%), K_2CO_3 (1 eq), acetonitrile (2.0 ml), N_2, 50 °C, 6h (monitored by TLC); [b]Isolated yield.

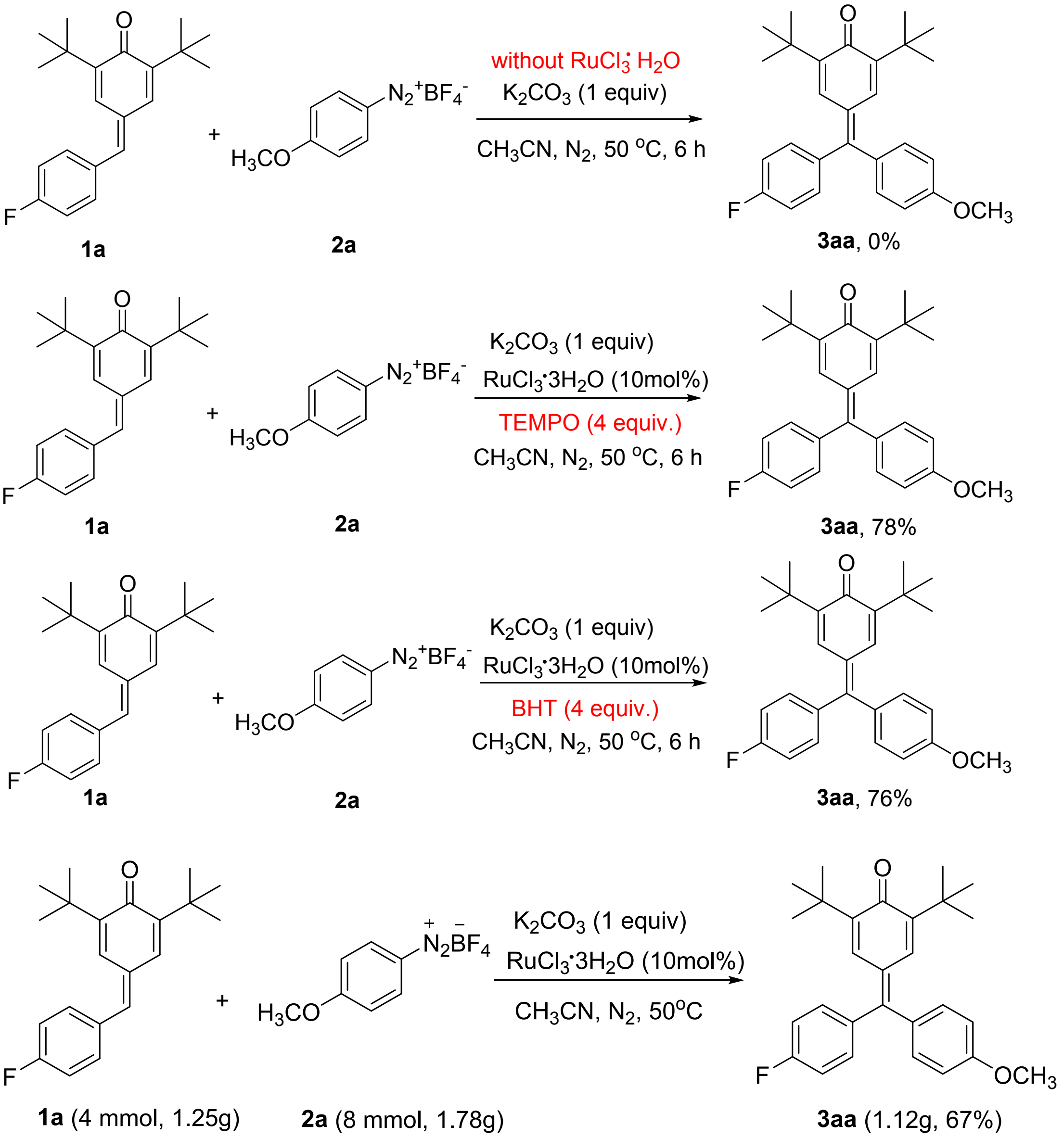
Subsequently, we investigated the scope of aryl diazonium salts **2** (Table 3). Different-substituted aryl diazonium salts **2b-2g** all showed good reaction activities. For instance, *para*-substituted diazonium salts **2b-2e** either with electron-withdrawing group (Me) or with electron-withdrawing groups (F, Cl, Br) reacted with diversified *p*-QMs **1** well, generating products **3ba-3ea** in high yields. Moreover, *ortho*-substituted diazonium salt **2f** was also well used in this preferred condition and given **3fa** with satisfying yield. Moreover, benzo[d][1,3]dioxole-5-diazonium salt **2g** also performed well in the synthesis, delivering products **3ga-3gh** in 81% to 92% yields. In these this synthetic scope, compounds **3bd**, **3db**, and **3gh** are the perfectly symmetrical structures.

Table 3. Scope of reactant **2**[a]



