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Electrochemical Radical δ-H Sulfonylation Reaction for the Synthesis of 4-((Aryl,Arylsul fonyl)methylene)-2,5-Cyclohexadiene Derivatives

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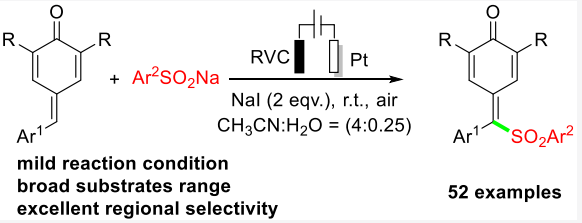
ABSTRACT: A novel and efficient electrochemical radical δ-H sulfonylation reaction of *para*-quinone methides (*p*-QMs) and sodium sulfinates has been achieved under common laboratory conditions. In this strategy, a new C(sp^2)−S bond was constructed for the synthesis of 4-((aryl,arylsulfonyl)methylene)-2,5-cyclohexadiene derivatives with a broad substrate scope, good functional group tolerance, and mild conditions. Further studies showed that the reaction had an excellent regional selectivity.



INTRODUCTION

Sulfone derivatives widely exist in a number of bioactive natural products and pharmaceuticals with various activities. For instance, intepirdine, **PVT-101**, could be used to treat Alzheimer's disease.[1] The indole skeleton containing a sulfone moiety (**K103N−Y181C 150**) is an important anti-HIV drug.[2] Vismodegib was a recently approved antitumor drug.[3] Bicalutamide is always used in treatment of prostate cancer (Figure 1).[4] Consequently, chemists have paid much attention to the synthesis of sulfone compounds.[5]

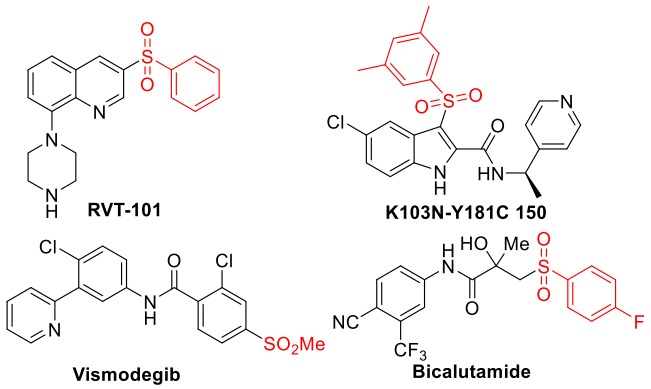


Figure 1. Bioactive compounds with a sulfone moiety.

para-Quinone methide (*p*-QM) derivatives are the significant structural motifs present in many naturally occurring compounds with important biological activities,[6] which were extensively used in lignin biosynthesis,[7] adrenergic receptors,[8] enzyme inhibition,[9] DNA alkylation,[10] and cross-linking reactions.[11] In general , *p*-QMs are well applied to organic synthesis with the three main approaches. First, *p*-QMs, as versatile Michael acceptors, are unique feedstocks for 1,6-addition[12] and 1,6-addition cyclization,[13] and these kinds of reactions are well developed (Scheme 1, previous work a). Second, many examples have been reported about *p*-QMs involving in 1,6-addition−dearomatization reactions (Scheme 1, previous work b).[14] Third, the radical mode 1,6-addition reactions of *p*-QMs were also reported by a few research groups (Scheme 1, previous work c).[15] Recently, the reactions of *p*-QMs with some sulfonation reagents ($ArSO_2Na$,[16] CF_3SO_2Na,[17] and $ArSO_2NHNH_2$[18]) to give corresponding products with a sulfone moiety (except for CF_3SO_2Na) have been reported by the different researchers; however, they were still the 1,6-conjugate addition reaction.

In recent years, organic electrosynthesis has been widely used in organic synthesis to give compounds with molecular diversity.[19] For instance, some vinyl sulfones derivatives were availably obtained via electrochemical synthesis.[20] As a part of our current study on the reactions of *p*-QMs,[21] herein, we developed an electrochemical radical δ-H sulfonylation reaction of *p*-QMs and sodium sulfinates to furnish 4-((aryl,arylsulfonyl)methylene)-2,5-cyclohexadiene derivatives (Scheme 1, this work).

RESULTS AND DISCUSSION

In order to achieve our assumption, we commenced the study by investigating the electrochemical reaction of 2,6-di*tert*-butyl-4-(2-methylbenzylidene)cyclohexa-2,5-dien-1-one **1a** and sodium benzenesulfinate **2a** (Table 1) in the presence of platinum plate as a cathode, the reticulated vitreous carbon

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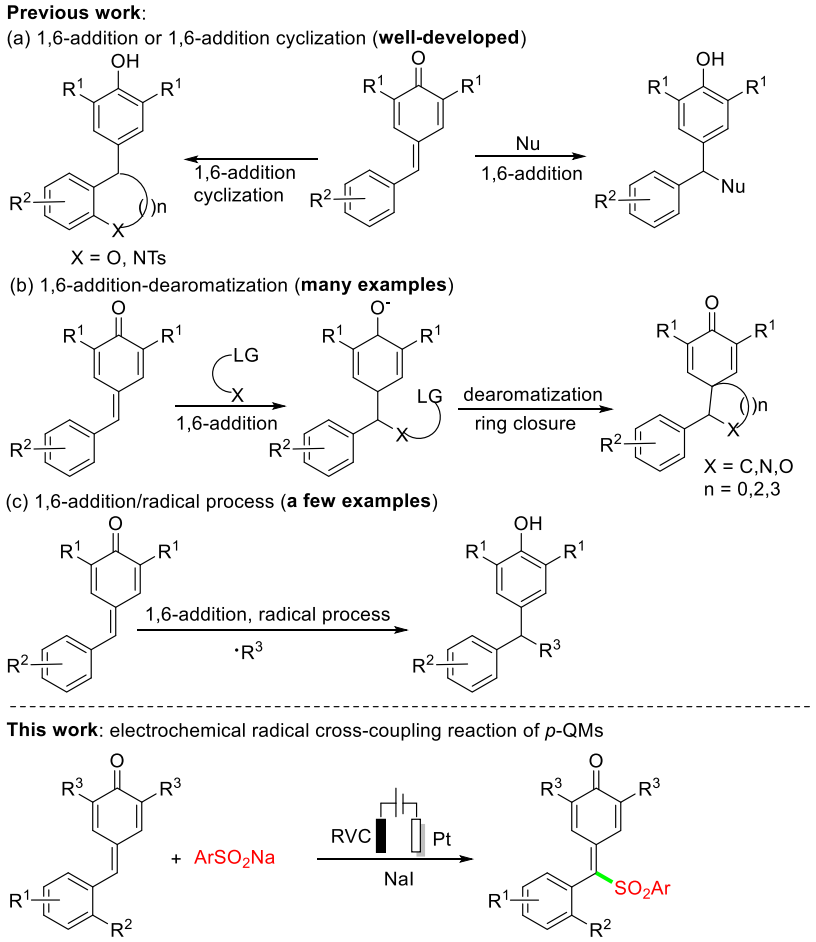
Scheme 1. Previous Work and the Current Reaction



(RVC) as a anode, along with NaI (2 equiv) as a additive in CH_3CN at room temperature under 10 mA current for 3 h. Pleasurably, the desired product **3a** was obtained in 26% yield (Table 1, entry 1). Then, other additives, such as KI, NH_4I, TBAI, and LiI, were tested in the reaction, but they all showed poor performance (Table 1, entries 2−5). Additionally, compared with CH_3CN, other aprotic solvents were not suitable for this reaction (Table 1, entries 6−8). To our delight, the reaction was significantly improved in the mixed solvents of CH_3CN and H_2O (entry 9), which prompted us to further investigate the reaction in different ratios of mixed solvents (entries 10−15). The results showed that the highest yield was obtained when the volume ratio of acetonitrile to water was 4:0.25 (entry 14). The amounts of NaI, constant current, and reaction time were all carefully screened (entries 16−23), which showed 2 equiv of NaI, a 5 mA current, and 3 h reaction time were sufficient to ensure the successful completion of the reaction. In addition, it was found that, when the reaction was carried out under a N_2 condition (Table 1, entry 24), the yield of the reaction did not change much. The results were summarized in Table 1.