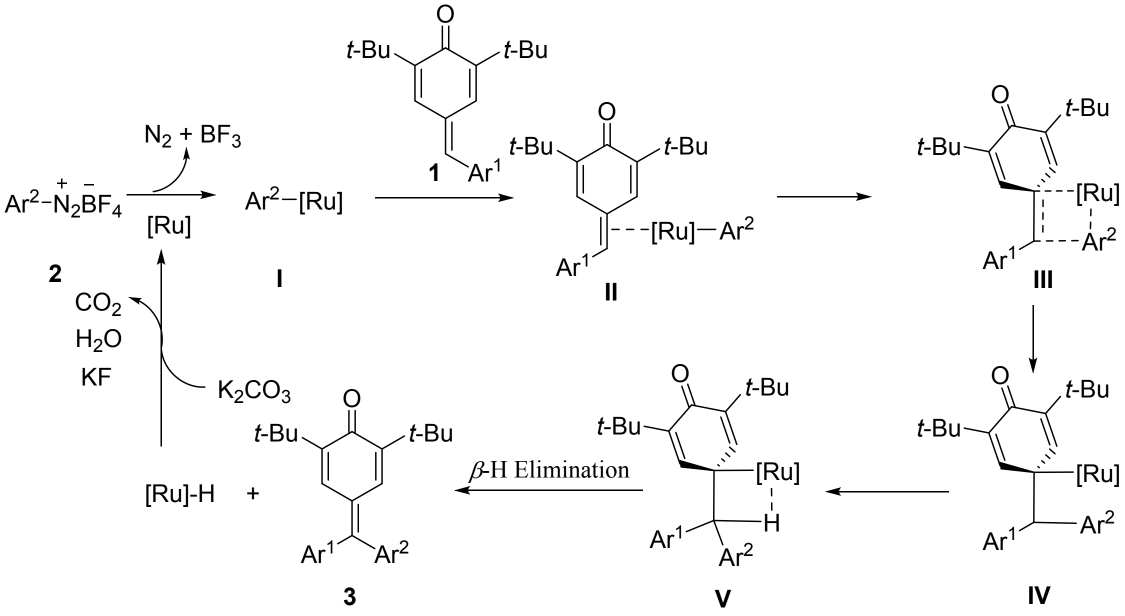
[a]Conditions: **1** (0.3 mmol), **2** (0.6 mol), RuCl$_3$·3H$_2$O (10 mol%), K$_2$CO$_3$ (1 eq), acetonitrile (2.0 ml), N$_2$, 50 ^{o}C, 6h (monitored by TLC); [b]Isolated yield.

To shed light on the reaction mechanism, some control reactions was investigated carefully (Scheme 2). When RuCl$_3$·3H$_2$O was absent in standard condition, the **3aa** was not obtained, which meant that the catalyst was indispensable. Subsequently, we added 4 equiv of radical scavenger TEMPO (2,2,6,6-Tetramethylpiperidine 1-oxyl) or BHT (2,6-Di-tert-butyl-4-methyl- phenol) into the model reaction, and found **3aa** was formed in 78% and 76% yields, respectively. These results illustrated the reaction should occurred via a non-radical pathway. In addition, the successful completion of gram-scale experiment indicates that this synthesis has a good application prospect.



Scheme 2. Control and gram-scale experiments

Based on our experimental results, a possible reaction mechanism was proposed as follows (Scheme 3). At first, aryl diazonium salt was inserted by [Ru] species to generate aryl-ruthenium intermediate **I** accompanying removal of N_2 and BF_3. Through the olefin insertion reaction of **I** and *p*-QMs **1** to afford intermediate **II** and intermediate **III,** which finally forms intermediate **IV**. The intermediate **V** is formed by the characteristic of easy coordination of hydrogen atom with ruthenium, After *β*-H elimination, the product **3** is obtained, and with the help of K_2CO_3, [Ru] species is freshly generated again.



Scheme 3. Possible mechanism

CONCLUSION

In conclusion, we have developed a novel reaction mode and efficient ruthenium-catalyzed arylation of *p*-QMs with aryl diazonium salts to synthesize fuchsones derivatives. A variety of reactants survive in the conditions and symmetrical or unsymmetrical products are formed in high yields. This reaction represents a new Matsuda–Heck-type reaction by employing *p*-QMs as the coupling partner to construct Csp^2-Csp^2 bond with diazonium salts for the first time.

EXPERIMENTAL SECTION

General Information.

Unless stated otherwise, all reactions were conducted in Schlenk tube under nitrogen condition. All solvents and reagents were received from commercial sources without further purification. *para*-Quinone methides[26] and aryl diazonium salts[27] were synthesized following reported protocols. All the reactions were monitored by TLC. Silica gel (particle size 10–50 μm) was used for flash column chromatography. NMR spectra were recorded on Bruker-400 spectrometer at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR). High resolution mass spectra (HRMS) were recorded on a

Bruker microTOF-Q 134 instrument with Electron Spray Ionization (ESI) resource.

General Procedure for the Synthesis Product 3.

To a mixture of $RuCl_3·3H_2O$ (0.03 mmol) and K_2CO_3 (0.3 mmol) in CH_3CN (2.0 mL) under N_2 atmosphere, *para*-quinone methides **1** (0.3 mmol) and aryl diazonium salts **2** (0.6 mmol) were added. The system was stirred at 50 °C using an oil bath for 6 h (the reaction was monitored by TLC). After the reaction was completed, the reaction mixture was filtered by diatomite. The filtere was diluted with brine (10 mL) and extracted with ethyl acetate (5 mL x 3). The organic layer was washed with water (10 mL), then separated, dried over Na_2SO_4, and concentrated under vacuum. The residue was further purified by flash column chromatography on silica gel (petroleum ether: EtOAc = 40:1) to afford desired product **3** as a yellow solid.

Procedure for the Control Reaction.

To a mixture of $RuCl_3·3H_2O$ (0.03 mmol) and K_2CO_3 (0.3 mmol) in CH_3CN (2.0 mL) under N_2 atmosphere, 2,2,6,6-tetramethylpiperidinooxy (TEMPO) (1.2 mmol) or butylated hydroxytoluene (BHT) (1.2 mmol), 2,6-di-tert-butyl-4-(4-fluorobenzyli dene)cyclohexa-2,5-dien-1-one **1a** (0.3 mmol) and 4-methoxybenzenediazonium salt **2a** (0.6 mmol) were added. The system was stirred at 50 °C for 6 h and the reaction was monitored by TLC.

Procedure for the Synthesis of 3aa on 4 mmol Scale.