Under the optimized conditions, the reaction scope about the *p*-QMs and the sodium sulfinates was examined carefully (Table 2). At first, the reaction of various substituted *p*-QMs and sodium benzensulfinate was tested under optimized conditions. In general, the yields of the electron-donating groups (Me, MeO) on the *ortho*-substituted phenol ring of *p*-QMs were better than that of electron-withdrawing (Cl) group. For instance, we clearly found that the yields of the *p*-QMs with 2-Me or 2-MeO groups are better than that of 2-Cl group (**3a** 89% and **3b** 85% vs **3c** 74%). The *p*-QMs with *para*-substituents have the similar reaction results (**3d**, **3f**, **3g** vs **3e**, **3h**). It also found when the number of electron-donoring groups in *p*-QMs increased to 2 and 3, and the yields of the reaction improved significantly (**3i**−**3l**). Next, we studied the reactions of sodium 4-methylbenzenesulfinate with *p*-QMs bearing different substituted groups, and corresponding products (**3m**−**3p**) could be obtained with good yields. In particular, the yields of the reaction increased significantly when electron-donating groups were both available on *p*-QMs and sodium sulfinate (**3o**, **3p**). Subsequently, other electron-donating groups (MeO, *t*-Bu) on sodium phenyl sulfinate could give similar results of sodium 4-methylbenzenesulfinate, in which both electron-withdrawing and electron-donating groups of *p*-QMs were well tolerated in the reaction condition to afford the corresponding products (**3q**−**3aa**) with high yields. We further investigated the reactions of sodium sulfinate with the halogen atom group (F, Cl). It was found that the reactions were worse than that of sodium benzensulfinate (**3ab**−**3ah**). The sodium sulfinate with the strong electron-withdrawing group (CF_3, NO_2) could also be used in this synthesis strategy (**3ai**, **3aj**), and sodium 2-naphthalenesulfinate was the efficient sulfonated reagent to give product **3ak** with 83% yield. As the isopropyl replaced the tertiary butyl in *p*-QMs, the reactions were carried out smoothly to give correspond-

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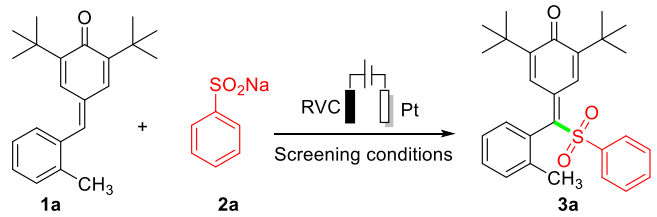
Table 1. Screening of the Reaction Conditions[a]



entry	additive	solvent	current (mA)	time (h)	yield (%[b])
1	NaI (2 equiv)	CH_3CN	10	3	26
2	KI (2 equiv)	CH_3CN	10	3	15
3	NH_4I (2 equiv)	CH_3CN	10	3	10
4	TBAI (2 equiv)	CH_3CN	10	3	trace
5	LiI (2 equiv)	CH_3CN	10	3	20
6	NaI (2 equiv)	DMSO	10	3	5
7	NaI (2 equiv)	THF	10	3	10
8	NaI (2 equiv)	toluene	10	3	trace
9	NaI (2 equiv)	CH_3CN/H_2O (1:1)	10	3	38
10	NaI (2 equiv)	CH_3CN/H_2O (2:1)	10	3	41
11	NaI (2 equiv)	CH_3CN/H_2O (3:1)	10	3	53
12	NaI (2 equiv)	CH_3CN/H_2O (4:1)	10	3	60
13	NaI (2 equiv)	CH_3CN/H_2O (4:0.5)	10	3	71
14	NaI (2 equiv)	CH_3CN/H_2O (4:0.25)	10	3	80
15	NaI (2 equiv)	CH_3CN/H_2O (4:0.1)	10	3	52
16	NaI (2 equiv)	CH_3CN/H_2O (4:0.25)	5	3	89
17	NaI (2 equiv)	CH_3CN/H_2O (4:0.25)	20	3	60
18	NaI (1 equiv)	CH_3CN/H_2O (4:0.25)	5	3	42
19	NaI (3 equiv)	CH_3CN/H_2O (4:0.25)	5	3	87
20		CH_3CN/H_2O (4:0.25)	5	3	NR[c]
21	NaI (2 equiv)	CH_3CN/H_2O (4:0.25)	0	3	NR
22	NaI (2 equiv)	CH_3CN/H_2O (4:0.25)	5	4	88
23	NaI (2 equiv)	CH_3CN/H_2O (4:0.25)	5	5	87
24	NaI (2 equiv)	CH_3CN/H_2O (4:0.25)	5	4	85[d]

[a]Undivided cell, RVC anode (100 PPI, 1 cm × 1 cm × 1.2 cm), Pt cathode (1 cm × 1 cm), constant current at 5.0 mA, **1a** (0.3 mmol), **2a** (0.6 mmol), additive (2.0 equiv), solvent (4−4.25 mL), room temperature, under air. [b]Isolated yield. [c]No reaction. [d]In N_2.

ing products (**3al**−**3ap**) with good yields. In addition, the structure of product was confirmed by the X-crystal diffraction analysis of **3l**. The results were listed in Table 2.

In order to further study this synthesis, we designed substrate **1′** to investigate the regioselectivity of the reaction. It could be found that the reactions were still taken place at the original alkene position, rather than the allyl (**4a**−**4h**) and alkyne bond (**4i**, **4j**), which indicated this electrochemical radical δ-H sulfonylation reaction had the high regioselectivity. The obtained crystal structure **4a** further confirmed this result (Table 3).

Then, a series of control experiments was performed to study the mechanism. Compounds **1b** and **2a** were carried out under standard conditions with TEMPO (2 equiv), and the trace **2b** could be found. While BHT (2 equiv) was used in the experiment, the reaction was completely inhibited, and the radical capture product **5** was obtained, which confirmed that this reaction was a radical pathway. In addition, the good yield could still be obtained after the substrates were increased 10-fold. The reactions were shown in Scheme 2.

On the basis of the above results and reported literature,[20] the possible electrochemical pathways was given in Scheme 3. Initially, iodine is oxidized at the anode to obtain elemental iodine, which reacted with sodium sulfinate to form sulfonyl iodide **A**. Then, radical **B** and iodine radical were generated by the homolysis of **A**. The iodine radical generated elemental iodine and participated in the reaction cycle again. Subsequently, **B** reacted with *p*-QMs **1** produce radical intermediate **C**, which loses an electron to the current to give intermediate **D**. Under the help of iodide, the desired product **3** could be obtained by elimination of a H^+, and then the H^+ participated in the reduction reaction on the cathode with H_2O to release H_2.

CONCLUSION

In summary, a novel electrochemical radical δ-H sulfonylation reaction of *p*-QMs and sodium arlysulfinate has been well established with the assistance of NaI under mild conditions. A wide range of substrates are tolerated in this transformation, and various products can be obtained in moderate to good yields. To the best of our knowledge, this is the first example of a radical reaction about *p*-QMs and sodium sulfinates.

EXPERIMENTAL SECTION

General Information. Unless otherwise noted, all reagents were purchased from commercial suppliers without further purification. All reactions were carried out under air conditions using IKA ElectraSyn 2.0 Pro with undivided cell. *para*-Quinone methides[14,22] and sodium sulfinates[23] were synthesized according to known literature procedures. Melting points were determined on an XT-5 microscopic melting point apparatus and were uncorrected. NMR

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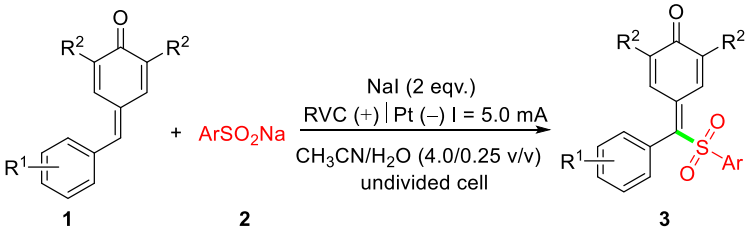
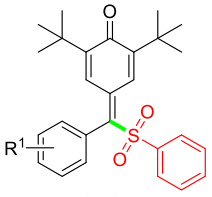
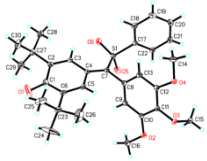
Table 2. Substrate Scope of the *p*-QMs and Sodium Sulfinate[a]



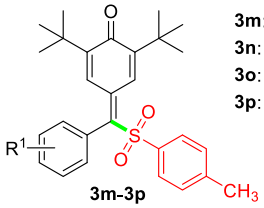


3a-3l

3a: R^1= 2-CH_3, (89%[b])
3b: R^1= 2-OCH_3, (85%)
3c: R^1= 2-Cl, (74%)
3d: R^1= 4-CH_3, (85%)
3e: R^1= 4-CN, (75%)
3f: R^1= 4-OCH_3, (84%)
3g: R^1= 4-SCH_3, (82%)
3h: R^1= 4-Br, (78%)
3i: R^1= 2,5-$(OCH_3)_2$, (86%)
3j: R^1= 2-OCH_3-5-Br, (81%)
3k: R^1= 3,4-OCH_2O, (86%)
3l: R^1= 3,4,5-$(OCH_3)_3$, (88%)