To a mixture of $RuCl_3·3H_2O$ (0.104 g, 0.4 mmol) and K_2CO_3 (0.55 g, 4 mmol) in CH_3CN (10.0 mL) under N_2 atmosphere, 2,6-di-tert-butyl-4-(4-fluorobenzylidene) cyclohexa-2,5-dien-1-one **1a** (1.25 g, 4 mmol) and 4-methoxybenzenediazonium salt **2a** (1.78 g, 8 mmol) were added. The system was stirred at 50 °C for 6 h (the reaction was monitored by TLC). After the reaction was completed, the reaction mixture was filtered by diatomite. The filtere was diluted with brine (40 mL) and extracted with ethyl acetate (20 mL X 3). The organic layer was washed with water (40 mL), then separated, dried over Na_2SO_4, and concentrated under vacuum. The residue was further purified by flash column chromatography on silica gel (petroleum ether: EtOAc = 40:1) to afford desired product **3aa** (1.12 g, 67%) as a yellow solid.

Characterization Data of Product 3.

*2,6-Di-tert-butyl-4-((4-fluorophenyl)(4-methoxyphenyl)methylene)cyclohexa-2,5-dien-1-one (**3aa**)* yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 79% (99 mg). mp: 169 - 170 ^{o}C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.30 - 7.26 (m, 3H), 7.23 - 7.20 (m, 2H), 7.18 - 7.13 (m, 3H), 6.99 (d, J = 8.8 Hz, 2H), 3.93 (s, 3H), 1.31 (s, 9H), 1.29 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.1, 163.4 (d, J_{C-F} = 249.2 Hz), 160.8, 154.9, 147.3 (double), 137.2 (d, J_{C-F} = 2.9 Hz), 134.1 (d, J_{C-F} = 8.3 Hz), 133.9, 133.1, 132.2, 132.0, 129.3, 115.2 (d, J_{C-F} = 21.6 Hz), 113.7, 55.5, 35.4 (double), 29.7, 29.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{28}H_{31}FNaO_2$ 441.2206; Found 441.2213.

*2,6-Di-tert-butyl-4-((4-chlorophenyl)(4-methoxyphenyl)methylene)cyclohexa-2,5-dien-1-one (**3ab**)* yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 78% (102 mg). mp: 160 - 161 ^{o}C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.44 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 2.8 Hz, 1H), 7.25 - 7.19 (m, 4H), 7.14 (d, J = 2.4 Hz, 1H), 7.01 - 6.96 (m, 2H), 3.93 (s, 3H), 1.31 (s, 9H), 1.29 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.1, 160.8, 154.5, 147.5, 147.4, 139.6, 135.5, 133.9, 133.4, 132.9, 132.1, 131.7, 129.5, 128.4, 113.7, 55.5, 35.4, 29.7, 29.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{28}H_{31}ClNaO_2$ 457.1910; Found 457.1899.

*2,6-Di-tert-butyl-4-((4-methoxyphenyl)(4-nitrophenyl)methylene)cyclohexa-2,5-dien-1-one (**3ac**)* yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 78% (104 mg). mp: 197 - 198 ^{o}C. ^1H

NMR (400 MHz, $CDCl_3$) δ: 8.32 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 2.8 Hz, 1H), 7.21 - 7.17 (m, 2H), 7.03 (d, *J* = 2.8 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 3.93 (s, 3H), 1.31 (s, 9H), 1.27 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.1, 161.0, 152.2, 148.4, 148.3, 147.9, 147.8, 133.7, 132.8, 132.2, 131.7, 130.9, 130.7, 123.3, 114.0, 55.6, 35.5, 35.5, 29.7, 29.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{28}H_{31}NNaO_4$ 468.2151; Found 468.2144.

*4-(Bis(4-methoxyphenyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one **(3ad)***

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 86% (111 mg). mp: 178 - 179 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.24 (s, 2H), 7.22 (s, 4H), 7.00 - 6.97 (m, 4H), 3.93 (s, 6H), 1.31 (s, 18H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.0, 160.8, 156.6, 146.7, 134.1, 133.5, 132.5, 128.6, 113.5, 55.5, 35.3, 29.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{29}H_{34}NaO_3$ 453.2406; Found 453.2397.

*2,6-Di-tert-butyl-4-((4-isopropylphenyl)(4-methoxyphenyl)methylene)cyclohexa-2,5-dien-1-one **(3ae)***

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 89% (118 mg). mp: 182 - 183 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.31 (d, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 2.0 Hz, 1H), 7.24 (d, *J* = 2.0 Hz, 2H), 7.22 (d, *J* = 2.8 Hz, 2H), 7.20 (s, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 3.93 (s, 3H), 3.02 (dt, *J* = 13.6, 6.8 Hz, 1H), 1.36 (s, 3H), 1.35 (s, 3H), 1.32 (s, 9H), 1.30 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.1, 160.6, 156.8, 150.4, 146.9, 146.8, 138.5, 134.0, 133.4, 132.5, 132.4, 128.9, 126.0, 113.4, 55.4, 35.3 (double), 34.0, 29.6 (double), 23.9. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{31}H_{38}NaO_2$ 465.2770; Found 465.2768.

*2,6-Di-tert-butyl-4-((4-methoxyphenyl)(o-tolyl)methylene)cyclohexa-2,5-dien-1-one **(3af)***

yellow solid, isolated yield 80% (99 mg). mp: 142 - 143 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.46

(d, J = 2.4 Hz, 1H), 7.39 - 7.35 (m, 1H), 7.31 - 7.27 (m, 2H), 7.24 (d, J = 8.8 Hz, 2H), 7.19 - 7.15 (m, 1H), 6.96 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 2.4 Hz, 1H), 3.91 (s, 3H), 2.05 (s, 3H), 1.35 (s, 9H), 1.22 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.3, 160.5, 155.4, 147.5, 147.2, 140.5, 137.1, 133.1, 132.3, 131.9, 131.3, 131.1, 130.5, 129.3, 128.7, 125.4, 113.7, 55.5, 35.4, 35.2, 29.7, 29.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{29}H_{34}NaO_2$ 437.2457; Found 437.2445.

*2,6-Di-tert-butyl-4-((2-chlorophenyl)(4-methoxyphenyl)methylene)cyclohexa-2,5-dien-1-one (**3ag**)*

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 80% (104 mg). mp: 126 - 127 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.51 (dd, J = 7.6, 2.0 Hz, 1H), 7.43 (d, J = 2.4 Hz, 1H), 7.42 - 7.38 (m, 2H), 7.29 (dd, J = 7.2, 2.0 Hz, 1H), 7.26 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.80 (d, J = 2.4 Hz, 1H), 3.91 (s, 3H), 1.34 (s, 9H), 1.23 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.4, 160.4, 151.6, 148.1, 147.5, 139.7, 134.1, 133.0, 132.4, 131.6, 131.4, 131.0, 130.1, 130.0, 129.9, 126.4, 113.7, 55.4, 35.5, 35.2, 29.7, 29.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{28}H_{31}ClNaO_2$ 457.1910; Found 457.1907.

*4-((2-Bromophenyl)(4-methoxyphenyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (**3ah**)*

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 81% (116 mg). mp: 123 - 124 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.71 (d, J = 8.0 Hz, 1H), 7.47 - 7.41 (m, 2H), 7.33 (dd, J = 8.0, 2.0 Hz, 1H), 7.30 (t, J = 2.0 Hz, 1H), 7.27 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.78 (d, J = 2.4 Hz, 1H), 3.91 (s, 3H), 1.34 (s, 9H), 1.23 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.4, 160.5, 153.0, 148.2, 147.5, 141.7, 133.4, 133.2, 132.4, 131.5, 131.4, 131.1, 130.0, 129.8, 127.1, 124.2, 113.7, 55.5, 35.6, 35.3, 29.8, 29.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{28}H_{31}BrNaO_2$ 501.1405; Found 501.1409.

*2,6-Di-tert-butyl-4-((4-methoxyphenyl)(m-tolyl)methylene)cyclohexa-2,5-dien-1-one (**3ai**)* yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 85% (106 mg). mp: 170 - 171 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 2.8 Hz, 2H), 7.25 - 7.22 (m, 2H), 7.21 (d, *J* = 2.4 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.93 (s, 3H), 2.42 (s, 3H), 1.32 (s, 9H), 1.29 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 186.2, 160.7, 156.7, 147.1, 146.9, 141.1, 137.6, 133.9, 133.3, 132.9, 132.5, 132.3, 130.1, 129.5, 129.2, 127.8, 113.5, 55.5, 35.4, 35.3, 29.7, 29.6, 21.4. HRMS (ESI-TOF) m/z: [M+Na]$^{+}$ Calculated for $C_{29}H_{34}NaO_2$ 437.2457; Found 437.2466.

*2,6-Di-tert-butyl-4-((3-methoxyphenyl)(4-methoxyphenyl)methylene)cyclohexa-2,5-dien-1-one **(3aj)***

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 86% (111 mg). mp: 174 - 175 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (t, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 2.4 Hz, 1H), 7.25 (s, 1H), 7.23 (s, 2H), 7.02 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.82 (s, 1H), 3.92 (s, 3H), 3.84 (s, 3H), 1.32 (s, 9H), 1.29 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 186.2, 160.7, 159.2, 156.1, 147.3, 147.0, 142.5, 133.9, 133.1, 132.3, 132.2, 129.2, 129.0, 124.8, 117.3, 115.2, 113.5, 55.5, 35.4, 35.4, 29.7 (double). HRMS (ESI-TOF) m/z: [M+Na]$^{+}$ Calculated for $C_{29}H_{34}NaO_3$ 453.2406; Found 453.2409.

*4-((2-Bromo-4-methylphenyl)(4-methoxyphenyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one **(3ak)***

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 84% (124 mg). mp: 169 - 170 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (s, 1H), 7.42 (d, *J* = 2.4 Hz, 1H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.22 (s, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 2.4 Hz, 1H), 3.91 (s, 3H), 2.45 (s, 3H), 1.34 (s, 9H), 1.24 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 186.4, 160.4, 153.3, 147.9, 147.3, 140.4, 138.7, 133.8, 133.2, 132.2, 131.7, 131.1, 129.8, 127.9, 124.0, 113.6, 55.4, 35.5, 35.2, 29.7, 29.6, 21.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{29}H_{33}BrNaO_2$ 515.1562; Found 515.1567.

2,6-Di-tert-butyl-4-((2,5-dimethoxyphenyl)(4-methoxyphenyl)methylene)cyclohexa-2,5-dien-1-one ***(3al)***

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 89% (123 mg). mp: 180 - 181 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (d, *J* = 2.8 Hz, 1H), 7.28 - 7.24 (m, 2H), 7.01 (d, *J* = 2.8 Hz, 1H), 6.98 (d, *J* = 2.8 Hz, 1H), 6.95 (d, *J* = 2.8 Hz, 2H), 6.93 (d, *J* = 3.2 Hz, 1H), 6.74 (d, *J* = 3.2 Hz, 1H), 3.91 (s, 3H), 3.82 (s, 3H), 3.60 (s, 3H), 1.32 (s, 9H), 1.25 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.4, 160.2, 153.2, 152.3, 151.8, 147.3, 146.8, 132.9, 132.7, 132.2, 131.4, 131.0, 129.6, 117.9, 115.5, 113.4, 113.2, 56.5, 56.0, 55.4, 35.4, 35.2, 29.7, 29.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{30}H_{36}NaO_4$ 483.2511; Found 483.2517.