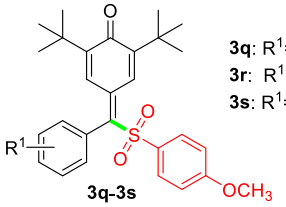


ORTEP drawing of **3l**



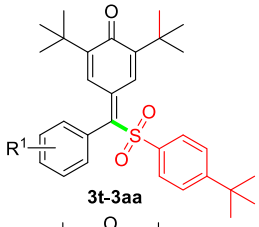
3m-3p

3m: R^1= 2-Cl, (80%)
3n: R^1= 4-CH_3, (82%)
3o: R^1= 2-OCH_3-5-Br, (86%)
3p: R^1= 3,4,5-$(OCH_3)_3$, (90%)



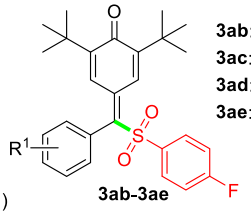
3q-3s

3q: R^1= 2-OCH_3, (83%)
3r: R^1= 4-OCH_3, (81%)
3s: R^1= 3,4,5-$(OCH_3)_3$, (90%)



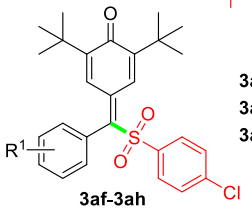
3t-3aa

3t: R^1= 2-OCH_3, (87%)
3u: R^1= 4-CH_3, (83%)
3v: R^1= 4-OCH_3, (88%)
3w: R^1= 4-Br, (80%)
3x: R^1= 2,5-$(OCH_3)_2$, (86%)
3y: R^1= 2-OCH_3-5-Br, (84%)
3z: R^1= 3,4-OCH_2O, (87%)
3aa: R^1= 3,4,5-$(OCH_3)_3$, (89%)



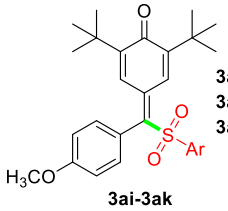
3ab-3ae

3ab: R^1= 4-OCH_3, (75%)
3ac: R^1= 2-OCH_3-5-Br, (75%)
3ad: R^1= 3,4-OCH_2O, (80%)
3ae: R^1= 3,4,5-$(OCH_3)_3$, (83%)



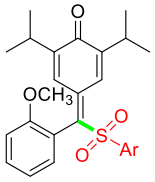
3af-3ah

3af: R^1= 2,5-$(OCH_3)_2$, (80%)
3ag: R^1= 2-OCH_3-5-Br, (81%)
3ah: R^1= 3,4,5-$(OCH_3)_3$, (85%)



3ai-3ak

3ai: Ar = 4-$CF_3C_6H_4$, (70%)
3aj: Ar = 4-$NO_2C_6H_4$, (73%)
3ak:Ar = 2-naphthyl (83%)



3al: Ar = C_6H_5, (80%)
3am: Ar = 4-$CH_3C_6H_4$, (82%)
3an: Ar = 4-ClC_6H_4, (75%)
3ao: Ar = 4-$OCH_3C_6H_4$, (85%)
3ap: Ar = 4-^{t}BuC_6H_4, (82%)

[a]Reaction conditions: undivided cell, RVC anode (100 PPI, 1 cm × 1 cm × 1.2 cm), Pt cathode (1 cm × 1 cm), constant current at 5.0 mA, **1a** (0.3 mmol), **2a** (0.6 mmol), NaI (2.0 equiv), CH_3CH/H_2O = 4:0.25 (4.25 mL), room temperature, 3−4 h (monitored by TLC), under air. [b]Isolated yield.

spectra were recorded on a Bruker 400 spectrometer (^{1}H, 400 MHz; ^{13}C, 100 MHz). Chemical shifts were reported in ppm downfield and referenced as follows: ^{1}H, residual internal $CDCl_3$ (δ 7.31 ppm); ^{13}C, internal $CDCl_3$ (δ 77.23 ppm). Coupling constants (J) were quoted in hertz (Hz). The following abbreviations were used to explain the multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). HRMS was obtained on a Bruker micrOTOF-Q 134 instrument; X-ray diffractions were recorded on a Siemens P4 or Simart-1000 diffractometer. All the reactions were monitored by thin-layer chromatography (TLC). Flash chromatography separations were performed on 300−400 mesh silica gel.

General Procedure for the Synthesis of 3 and 4. *para*-Quinone methides **1** or **1′** (0.3 mmol), sodium sulfinates **2** (0.6 mmol, 2 equiv), NaI (0.6 mmol, 2 equiv), and mixed solvents (4.25 mL, CH_3CN/H_2O = 4:0.25) were added in a reaction tube equipped with a reticulated vitreous carbon RVC (100 PPI, 1 cm × 1 cm × 1.2 cm) anode and a platinum plate (1 cm × 1 cm) cathode. The reaction was stirred at 5 mA under room temperature about 3−4 h until TLC revealed the absence of the starting material. Then the reaction was quenched by brine (10 mL), and the resultant mixture was extracted with EtOAc (3 × 5 mL). The combined extracts were washed sequentially with water (10 mL) and brine (10 mL) and dried over $NaSO_4$. The extract was concentrated under reduced pressure, and the residue was purified by flash column chromatography (petroleum ether/EtOAc = 10:1−40:1) to yield the corresponding product **3** and **4**.

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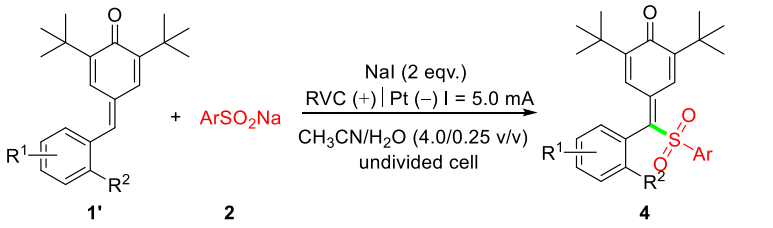
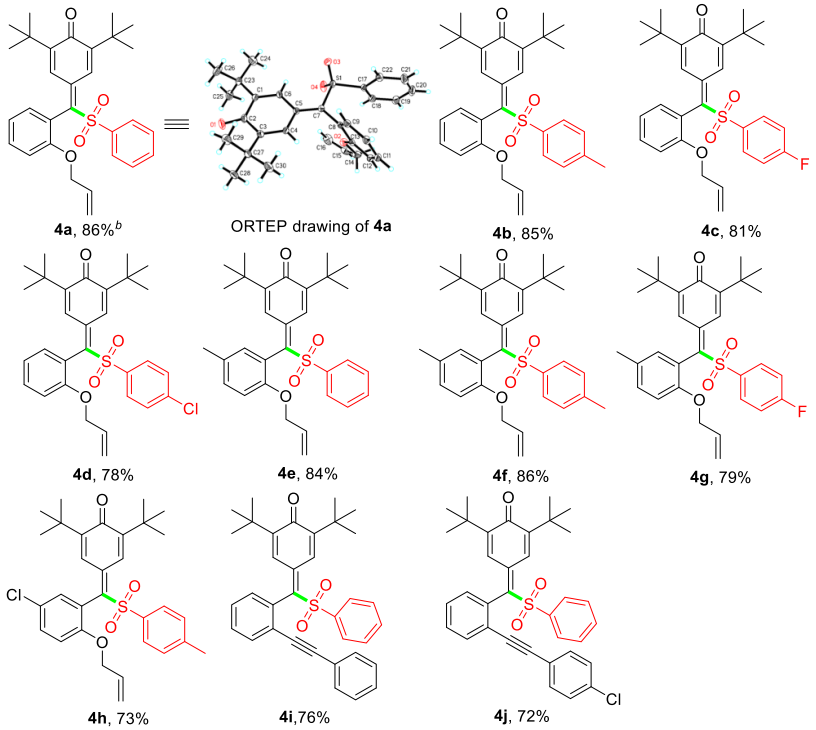
Table 3. Substrate Scope of the Allyl *p*-QMs and Sodium Sulfinate[a]





[a]Reaction conditions: undivided cell, RVC anode (100 PPI, 1 cm × 1 cm × 1.2 cm), Pt cathode (1 cm × 1 cm), constant current at 5.0 mA, **1a** (0.3 mmol), **2a** (0.6 mmol), NaI (2.0 equiv), CH_3CH/H_2O = 4:0.25 (4.25 mL), room temperature, 3−4 h (monitored by TLC), under air. [b]Isolated yield.

General Procedure for Radical Trapping Reaction. *para*-Quinone methide **1b** (0.3 mmol), sodium sulfinates **2a** (0.6 mmol), sodium iodide (2 equiv, 90 mg), BHT (0.6 mmol, 132 mg), and mixed solvent CH_3CN/H_2O (v/v = 4:0.25, 4.25 mL) were added in a reaction flask. The reaction flask was equipped with an RVC electrode (1.0 × 1.0 × 1.2 cm^3) as an anode and a Pt electrode as a cathode (1.0 × 1.0 cm^2). The solution was stirred and electrolyzed at a constant current (5 mA) without a reference electrode for 4 h at room temperature, and the radical capture product **5** was obtained.