2,6-Di-tert-butyl-4-((3,4-dimethylphenyl)(4-methoxyphenyl)methylene)cyclohexa-2,5-dien-1-one ***(3am)***

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 87% (112 mg). mp: 190 - 200 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26 (s, 2H), 7.22 (t, *J* = 8.4 Hz, 3H), 7.06 (s, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 3.93 (s, 3H), 2.38 (s, 3H), 2.32 (s, 3H), 1.32 (s, 9H), 1.31 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.1, 160.6, 157.0, 146.8, 146.6, 138.6, 138.3, 136.2, 134.0, 133.6, 133.4, 132.6, 132.4, 130.0, 129.2, 128.8, 113.4, 55.4, 35.3 (double), 29.6 (double) 19.8, 19.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{30}H_{36}NaO_2$ 451.2613; Found 451.2601.

4-(Benzo[d][1,3]dioxol-5-yl(4-methoxyphenyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-o *ne (**3an**)*

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 90% (120 mg). mp: 177 - 178 ^{o}C. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.24 (d, *J* = 1.6 Hz, 2H), 7.22 (s, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.84 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.72 (d, *J* = 1.2 Hz, 1H), 6.09 (s, 2H), 3.93 (s, 3H), 1.32 (s, 9H), 1.31 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ: 186.1, 160.8, 156.1, 148.8, 147.6, 146.9, 146.8, 135.1, 134.0, 133.3, 132.4, 132.3, 129.0, 127.3, 113.5, 112.3, 107.8, 101.6, 55.5, 35.3, 29.7. HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calculated for $C_{29}H_{32}NaO_4$ 467.2198; Found 467.2193.

*2,6-Di-tert-butyl-4-((4-methoxyphenyl)(3,4,5-trimethoxyphenyl)methylene)cyclohexa-2,5-dien-1-one (**3ao**)*

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 92% (135 mg). mp: 136 - 137 ^{o}C. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.29 - 7.26 (m, 2H), 7.25 (d, *J* = 2.8 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.51 (s, 2H), 3.99 (s, 3H), 3.94 (s, 3H), 3.84 (s, 6H), 1.32 (s, 9H), 1.31 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ: 186.2, 160.8, 156.3, 152.6, 147.1, 146.9, 139.2, 136.4, 134.1, 132.9, 132.4, 132.3, 129.1, 113.5, 110.0, 61.1, 56.3, 55.5, 35.4, 29.8, 29.7. HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calculated for $C_{31}H_{38}NaO_5$ 513.2617; Found 513.2624.

*2,6-Di-tert-butyl-4-((4-methoxyphenyl)(naphthalen-2-yl)methylene)cyclohexa-2,5-dien-1-one (**3ap**)*

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 87% (118 mg). mp: 173 - 174 ^{o}C. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.96 (dd, *J* = 11.6, 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.60 - 7.56 (m, 2H), 7.53 - 7.49 (m, 1H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.33 (d, *J* = 2.0 Hz, 1H), 7.31 (d, *J* = 2.4 Hz, 1H), 6.95 - 6.92 (m, 2H), 6.79 (d, *J* = 2.8 Hz, 1H), 3.88 (s, 3H), 1.39 (s, 9H), 1.10 (s, 9H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.4, 160.5, 153.9, 147.6, 147.0, 138.6, 133.7, 133.1, 132.9, 132.4, 132.2, 131.3, 130.5, 129.3 (double), 128.4, 126.5, 126.3, 126.0, 124.5, 113.7, 55.4, 35.4, 35.1, 29.7, 29.3. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{32}H_{34}NaO_2$ 473.2457; Found 473.2448.

*2,6-Di-tert-butyl-4-((4-methoxyphenyl)(thiophen-2-yl)methylene)cyclohexa-2,5-dien-1-one (**3aq**)*

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 84% (102 mg). mp: 173 - 174 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.69 (d, J = 2.4 Hz, 1H), 7.64 (dd, J = 4.8, 2.0 Hz, 1H), 7.34 - 7.30 (m, 2H), 7.23 - 7.19 (m, 2H), 7.11 (d, J = 2.8 Hz, 1H), 7.02 - 6.98 (m, 2H), 3.94 (s, 3H), 1.38 (s, 9H), 1.28 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.2, 161.0, 147.9, 147.5, 147.0, 144.1, 133.8, 133.3, 133.2, 132.3, 131.6, 131.1, 129.4, 127.7, 113.5, 55.5, 35.5, 35.4, 29.7, 29.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{26}H_{30}NaO_2S$ 429.1864; Found 429.1859.

*2,6-Di-tert-butyl-4-((2-methoxyphenyl)(p-tolyl)methylene)cyclohexa-2,5-dien-1-one (**3ba**)*

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 85% (106 mg). mp: 146 - 147 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.47 - 7.41 (m, 1H), 7.39 (d, J = 2.8 Hz, 1H), 7.21 (s, 4H), 7.17 (dd, J = 7.6, 1.6 Hz, 1H), 7.06 (t, J = 7.6 Hz, 1H), 7.02 - 6.98 (m, 2H), 3.67 (s, 3H), 2.44 (s, 3H), 1.32 (s, 9H), 1.24 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.4, 157.4, 152.9, 147.2, 146.9, 138.7, 137.7, 132.4, 132.1, 131.4, 130.9, 130.4, 130.0, 129.9, 128.6, 120.3, 111.6, 55.7, 35.3, 35.1, 29.6, 29.5, 21.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Ccalculated for $C_{29}H_{34}NaO_2$ 437.2457; Found 437.2450.