*2,6-Di-tert-butyl-4-((phenylsulfonyl)(o-tolyl)methylene)-cyclohexa-2,5-dien-1-one (**3a**).* Yellow solid. Isolated yield: 89% (120 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 130−131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.70 (d, J = 2.8 Hz, 1H), 7.70−7.66 (m, 2H), 7.61−7.55 (m, 1H), 7.47−7.41 (m, 2H), 7.31−7.27 (m, 1H), 7.18−7.12 (m, 2H), 6.97 (d, J = 6.8 Hz, 1H), 6.32 (d, J = 2.4 Hz, 1H), 1.98 (s, 3H), 1.37 (s, 9H), 1.03 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.1, 151.9, 151.1, 147.2, 140CH_3CN:H_2O.0, 138.6, 136.5, 133.7, 132.1, 131.1, 130.2, 130.1, 129.8, 128.9, 128.7, 126.3, 125.4, 36.1, 35.5, 29.7, 29.3, 20.0. HRMS (ESI-TOF): m/z calcd for $C_{28}H_{32}NaO_3S^+$, 471.1970; found $[M + Na]^+$, 471.1963.

*2,6-Di-tert-butyl-4-((2-methoxyphenyl)(phenylsulfonyl)-methylene)cyclohexa-2,5-dien-1-one (**3b**).* Yellow solid. Isolated yield: 85% (118 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 152−153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.51 (d, J = 2.8 Hz, 1H), 7.75−7.71 (m, 2H), 7.55−7.51 (m, 1H), 7.43−7.38 (m, 2H), 7.38−7.34 (m, 1H), 7.21 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.02−6.98 (m, 1H), 6.74 (d, J = 8.0 Hz, 1H), 6.45 (d, J = 2.4 Hz, 1H), 3.53 (s, 3H), 1.33 (s, 9H), 1.06 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.3, 157.4, 151.1, 150.6, 145.6, 140.8, 136.5, 133.3, 132.3, 131.6, 130.8, 128.5, 128.4, 126.5, 121.4, 120.4, 110.6, 55.3, 36.0, 35.5, 29.7, 29.3. HRMS (ESI-TOF): m/z calcd for $C_{28}H_{32}NaO_4S^+$, 487.1919; found $[M + Na]^+$, 487.1923.

*2,6-Di-tert-butyl-4-((2-chlorophenyl)(phenylsulfonyl)methylene)-cyclohexa-2,5-dien-1-one (**3c**).* Yellow solid. Isolated yield: 74% (104 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 137−138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.62 (d, J = 2.4 Hz, 1H), 7.74−7.71 (m, 2H), 7.58 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 8.0 Hz, 2H), 7.39−7.36 (m, 1H), 7.36−7.30 (m, 3H), 6.31 (d, J = 2.8 Hz, 1H), 1.36 (s, 9H), 1.06 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.1, 152.1, 151.5, 144.2, 139.9, 137.3, 135.2, 133.8, 132.9, 131.6, 131.1, 130.1, 129.5, 128.9, 128.7, 126.6, 126.1, 36.2, 35.6, 29.7, 29.3. HRMS (ESI-TOF): m/z calcd for $C_{27}H_{29}ClNaO_3S^+$, 491.1424; found $[M + Na]^+$, 491.1420.

*2,6-Di-tert-butyl-4-((phenylsulfonyl)(p-tolyl)methylene)-cyclohexa-2,5-dien-1-one (**3d**).* Yellow solid. Isolated yield: 85% (114 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 188−189 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.67 (s, 1H), 7.66 (d, J = 7.6 Hz, 2H), 7.56 (t, J = 6.8 Hz, 1H), 7.44 (t, J = 7.2 Hz, 2H),

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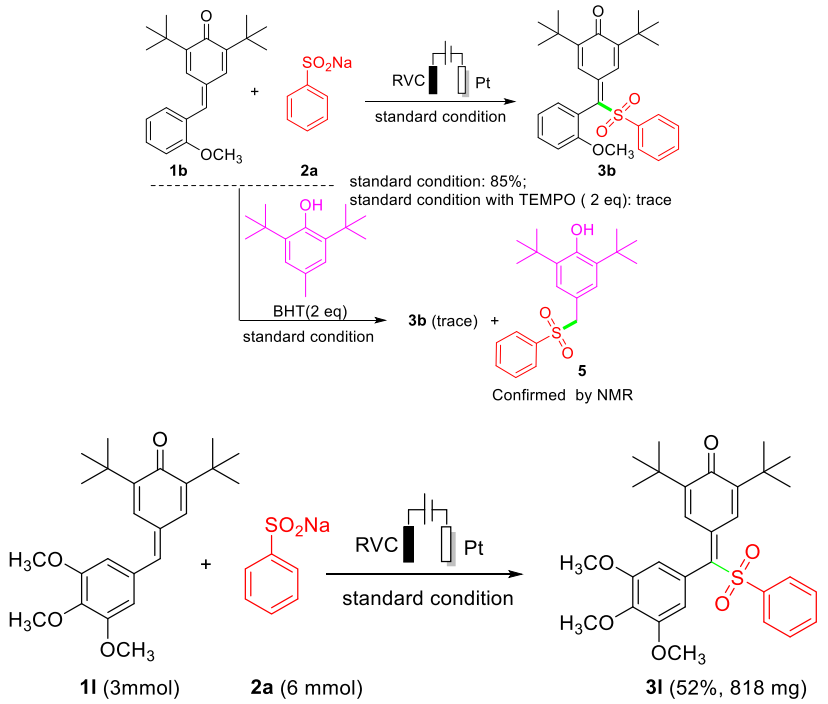
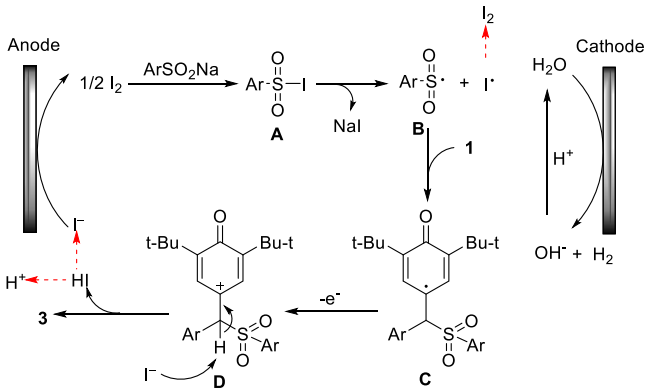
Scheme 2. Radical Trapping, Control Reaction, and Scalability



Scheme 3. A Plausible Mechanism



7.14 (d, J = 7.2 Hz, 2H), 7.00 (d, J = 7.2 Hz, 2H), 6.50 (s, 1H), 2.38 (s, 3H), 1.35 (s, 9H), 1.06 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.2, 151.3, 151.0, 147.9, 140.6, 139.7, 136.5, 133.5, 131.5, 130.9, 129.7, 129.0, 128.7, 128.3, 126.7, 36.2, 35.6, 29.8, 29.4, 21.5. HRMS (ESI-TOF): m/z calcd for $C_{28}H_{32}NaO_3S^+$, 471.1970; found $[M + Na]^+$, 471.1975.

*4-((3,5-Di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)(phenylsulfonyl)methyl)benzonitrile (**3e**).* Yellow solid. Isolated yield: 75% (103 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 209−210 °C. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.71 (d, J = 2.4 Hz, 1H), 7.70 (d, J = 8.0 Hz, 4H), 7.65 (d, J = 8.0 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.33 (d, J = 2.8 Hz, 1H), 1.42 (s, 9H), 1.09 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 185.9, 152.6, 152.1, 144.9, 139.9, 137.8, 137.2, 134.2, 132.3, 131.8, 129.6, 129.4, 128.2, 126.1, 118.1, 113.5, 36.3, 35.8, 29.7, 29.3. HRMS (ESI-TOF): m/z calcd for $C_{28}H_{29}NNaO_3S^+$, 482.1766; found $[M + Na]^+$, 482.1771.

*2,6-Di-tert-butyl-4-((4-methoxyphenyl)(phenylsulfonyl)methylene)cyclohexa-2,5-dien-1-one (**3f**).* Yellow solid. Isolated yield: 84% (117 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 113−114 °C. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.67 (d, J = 2.8 Hz, 1H), 7.67−7.64 (m, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.06 (d, J = 8.8 Hz, 2H), 6.87−6.84 (m, 2H), 6.53 (d, J = 2.8 Hz, 1H), 3.85 (s, 3H), 1.35 (s, 9H), 1.07 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.2, 160.5, 151.2, 150.9, 147.5, 140.6, 136.6, 133.5, 133.2, 130.9, 129.0, 128.1, 126.7, 124.5, 113.5, 55.4, 36.1, 35.6, 29.7, 29.3. HRMS (ESI-TOF): m/z calcd for $C_{28}H_{32}NaO_4S^+$, 487.1919; found $[M + Na]^+$, 487.1928.