*2,6-Di-tert-butyl-4-((2-chlorophenyl)(p-tolyl)methylene)cyclohexa-2,5-dien-1-one (**3bb**)*

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 83% (104 mg). mp: 143 - 144 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.53 - 7.49 (m, 1H), 7.42 (d, J = 2.8 Hz, 1H), 7.40 (dd, J = 4.0, 2.0 Hz, 1H), 7.39 - 7.36 (m, 1H), 7.31 - 7.28 (m, 1H), 7.23 (q, *J* = 8.4 Hz, 4H), 6.82 (d, *J* = 2.4 Hz, 1H), 2.45 (s, 3H), 1.33 (s, 9H), 1.23 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.4, 151.7, 148.1, 147.7, 139.6, 139.3, 136.2, 134.0, 132.2, 131.3, 131.2, 130.9, 130.3, 130.1, 129.8, 128.9, 126.4, 35.4, 35.2, 29.6, 29.4, 21.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{28}H_{31}ClNaO$ 441.1961; Found 441.1958.

*4-((2-Bromophenyl)(p-tolyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (**3bc**)*

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 80% (111 mg). mp: 145 - 146 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.72 - 7.69 (m, 1H), 7.46 - 7.41 (m, 2H), 7.35 - 7.32 (m, 1H), 7.29 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.24 (s, 4H), 6.80 (d, *J* = 2.4 Hz, 1H), 2.45 (s, 3H), 1.33 (s, 9H), 1.23 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.4, 153.0, 148.2, 147.7, 141.6, 139.3, 135.9, 133.2, 132.2, 131.4, 131.3, 130.9, 130.2, 129.8, 128.9, 127.0, 124.0, 35.4, 35.2, 29.6, 29.4, 21.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{28}H_{31}BrNaO$ 485.1456; Found 485.1447.

*2,6-Di-tert-butyl-4-(di-p-tolylmethylene)cyclohexa-2,5-dien-1-one (**3bd**)*

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 83% (99 mg). mp: 198 - 199 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.26 (s, 2H), 7.25 (d, *J* = 6.4 Hz, 4H), 7.17 (d, *J* = 8.0 Hz, 4H), 2.47 (s, 6H), 1.31 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 186.2, 156.8, 147.0, 139.5, 138.1, 132.3, 132.2, 129.2, 128.7, 35.3, 29.6, 21.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{29}H_{34}NaO$ 421.2507; Found 421.2496.

*4-((2-Bromo-4-methylphenyl)(p-tolyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (**3be**)*

yellow solid, isolated yield 83% (119 mg). mp: 184 - 185 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.53 (s, 1H), 7.41 (d, *J* = 2.4 Hz, 1H), 7.23 (d, *J* = 3.2 Hz, 5H), 7.15 (d, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 2.8 Hz, 1H), 2.45 (s, 3H), 2.44 (s, 3H), 1.33 (s, 9H), 1.24 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz,

$CDCl_3$) δ: 186.4, 153.4, 148.0, 147.5, 140.3, 139.3, 138.6, 136.3, 133.8, 132.1, 131.6, 131.5, 131.1, 130.2, 128.9, 127.9, 123.8, 35.5, 35.3, 29.7, 29.6, 21.5, 21.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{29}H_{33}BrNaO$ 499.1612; Found 499.1605.

*2,6-Di-tert-butyl-4-((4-fluorophenyl)(2-methoxyphenyl)methylene)cyclohexa-2,5-dien-1-one (**3ca**)*

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 78% (94 mg). mp: 140 - 141 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.48 - 7.43 (m, 1H), 7.31 - 7.27 (m, 3H), 7.19 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.14 - 7.07 (m, 3H), 7.01 (s, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 3.66 (s, 3H), 1.31 (s, 9H), 1.24 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.4, 162.8 (d, J_{C-F} = 248.1 Hz), 157.4, 151.4, 147.7, 147.3, 136.7 (d, J_{C-F} = 2.6 Hz), 132.6 (d, J_{C-F} = 8.2 Hz), 132.5, 131.9, 130.9, 130.7, 130.3, 129.6, 120.4, 114.9 (d, J_{C-F} = 21.5 Hz), 111.7, 55.6, 35.4, 35.2, 29.6 (double). HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{28}H_{31}FNaO_2$ 441.2206; Found 441.2199.

*2,6-Di-tert-butyl-4-((3,4-dimethylphenyl)(4-fluorophenyl)methylene)cyclohexa-2,5-dien-1-one (**3cb**)*

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 80% (100 mg). mp: 166 - 167 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.30 - 7.25 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 4.4 Hz, 1H), 7.14 (d, *J* = 8.8 Hz, 2H), 7.04 (s, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 2.38 (s, 3H), 2.32 (s, 3H), 1.31 (s, 9H), 1.30 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.1, 163.2 (d, J_{C-F} = 249.1 Hz), 155.3, 147.4, 147.2, 138.5, 138.2, 137.1 (d, J_{C-F} = 3.0 Hz), 136.4, 133.9 (d, J_{C-F} = 8.1 Hz), 133.3, 132.2, 131.8, 129.8, 129.5, 129.4, 115.1 (d, J_{C-F} = 21.4 Hz), 35.3, 29.6 (double), 19.8, 19.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{29}H_{33}FNaO$ 439.2413; Found 439.2403.