*2,6-Di-tert-butyl-4-((4-(methylthio)phenyl)(phenylsulfonyl)methylene)cyclohexa-2,5-dien-1-one (**3g**).* Yellow solid. Isolated yield: 82% (118 mg) (eluent: petroleum ether/EtOAc = 40:1). Mp: 189−190 °C. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.71 (d, J = 2.4 Hz, 1H), 7.71 (d, J = 8.0 Hz, 2H), 7.62 (t, J = 7.2 Hz, 1H), 7.50 (t, J = 7.8 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 6.56 (d, J = 2.4 Hz, 1H), 2.56 (s, 3H), 1.40 (s, 9H), 1.12 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.2, 151.5, 151.1, 147.2, 141.4, 140.5, 136.7, 133.7, 132.0, 130.7, 129.1, 128.8, 128.2, 126.7, 125.0, 36.2, 35.7, 29.7, 29.4, 15.1. HRMS (ESI-TOF): m/z calcd for $C_{28}H_{32}NaO_3S_2^+$, 503.1691; found $[M + Na]^+$, 503.1695.

*4-((4-Bromophenyl)(phenylsulfonyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (**3h**).* Yellow solid. Isolated yield: 78% (120 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 140−141 °C. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.68 (d, J = 2.4 Hz, 1H), 7.66 (d, J = 7.2 Hz, 2H), 7.59 (t, J = 7.6 Hz, 1H), 7.51−7.44 (m, 4H), 6.99 (d, J = 8.4 Hz, 2H), 6.42 (d, J = 2.8 Hz, 1H), 1.36 (s, 9H), 1.07 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.1, 152.0, 151.5, 146.0, 140.2, 136.9, 133.9, 133.1, 131.7, 131.4, 130.2, 129.2, 128.2, 126.4, 124.3, 36.2, 35.8, 29.8, 29.4. HRMS (ESI-TOF): m/z calcd for $C_{27}H_{29}BrNaO_3S^+$, 535.0918; found $[M + Na]^+$, 535.0905.

*2,6-Di-tert-butyl-4-((2,5-dimethoxyphenyl)(phenylsulfonyl)methylene)cyclohexa-2,5-dien-1-one (**3i**).* Yellow solid. Isolated yield: 86% (128 mg) (eluent: petroleum ether/EtOAc = 10:1). Mp: 150−151 °C. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.51 (d, J = 2.8 Hz, 1H), 7.79−7.74 (m, 2H), 7.56−7.51 (m, 1H), 7.44−7.39 (m, 2H), 6.91 (dd, J_1 = 9.2 Hz, J_2 = 3.2 Hz, 1H), 6.78 (d, J = 3.2 Hz, 1H), 6.67 (d, J = 9.2 Hz, 1H), 6.47 (d, J = 2.8 Hz, 1H), 3.77 (s, 3H), 3.48 (s, 3H), 1.33 (s, 9H), 1.07 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.3, 153.1, 151.6, 151.3, 150.7, 145.0, 140.9, 136.7, 133.3, 130.8, 128.5, 126.5, 121.8, 117.3, 117.1, 111.6, 56.0, 55.7, 36.1, 35.6, 29.7, 29.4. HRMS (ESI-TOF): m/z calcd for $C_{29}H_{34}NaO_5S^+$, 517.2025; found $[M + Na]^+$, 517.2010.

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*4-((5-Bromo-2-methoxyphenyl)(phenylsulfonyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (**3j**).* Yellow solid. Isolated yield: 81% (132 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 178−179 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.48 (d, J = 2.4 Hz, 1H), 7.77−7.73 (m, 2H), 7.58−7.54 (m, 1H), 7.49−7.43 (m, 3H), 7.32 (d, J = 2.4 Hz, 1H), 6.65 (d, J = 8.8 Hz, 1H), 6.40 (d, J = 2.8 Hz, 1H), 3.54 (s, 3H), 1.32 (s, 9H), 1.08 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.2, 156.6, 151.7, 151.1, 143.5, 140.7, 137.1, 134.6, 134.2, 133.5, 130.3, 128.7, 128.5, 126.3, 123.5, 112.5, 112.3, 55.7, 36.2, 35.6, 29.7, 29.4. HRMS (ESI-TOF): m/z calcd for $C_{28}H_{31}BrNaO_4S^+$, 565.1024; found [M + Na]$^+$, 565.1020.

*4-(Benzo[d][1,3]dioxol-5-yl(phenylsulfonyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (**3k**).* Yellow solid. Isolated yield: 86% (123 mg) (eluent: petroleum ether/EtOAc = 15:1). Mp: 148−149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.64 (d, J = 2.4 Hz, 1H), 7.72−7.68 (m, 2H), 7.58 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 6.77−6.72 (m, 2H), 6.56 (d, J = 2.8 Hz, 1H), 6.47 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 6.04 (d, J = 8.0 Hz, 2H), 1.35 (s, 9H), 1.09 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.2, 151.4, 151.0, 148.8, 147.5, 147.1, 140.5, 136.8, 133.6, 130.7, 129.0, 128.1, 126.6, 126.2, 125.9, 111.8, 107.8, 101.7, 36.1, 35.6, 29.7, 29.4. HRMS (ESI-TOF): m/z calcd for $C_{28}H_{30}NaO_5S^+$, 501.1712; found [M + Na]$^+$, 501.1720.

*2,6-Di-tert-butyl-4-((phenylsulfonyl)(3,4,5-trimethoxyphenyl)-methylene)cyclohexa-2,5-dien-1-one (**3l**).* Yellow solid. Isolated yield: 88% (138 mg) (eluent: petroleum ether/EtOAc = 10:1). Mp: 144−145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.72 (d, J = 2.8 Hz, 1H), 7.73−7.69 (m, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 8.4 Hz, 2H), 6.56 (d, J = 2.4 Hz, 1H), 6.29 (s, 2H), 3.88 (s, 3H), 3.72 (s, 6H), 1.37 (s, 9H), 1.09 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.2, 152.7, 151.5, 151.3, 147.2, 140.3, 139.0, 136.5, 133.7, 130.7, 129.0, 128.5, 127.7, 126.5, 109.2, 61.2, 56.3, 36.2, 35.7, 29.8, 29.4. HRMS (ESI-TOF): m/z calcd for $C_{30}H_{36}NaO_6S^+$, 547.2130; found [M + Na]$^+$, 547.2132.

*2,6-Di-tert-butyl-4-((2-chlorophenyl)(tosyl)methylene)-cyclohexa-2,5-dien-1-one (**3m**).* Yellow solid. Isolated yield: 80% (116 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 156−157 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.62 (d, J = 2.8 Hz, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.37−7.32 (m, 4H), 7.23 (d, J = 8.0 Hz, 2H), 6.31 (d, J = 2.8 Hz, 1H), 2.41 (s, 3H), 1.36 (s, 9H), 1.06 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.1, 151.9, 151.4, 145.0, 144.6, 137.1, 137.0, 135.2, 132.9, 131.9, 131.1, 130.2, 129.6, 129.5, 128.8, 126.6, 126.2, 36.2, 35.6, 29.8, 29.3, 21.8. HRMS (ESI-TOF): m/z calcd for $C_{28}H_{31}ClNaO_3S^+$, 505.1580; found [M + Na]$^+$, 505.1575.

*2,6-Di-tert-butyl-4-(p-tolyl(tosyl)methylene)cyclohexa-2,5-dien-1-one (**3n**).* Yellow solid. Isolated yield: 82% (114 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 188−189 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.67 (d, J = 2.8 Hz, 1H), 7.54 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 7.6 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 6.49 (d, J = 2.8 Hz, 1H), 2.40 (s, 3H), 2.39 (s, 3H), 1.35 (s, 9H), 1.05 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.3, 151.1, 150.8, 148.3, 144.6, 139.6, 137.7, 136.2, 131.5, 131.0, 129.8, 129.7, 128.7, 128.3, 126.8, 36.1, 35.6, 29.8, 29.4, 21.8, 21.5. HRMS (ESI-TOF): m/z calcd for $C_{29}H_{34}NaO_3S^+$, 485.2126; found [M + Na]$^+$, 485.2135.

*4-((5-Bromo-2-methoxyphenyl)(tosyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (**3o**).* Yellow solid; solated yield: 86% (143 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 207−208 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.49 (s, 1H), 7.62 (d, J = 7.6 Hz, 2H), 7.47 (d, J = 8.4 Hz, 1H), 7.29−7.22 (m, 3H), 6.68 (d, J = 8.8 Hz, 1H), 6.40 (s, 1H), 3.57 (s, 3H), 2.40 (s, 3H), 1.33 (s, 9H), 1.07 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.2, 156.7, 151.5, 150.9, 144.6, 144.0, 137.8, 136.8, 134.6, 134.1, 130.4, 129.3, 128.5, 126.4, 123.7, 112.4, 55.8, 36.1, 35.6, 29.7, 29.4, 21.7. HRMS (ESI-TOF): m/z calcd for $C_{29}H_{33}BrNaO_4S^+$, 579.1181; found [M + Na]$^+$, 579.1172.