*2,6-Di-tert-butyl-4-((4-chlorophenyl)(2-methoxyphenyl)methylene)cyclohexa-2,5-dien-1-one (**3da**)*

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 77% (100 mg). mp: 152 - 153 ^oC. ^1H

NMR (400 MHz, $CDCl_3$) δ: 7.48 - 7.43 (m, 1H), 7.40 - 7.37 (m, 2H), 7.29 (d, *J* = 2.4 Hz, 1H), 7.27 - 7.23 (m, 2H), 7.19 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.07 (td, *J* = 7.2, 0.8 Hz, 1H), 7.01 (s, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 3.65 (s, 3H), 1.31 (s, 9H), 1.24 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.4, 157.4, 151.1, 147.8, 147.5, 139.1, 134.6, 132.5, 132.1, 131.9, 130.8, 130.7, 130.5, 129.4, 128.1, 120.4, 111.7, 55.6, 35.5, 35.3, 29.7, 29.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{28}H_{31}ClNaO_2$ 457.1910; Found 457.1919.

4-(Bis(4-chlorophenyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one ***(3db)***

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 75% (99 mg). mp: 175 - 176 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.47 - 7.43 (m, 4H), 7.23 - 7.19 (m, 4H), 7.16 (s, 2H), 1.29 (s, 18H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.1, 152.4, 148.2, 138.9, 135.7, 133.2, 131.3, 130.4, 128.6, 35.5, 29.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{27}H_{28}Cl_2NaO$ 461.1415; Found 461.1421.

2,6-Di-tert-butyl-4-((4-chlorophenyl)(3,4-dimethylphenyl)methylene)cyclohexa-2,5-dien-1-one ***(3de)***

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 79% (102 mg). mp: 201 - 202 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.45 - 7.41 (m, 2H), 7.28 (d, *J* = 2.8 Hz, 1H), 7.25 - 7.23 (m, 1H), 7.22 (s, 1H), 7.21 (d, *J* = 4.4 Hz, 1H), 7.15 (d, *J* = 2.4 Hz, 1H), 7.03 (s, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 2.38 (s, 3H), 2.32 (s, 3H), 1.30 (s, 9H), 1.30 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.2, 155.0, 147.6, 147.4, 139.5, 138.5, 138.0, 136.5, 135.3, 133.3, 132.2, 131.7, 129.9, 129.7, 129.5, 128.3, 35.4, 29.7, 19.9, 19.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{29}H_{33}ClNaO$ 455.2118; Found 455.2110.

4-((4-Bromophenyl)(2-methoxyphenyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one ***(3ea)*** yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 77% (110 mg). mp: 158 - 159 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.54 (d, *J* = 8.4 Hz, 2H), 7.48 - 7.43 (m, 1H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.20 - 7.16 (m, 3H), 7.07 (t, *J* = 7.2 Hz, 1H), 7.00 (s, 1H), 6.99 (d, *J* = 5.2 Hz, 1H), 3.66 (s, 3H), 1.31 (s, 9H), 1.24 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ: 186.4, 157.4, 151.1, 147.9, 147.5, 139.6, 132.5, 132.3, 131.8, 131.1, 130.7, 130.7, 130.5, 129.3, 122.9, 120.4, 111.7, 55.6, 35.5, 35.3, 29.6, 29.5. HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calculated for $C_{28}H_{31}BrNaO_2$ 501.1405; Found 501.1397.

*4-((2-Bromophenyl)(3,4-dimethylphenyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one **(3fa)***

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 81% (116 mg). mp: 140 - 141 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.71 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 2.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.34 - 7.31 (m, 1H), 7.30 - 7.27 (m, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.11 (s, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 2.4 Hz, 1H), 2.35 (s, 3H), 2.31 (s, 3H), 1.34 (s, 9H), 1.23 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ: 186.4, 153.3, 148.0, 147.6, 141.7, 138.2, 136.4, 136.3, 133.2, 132.6, 132.2, 131.5, 131.2, 130.1, 129.9, 129.4, 129.2, 127.1, 124.0, 35.5, 35.2, 29.7, 29.5, 19.9. HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calculated for $C_{29}H_{33}BrNaO$ 499.1612; Found 499.1605.

*4-(Benzo[d][1,3]dioxol-5-yl(o-tolyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one **(3ga)***

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 85% (109 mg). mp: 172 - 173 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.45 (d, *J* = 2.4 Hz, 1H), 7.39 - 7.34 (m, 1H), 7.31 - 7.26 (m, 2H), 7.16 (d, *J* = 7.2 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.86 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.82 (d, *J* = 2.4 Hz, 1H), 6.73 (d, *J* = 1.2 Hz, 1H), 6.07 (s, 2H), 2.08 (s, 3H), 1.35 (s, 9H), 1.21 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ: 186.3, 154.9, 148.5, 147.7, 147.6, 147.3, 140.3, 137.0, 133.9, 131.8, 131.0 (double), 130.5, 129.7, 128.8, 126.4, 125.5, 111.3, 108.0, 101.6, 35.4, 35.1, 29.6, 29.5, 20.3. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{29}H_{32}NaO_3$ 451.2249; Found 451.2238.

*4-(Benzo[d][1,3]dioxol-5-yl(2-bromophenyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one **(3gb)***

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 82% (121 mg). mp: 168 - 169 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.46 - 7.42 (m, 2H), 7.33 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.28 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.87 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.77 (d, *J* = 1.2 Hz, 1H), 6.75 (d, *J* = 2.8 Hz, 1H), 6.07 (s, 2H), 1.34 (s, 9H), 1.22 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.4, 152.5, 148.6, 148.2, 147.7, 147.6, 141.5, 133.3, 132.8, 132.2, 131.4, 130.7, 130.2, 130.0, 127.1, 126.6, 124.0, 111.3, 108.0, 101.6, 35.4, 35.2, 29.6, 29.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{28}H_{29}BrNaO_3$ 515.1198; Found 515.1192.

*4-(Benzo[d][1,3]dioxol-5-yl(p-tolyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one **(3gc)***

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 88% (113 mg). mp: 167 - 168 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (s, 2H), 7.25 (s, 1H), 7.21 (d, *J* = 2.8 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.83 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.70 (d, *J* = 1.6 Hz, 1H), 6.08 (s, 2H), 2.47 (s, 3H), 1.32 (s, 9H), 1.29 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.1, 156.2, 148.7, 147.6, 147.0, 139.6, 138.0, 135.0, 132.3, 132.2, 132.1, 129.3, 128.8, 127.1, 112.1, 107.8, 101.6, 35.3 (double), 29.6 (double), 21.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{29}H_{32}NaO_3$ 451.2249; Found 451.2256.

*4-(Benzo[d][1,3]dioxol-5-yl(4-bromophenyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one **(3gd)***

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 81% (120 mg). mp: 153 - 154 ^{o}C. ^{1}H

NMR (400 MHz, $CDCl_3$) δ: 7.60 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 2.4 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 2.4 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.81 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.68 (d, *J* = 1.6 Hz, 1H), 6.10 (s, 2H), 1.31 (s, 9H), 1.29 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.1, 154.0, 148.9, 147.8 147.6, 147.5, 139.8, 134.3, 133.5, 131.8, 131.5, 131.3, 129.8, 127.1, 123.8, 112.0, 107.9, 101.7, 35.3, 29.6, 29.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{28}H_{29}BrNaO_3$ 515.1198; Found 515.1187.

*4-(Benzo[d][1,3]dioxol-5-yl(5-bromo-2-methoxyphenyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one **(3ge)***

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 85% (133 mg). mp: 196 - 197 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.54 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.36 (d, *J* = 2.8 Hz, 1H), 7.28 (d, *J* = 2.4 Hz, 1H), 6.89 (d, *J* = 2.4 Hz, 2H), 6.87 (s, 1H), 6.83 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.74 (d, *J* = 1.6 Hz, 1H), 6.07 (s, 2H), 3.70 (s, 3H), 1.32 (s, 9H), 1.25 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.4, 156.5, 149.8, 148.4, 147.7 (double), 147.4, 134.7, 134.0, 133.0, 131.8, 131.6, 130.9, 130.4, 125.8, 113.3, 112.7, 111.0, 108.0, 101.6, 56.0, 35.5, 35.3, 29.7, 29.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{29}H_{31}BrNaO_4$ 545.1303; Found 545.1307.

*4-(Benzo[d][1,3]dioxol-5-yl(2-bromo-4-methylphenyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one **(3gf)***

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 84% (128 mg). mp: 174 - 175 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.53 (s, 1H), 7.42 (d, *J* = 2.4 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.85 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.80 (d, *J* = 2.4 Hz, 1H), 6.75 (d, *J* = 1.6 Hz, 1H), 6.06 (s, 2H), 2.45 (s, 3H), 1.34 (s, 9H), 1.23 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.4, 152.8, 148.5, 148.0, 147.7, 147.4, 140.4, 138.5, 133.8, 133.2, 132.2, 131.6, 130.9, 130.2, 127.9, 126.6, 123.9, 111.4, 108.0, 101.6, 35.4, 35.2, 29.6, 29.5, 21.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{29}H_{31}BrNaO_3$ 529.1354; Found 529.1346.

*4-(Benzo[d][1,3]dioxol-5-yl(3,4-dimethylphenyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one **(3gg)***

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 90% (119 mg). mp: 202 - 203 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25 (dd, *J* = 8.8, 2.4 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.06 - 7.00 (m, 2H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.84 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.71 (d, *J* = 1.6 Hz, 1H), 6.09 (s, 2H), 2.38 (s, 3H), 2.32 (s, 3H), 1.32 (s, 9H), 1.30 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.1, 156.5, 148.7, 147.6, 146.9, 146.8, 138.4, 138.3, 136.2, 135.0, 133.4, 132.5, 132.2, 129.9, 129.3, 129.2, 127.1, 112.2, 107.7, 101.6, 35.3 (double), 29.6(double), 19.8, 19.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{30}H_{34}NaO_3$ 465.2406; Found 465.2418.

*4-(Bis(benzo[d][1,3]dioxol-5-yl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one **(3gh)***

yellow solid (petroleum ether: EtOAc = 40:1), isolated yield 92% (126 mg). mp: 198 - 199 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.22 (s, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.84 (dd, *J* = 8.0, 1.6 Hz, 2H), 6.71 (d, *J* = 1.6 Hz, 2H), 6.09 (s, 4H), 1.31 (s, 18H). ^{13}C $\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.1, 155.5, 148.8, 147.6, 146.9, 134.8, 132.1, 129.3, 127.2, 112.1, 107.8, 101.6, 35.3, 29.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calculated for $C_{29}H_{30}NaO_5$ 481.1991; Found: 481.1988.

ASSOCIATED CONTENT

*Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

^{1}H NMR, $^{13}C\{^1H\}$ NMR spectra for all products (PDF).

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: lcrong@jsnu.edu.cn; xiaopangpeng@126.com

ORCID

Liangce Rong:0000-0003-0561-1137

Notes

The authors declare no competing financial interest.

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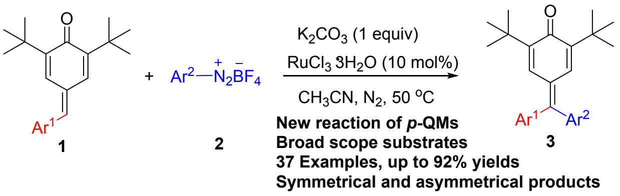
Table of Contents Graphic:



New reaction of *p*-QMs
Broad scope substrates
37 Examples, up to 92% yields
Symmetrical and asymmetrical products

A novel reaction mode and efficient ruthenium-catalyzed Matsuda−Heck-type arylation of *para*-quinone methides (*p*-QMs) with aryl diazonium salts has been developed for the synthesis of fuchsones.