*2,6-Di-tert-butyl-4-(tosyl(3,4,5-trimethoxyphenyl)methylene)-cyclohexa-2,5-dien-1-one (**3p**).* Yellow solid. Isolated yield: 90% (145 mg) (eluent: petroleum ether/EtOAc = 10:1). Mp: 155−156 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.70 (d, J = 2.0 Hz, 1H), 7.58 (d, J = 7.6 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 6.55 (d, J = 2.0 Hz, 1H), 6.29 (s, 2H), 3.88 (s, 3H), 3.73 (s, 6H), 2.40 (s, 3H), 1.36 (s, 9H), 1.08 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.2, 152.6, 151.3, 151.1, 147.7, 144.8, 138.9, 137.4, 136.1, 130.8, 129.5, 128.5, 127.9, 126.6, 109.1, 61.1, 56.3, 36.1, 35.6, 29.7, 29.4, 21.6. HRMS (ESI-TOF): m/z calcd for $C_{31}H_{38}NaO_6S^+$, 561.2287; found [M + Na]$^+$, 561.2276.

*2,6-Di-tert-butyl-4-((2-methoxyphenyl)((4-methoxyphenyl)-sulfonyl)methylene)cyclohexa-2,5-dien-1-one (**3q**).* Yellow solid. Isolated yield: 83% (123 mg) (eluent: petroleum ether/EtOAc = 15:1). Mp: 179−180 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.57 (d, J = 2.4 Hz, 1H), 7.65−7.61 (m, 2H), 7.39−7.34 (m, 1H), 7.18 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 6.99 (td, J_1 = 7.2 Hz, J_2 = 0.8 Hz, 1H), 6.87−6.84 (m, 2H), 6.76 (d, J = 8.0 Hz, 1H), 6.43 (d, J = 2.4 Hz, 1H), 3.84 (s, 3H), 3.56 (s, 3H), 1.35 (s, 9H), 1.05 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.3, 163.5, 157.3, 150.9, 150.4, 146.2, 135.9, 132.3, 132.2, 131.5, 130.9, 130.8, 126.6, 121.7, 120.3, 113.6, 110.5, 55.7, 55.3, 36.0, 35.4, 29.7, 29.3. HRMS (ESI-TOF): m/z calcd for $C_{29}H_{34}NaO_5S^+$, 517.2025; found [M + Na]$^+$, 517.2036.

*2,6-Di-tert-butyl-4-((4-methoxyphenyl)((4-methoxyphenyl)-sulfonyl)methylene)cyclohexa-2,5-dien-1-one (**3r**).* Yellow solid. Isolated yield: 81% (120 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 171−172 °C. ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 8.61 (d, J = 2.4 Hz, 1H), 7.56 (d, J = 8.8 Hz, 2H), 7.11 (dd, J_1 = 8.8 Hz, J_2 = 5.6 Hz, 4H), 6.99 (s, 1H), 6.96 (s, 1H) 6.52 (d, J = 2.4 Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 1.30 (s, 9H), 1.02 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) (δ, ppm) 185.9, 164.0, 160.7, 150.4, 150.1, 150.0, 134.9, 133.4, 131.7, 131.5, 130.5, 127.1, 124.4, 115.4, 114.0, 56.5, 55.9, 36.2, 35.7, 29.9, 29.4. HRMS (ESI-TOF): m/z calcd for $C_{29}H_{34}NaO_5S^+$, 517.2025; found [M + Na]$^+$, 517.2020.

*2,6-Di-tert-butyl-4-(((4-methoxyphenyl)sulfonyl)(3,4,5-trimethoxyphenyl)methylene)cyclohexa-2,5-dien-1-one (**3s**).* Yellow solid. Isolated yield: 90% (150 mg) (eluent: petroleum ether/EtOAc = 10:1). Mp: 144−145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.73 (d, J = 2.8 Hz, 1H), 7.61 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 9.2 Hz, 2H), 6.54 (d, J = 2.8 Hz, 1H), 6.30 (s, 2H), 3.88 (s, 3H), 3.84 (s, 3H), 3.73 (s, 6H), 1.37 (s, 9H), 1.08 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.3, 163.8, 152.6, 151.3, 151.1, 147.9, 139.0, 135.8, 131.8, 130.9, 130.8, 128.1, 126.7, 114.2, 109.2, 61.2, 56.4, 55.8, 36.2, 35.6, 29.8, 29.4. HRMS (ESI-TOF): m/z calcd for $C_{31}H_{38}NaO_7S^+$, 577.2236; found [M + Na]$^+$, 577.2243.

*2,6-Di-tert-butyl-4-(((4-(tert-butyl)phenyl)sulfonyl)(2-methoxyphenyl)methylene)cyclohexa-2,5-dien-1-one (**3t**).* Yellow solid. Isolated yield: 87% (136 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 164−165 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.48 (d, J = 2.4 Hz, 1H), 7.66−7.63 (m, 2H), 7.43−7.40 (m, 2H), 7.39−7.35 (m, 1H), 7.20 (dd, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H), 7.00 (td, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 1H), 6.75 (d, J = 8.4 Hz, 1H), 6.45 (d, J = 2.4 Hz, 1H), 3.53 (s, 3H), 1.32 (s, 9H), 1.31 (s, 9H), 1.05 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.4, 157.4, 157.2, 151.0, 150.5, 146.1, 137.9, 136.2, 132.3, 131.5, 130.9, 128.3, 126.7, 125.5, 121.6, 120.4, 110.5, 55.3, 36.0, 35.4, 35.2, 31.1, 29.7, 29.3. HRMS (ESI-TOF): m/z calcd for $C_{32}H_{40}NaO_4S^+$, 543.2545; found [M + Na]$^+$, 543.2534.

*2,6-Di-tert-butyl-4-(((4-(tert-butyl)phenyl)sulfonyl)(p-tolyl)-methylene)cyclohexa-2,5-dien-1-one (**3u**).* Yellow solid. Isolated yield: 83% (126 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 155−156 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.67 (d, J = 2.8 Hz, 1H), 7.64 (d, J = 8.8 Hz, 2H), 7.49 (d, J = 8.8 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 8.4 Hz, 2H), 6.56 (d, J = 2.4 Hz, 1H), 2.44 (s, 3H), 1.40 (s, 9H), 1.36 (s, 9H), 1.11 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.3, 157.6, 151.1, 150.8, 148.5, 139.6, 137.6, 136.1, 131.3, 131.0, 129.8, 128.7, 128.1, 126.9, 126.0, 36.1, 35.6, 35.3, 31.1, 29.7, 29.3, 21.5. HRMS (ESI-TOF): m/z calcd for $C_{32}H_{40}NaO_3S^+$, 527.2596; found [M + Na]$^+$, 527.2587.

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*2,6-Di-tert-butyl-4-(((4-(tert-butyl)phenyl)sulfonyl)(4-methoxyphenyl)methylene)cyclohexa-2,5-dien-1-one (**3v**).* Yellow solid. Isolated yield: 88% (137 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 140−141 °C. ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 8.42 (d, J = 2.8 Hz, 1H), 7.65−7.60 (m, 4H), 7.18−7.13 (m, 2H), 7.01−6.97 (m, 2H), 6.56 (d, J = 2.4 Hz, 1H), 3.81 (s, 3H), 1.28 (s, 9H), 1.25 (s, 9H), 1.02 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) (δ, ppm) 185.9, 160.7, 157.9, 150.5, 150.1, 149.9, 137.9, 135.2, 133.4, 131.3, 127.8, 127.0, 124.2, 114.0, 55.8, 36.1, 35.6, 35.5, 31.1, 29.7, 29.3. HRMS (ESI-TOF): m/z calcd for $C_{32}H_{40}NaO_4S^+$, 543.2545; found $[M + Na]^+$, 543.2557.

*4-((4-Bromophenyl)((4-(tert-butyl)phenyl)sulfonyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (**3w**).* Yellow solid. Isolated yield: 80% (136 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 150−151 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.63 (d, J = 2.4 Hz, 1H), 7.57 (d, J = 8.8 Hz, 2H), 7.50−7.45 (m, 4H), 7.00 (d, J = 8.4 Hz, 2H), 6.43 (d, J = 2.8 Hz, 1H), 1.35 (s, 9H), 1.32 (s, 9H), 1.07 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.1, 158.0, 151.7, 151.3, 146.7, 137.2, 136.5, 133.0, 131.8, 131.3, 130.3, 128.1, 126.5, 126.2, 124.2, 36.1, 35.7, 35.4, 31.1, 29.7, 29.3. HRMS (ESI-TOF): m/z calcd for $C_{31}H_{37}BrNaO_3S^+$, 591.1544; found $[M + Na]^+$, 591.1534.

*2,6-Di-tert-butyl-4-(((4-(tert-butyl)phenyl)sulfonyl)(2,5-dimethoxyphenyl)methylene)cyclohexa-2,5-dien-1-one (**3x**).* Yellow solid. Isolated yield: 86% (142 mg) (eluent: petroleum ether/EtOAc = 10:1). Mp: 170−161 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.48 (d, J = 2.4 Hz, 1H), 7.67 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 6.91 (dd, J_1 = 8.8 Hz, J_2 = 3.2 Hz, 1H), 6.76 (d, J = 3.2 Hz, 1H), 6.68 (d, J = 8.8 Hz, 1H), 6.47 (d, J = 2.4 Hz, 1H), 3.76 (s, 3H), 3.48 (s, 3H), 1.32 (s, 9H), 1.31 (s, 9H), 1.07 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.4, 157.3, 153.0, 151.7, 151.2, 150.6, 145.7, 137.9, 136.4, 130.9, 128.4, 126.6, 125.5, 122.0, 117.3, 117.0, 111.5, 56.0, 55.7, 36.1, 35.5, 35.3, 31.1, 29.7, 29.4. HRMS (ESI-TOF): m/z calcd for $C_{33}H_{42}NaO_5S^+$, 573.2651; found $[M + Na]^+$, 573.2653.

*4-((5-Bromo-2-methoxyphenyl)((4-(tert-butyl)phenyl)sulfonyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (**3y**).* Yellow solid. Isolated yield: 84% (151 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 120−121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.47 (d, J = 2.8 Hz, 1H), 7.66 (d, J = 8.8 Hz, 2H), 7.48−7.44 (m, 3H), 7.26 (s, 1H), 6.66 (d, J = 8.8 Hz, 1H), 6.40 (d, J = 2.8 Hz, 1H), 3.55 (s, 3H), 1.32 (s, 9H), 1.31 (s, 9H), 1.08 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.2, 157.6, 156.7, 151.6, 150.9, 144.0, 137.6, 136.7, 134.6, 134.1, 130.4, 128.4, 126.4, 125.7, 123.7, 112.4, 112.3, 55.7, 36.1, 35.6, 35.4, 31.1, 29.7, 29.4. HRMS (ESI-TOF): m/z calcd for $C_{32}H_{39}BrNaO_4S^+$, 621.1650; found $[M + Na]^+$, 621.1646.

*4-(Benzo[d][1,3]dioxol-5-yl((4-(tert-butyl)phenyl)sulfonyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (**3z**).* Yellow solid. Isolated yield: 87% (139 mg) (eluent: petroleum ether/EtOAc = 15:1). Mp: 165−166 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.60 (d, J = 2.4 Hz, 1H), 7.62 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.8 Hz, 2H), 6.75 (d, J = 8.0 Hz, 1H), 6.73 (d, J = 1.6 Hz, 1H), 6.57 (d, J = 2.4 Hz, 1H), 6.50 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 6.03 (d, J = 12.4 Hz, 2H), 1.34 (s, 9H), 1.32 (s, 9H), 1.09 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.2, 157.7, 151.2, 150.9, 148.8, 147.8, 147.5, 137.6, 136.5, 130.9, 128.1, 126.8, 126.2, 126.1, 111.8, 107.8, 101.7, 36.2, 35.7, 35.4, 31.1, 29.8, 29.4. HRMS (ESI-TOF): m/z calcd for $C_{32}H_{38}NaO_5S^+$, 557.2338; found $[M + Na]^+$, 557.2331.

*2,6-Di-tert-butyl-4-(((4-(tert-butyl)phenyl)sulfonyl)(3,4,5-rimethoxyphenyl)methylene)cyclohexa-2,5-dien-1-one (**3aa**).* Yellow solid. Isolated yield: 89% (155 mg) (eluent: petroleum ether/EtOAc = 10:1). Mp: 170−171 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.71 (d, J = 2.4 Hz, 1H), 7.61 (d, J = 8.8 Hz, 2H), 7.47−7.43 (m, 2H), 6.55 (d, J = 2.4 Hz, 1H), 6.27 (s, 2H), 3.87 (s, 3H), 3.71 (s, 6H), 1.36 (s, 9H), 1.31 (s, 9H), 1.08 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.3, 157.8, 152.6, 151.4, 151.1, 147.7, 138.9, 137.2, 136.0, 130.8, 128.4, 127.9, 126.6, 125.9, 109.0, 61.1, 56.2, 36.1, 35.6, 35.3, 31.1, 29.7, 29.4. HRMS (ESI-TOF): m/z calcd for $C_{34}H_{44}NaO_6S^+$, 603.2756; found $[M + Na]^+$, 603.2765.

*2,6-Di-tert-butyl-4-(((4-fluorophenyl)sulfonyl)(4-methoxyphenyl)methylene)cyclohexa-2,5-dien-1-one (**3ab**).* Yellow solid. Isolated yield: 75% (108 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 180−181 °C. ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 8.57 (s, 1H), 7.71 (s, 2H), 7.44 (t, J = 8.4 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 6.53 (s, 1H), 3.79 (s, 3H), 1.29 (s, 9H), 1.03 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) (δ, ppm) 185.9, 165.6 (d, J_{C-F} = 252.8 Hz), 160.8, 150.7, 150.4, 148.9, 136.5 (d, J_{C-F} = 2.3 Hz), 135.6, 133.5, 131.5, 131.3 (d, J_{C-F} = 5.7 Hz), 126.8, 124.0, 117.4 (d, J_{C-F} = 23.0 Hz), 114.1, 55.9, 36.2, 35.7, 29.8, 29.4. HRMS (ESI-TOF): m/z calcd for $C_{28}H_{31}FNaO_4S^+$, 505.1825; found $[M + Na]^+$, 505.1834.

*4-((5-Bromo-2-methoxyphenyl)((4-fluorophenyl)sulfonyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (**3ac**).* Yellow solid. Isolated yield: 75% (126 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 189−190 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.50 (d, J = 2.8 Hz, 1H), 7.76−7.70 (m, 2H), 7.48 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 7.35 (d, J = 2.4 Hz, 1H), 7.10 (t, J = 8.4 Hz, 2H), 6.65 (d, J = 9.2 Hz, 1H), 6.37 (d, J = 2.4 Hz, 1H), 3.54 (s, 3H), 1.34 (s, 9H), 1.08 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.1, 156.5, 151.9, 151.3, 142.8, 137.2, 136.5(d, J_{C-F} = 2.7 Hz), 134.8, 134.4, 131.4 (d, J_{C-F} = 9.6 Hz), 130.2, 126.1, 123.4, 115.9 (d, J_{C-F} = 22.6 Hz), 112.6, 112.3, 55.7, 36.2, 35.6, 29.7, 29.4. HRMS (ESI-TOF): m/z calcd for $C_{28}H_{30}BrFNaO_4S^+$, 583.0930; found $[M + Na]^+$, 583.0919.

*4-(Benzo[d][1,3]dioxol-5-yl((4-fluorophenyl)sulfonyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (**3ad**).* Yellow solid. Isolated yield: 80% (119 mg) (eluent: petroleum ether/EtOAc = 15:1). Mp: 174−175 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.71 (d, J = 2.4 Hz, 1H), 7.76−7.71 (m, 2H), 7.18 (t, J = 8.8 Hz, 2H), 6.80 (d, J = 2.0 Hz, 1H), 6.78 (d, J = 4.0 Hz, 1H), 6.59 (d, J = 2.4 Hz, 1H), 6.50 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 6.09 (d, J = 6.4 Hz, 2H), 1.41 (s, 9H), 1.14 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.1, 165.7 (d, J_{C-F} = 255.6 Hz), 151.6, 151.3, 148.9, 147.6, 146.6, 136.9, 136.4(d, J_{C-F} = 2.8 Hz), 131.1 (d, J_{C-F} = 9.6 Hz), 130.6, 126.4, 126.2, 125.8, 116.4 (d, J_{C-F} = 22.4 Hz), 111.8, 107.9, 101.8, 36.2, 35.7, 29.8, 29.4. HRMS (ESI-TOF): m/z calcd for $C_{28}H_{29}FNaO_5S^+$, 519.1617; found $[M + Na]^+$, 519.1612.

*2,6-Di-tert-butyl-4-(((4-fluorophenyl)sulfonyl)(3,4,5-trimethoxyphenyl)methylene)cyclohexa-2,5-dien-1-one (**3ae**).* Yellow solid. Isolated yield: 83% (135 mg) (eluent: petroleum ether/EtOAc = 10:1). Mp: 162−163 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.71 (d, J = 2.8 Hz, 1H), 7.73−7.67 (m, 2H), 7.12 (t, J = 8.4 Hz, 2H), 6.55 (d, J = 2.4 Hz, 1H), 6.30 (s, 2H), 3.88 (s, 3H), 3.74 (s, 6H), 1.37 (s, 9H), 1.09 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.1, 165.7 (d, J_{C-F} = 255.8 Hz), 152.7, 151.7, 151.5, 146.7, 139.1, 136.5, 136.2 (d, J_{C-F} = 3.1 Hz), 131.3 (d, J_{C-F} = 9.5 Hz), 130.6, 127.5, 126.3, 116.2 (d, J_{C-F} = 22.5 Hz), 109.2, 61.1, 56.3, 36.1, 35.6, 29.7, 29.4. HRMS (ESI-TOF): m/z calcd for $C_{30}H_{35}FNaO_6S$, 565.2036; found $[M + Na]^+$, 565.2028.

*2,6-Di-tert-butyl-4-(((4-chlorophenyl)sulfonyl)(2,5-dimethoxyphenyl)methylene)cyclohexa-2,5-dien-1-one (**3af**).* Yellow solid. Isolated yield: 80% (127 mg) (eluent: petroleum ether/EtOAc = 10:1). Mp: 186−187 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.51 (d, J = 2.8 Hz, 1H), 7.66 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.8 Hz, 2H), 6.92 (dd, J_1 = 9.2 Hz, J_2 = 3.2 Hz, 1H), 6.80 (d, J = 2.8 Hz, 1H), 6.67 (d, J = 8.8 Hz, 1H), 6.44 (d, J = 2.8 Hz, 1H), 3.78 (s, 3H), 3.48 (s, 3H), 1.34 (s, 9H), 1.07 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.2, 153.2, 151.5, 151.4, 151.0, 144.1, 140.1, 139.1, 137.0, 130.7, 130.0, 128.7, 126.3, 121.6, 117.4, 117.2, 111.5, 56.0, 55.6, 36.1, 35.6, 29.7, 29.4. HRMS (ESI-TOF): m/z calcd for $C_{29}H_{33}ClNaO_5S^+$, 551.1635; found $[M + Na]^+$, 551.1627.

*4-((5-Bromo-2-methoxyphenyl)((4-chlorophenyl)sulfonyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (**3ag**).* Yellow solid. Isolated yield: 81% (140 mg) (eluent: petroleum ether/EtOAc = 15:1). Mp: 175−176 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.48 (d, J = 2.8 Hz, 1H), 7.66 (d, J = 8.4 Hz, 2H), 7.49 (dd,

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J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 7.41 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 2.4 Hz, 1H), 6.66 (d, J = 8.8 Hz, 1H), 6.37 (d, J = 2.4 Hz, 1H), 3.54 (s, 3H), 1.33 (s, 9H), 1.08 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.1, 156.5, 151.9, 151.4, 142.6, 139.0, 137.4, 134.7, 134.4, 130.2, 130.0, 128.9, 126.0, 123.2, 112.6, 112.3, 55.7, 36.2, 35.7, 29.7, 29.4. HRMS (ESI-TOF): m/z calcd for $C_{28}H_{30}BrClNaO_4S^+$, 599.0634; found $[M + Na]^+$, 599.0646.

*2,6-Di-tert-butyl-4-(((4-chlorophenyl)sulfonyl)(3,4,5-trimethoxyphenyl)methylene)cyclohexa-2,5-dien-1-one (**3ah**).* Yellow solid. Isolated yield: 85% (142 mg) (eluent: petroleum ether/EtOAc = 10:1). Mp: 147−148 °C. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.68 (d, J = 2.4 Hz, 1H), 7.62 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 6.55 (d, J = 2.4 Hz, 1H), 6.29 (s, 2H), 3.89 (s, 3H), 3.74 (s, 6H), 1.37 (s, 9H), 1.09 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.1, 152.7, 151.7, 151.5, 146.5, 140.5, 139.2, 138.7, 136.7, 130.5, 129.9, 129.2, 127.4, 126.3, 109.2, 61.1, 56.3, 36.2, 35.6, 29.7, 29.4. HRMS (ESI-TOF): m/z calcd for $C_{30}H_{35}ClNaO_6S^+$, 581.1741; found $[M + Na]^+$, 581.1726.

*2,6-Di-tert-butyl-4-((4-methoxyphenyl)((4-trifluoromethyl)-phenyl)sulfonyl)methylene)cyclohexa-2,5-dien-1-one (**3ai**).* Yellow solid. Isolated yield: 70% (112 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 147−148 °C. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.70 (d, J = 2.4 Hz, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 6.58 (d, J = 2.4 Hz, 1H), 3.90 (s, 3H), 1.41 (s, 9H), 1.12 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.2, 160.8, 151.8, 151.5, 146.1, 144.1, 137.5, 133.3, 130.7, 128.7, 126.3, 126.1 (d, J_{C-F} = 3.0 Hz), 125.7 (q, J_{C-F} = 195.2 Hz)124.1, 113.7, 55.5, 36.2, 35.7, 30.4, 29.7, 29.4. HRMS (ESI-TOF): m/z calcd for $C_{29}H_{31}F_3NaO_4S^+$, 555.1793; found $[M + Na]^+$, 555.1780.

*2,6-Di-tert-butyl-4-((4-methoxyphenyl)((4-nitrophenyl)sulfonyl)-methylene)cyclohexa-2,5-dien-1-one (**3aj**).* Yellow solid. Isolated yield: 73% (112 mg) (eluent: petroleum ether/EtOAc = 10:1). Mp: 139−140 °C. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.72 (d, J = 2.4 Hz, 1H), 8.31 (d, J = 8.8 Hz, 2H), 7.86 (d, J = 8.8 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 6.91 (d, J = 8.4 Hz, 2H), 6.58 (d, J = 2.8 Hz, 1H), 3.90 (s, 3H), 1.42 (s, 9H), 1.13 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.1, 160.9, 152.1, 151.8, 146.1, 145.3, 138.0, 133.4, 130.5, 129.5, 126.1, 124.1, 123.7, 113.9, 55.5, 36.3, 35.8, 29.8, 29.4. HRMS (ESI-TOF): m/z calcd for $C_{28}H_{31}NNaO_6S^+$, 532.1770; found $[M + Na]^+$, 532.1753.

*2,6-Di-tert-butyl-4-((4-methoxyphenyl)(naphthalen-2-ylsulfonyl)methylene)cyclohexa-2,5-dien-1-one (**3ak**).* Yellow solid. Isolated yield: 83% (128 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 189−190 °C. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.81 (d, J = 2.4 Hz, 1H), 8.31 (s, 1H), 7.96−7.91 (m, 3H), 7.71 (t, J = 7.6 Hz, 1H), 7.65 (t, J = 7.6 Hz, 2H), 7.13 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 6.59 (d, J = 2.4 Hz, 1H), 3.88 (s, 3H), 1.42 (s, 9H), 1.11 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.3, 160.7, 151.3, 151.0, 147.7, 137.6, 136.7, 135.2, 133.3, 132.1, 131.0, 130.0, 129.5, 129.4, 129.3, 128.1, 127.8, 126.9, 124.7, 123.0, 113.6, 55.4, 36.2, 35.7, 29.8, 29.4. HRMS (ESI-TOF): m/z calcd for $C_{32}H_{34}NaO_4S^+$, 537.2075; found $[M + Na]^+$, 537.2078.

*2,6-Diisopropyl-4-((2-methoxyphenyl)(phenylsulfonyl)-methylene)cyclohexa-2,5-dien-1-one (**3al**).* Yellow solid. Isolated yield: 80% (105 mg) (eluent: petroleum ether/EtOAc = 30:1). Mp: 181−182 °C. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.51 (d, J = 1.6 Hz, 1H), 7.73 (d, J = 7.6 Hz, 2H), 7.53 (t, J = 7.2 Hz, 1H), 7.44−7.35 (m, 3H), 7.22 (d, J = 7.2 Hz, 1H), 7.01 (t, J = 7.2 Hz, 1H), 6.74 (d, J = 8.4 Hz, 1H), 6.40 (d, J = 2.4 Hz, 1H), 3.52 (s, 3H), 3.18−3.10 (m, 1H), 3.03−2.94 (m, 1H), 1.18 (t, J = 6.0 Hz, 6H), 0.88 (dd, J = 6.8, 2.0 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 185.2, 157.5, 149.1, 148.5, 145.8, 140.9, 136.4, 133.3, 132.4, 131.7, 130.7, 128.6, 128.5, 126.4, 121.4, 120.5, 110.6, 55.3, 27.5, 27.1, 22.1, 21.9, 21.7. HRMS (ESI-TOF): m/z calcd for $C_{26}H_{28}NaO_4S$, 459.1606; found $[M + Na]^+$, 459.1608.

*2,6-Diisopropyl-4-((2-methoxyphenyl)(tosyl)methylene)-cyclohexa-2,5-dien-1-one (**3am**).* Yellow solid. Isolated yield: 82% (111 mg) (eluent: petroleum ether/EtOAc = 30:1). Mp: 175−176 °C. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.50 (d, J = 2.8 Hz, 1H), 7.61 (d, J = 8.0 Hz, 2H), 7.41−7.37 (m, 1H), 7.23−7.17 (m, 3H), 7.01 (t, J = 7.2 Hz, 1H), 6.78 (d, J = 8.4 Hz, 1H), 6.40 (d, J = 2.8 Hz, 1H), 3.55 (s, 3H), 3.18−3.11 (m, 1H), 3.03−2.93 (m, 1H), 2.39 (s, 3H), 1.19 (dd, J = 7.2, 4.8 Hz, 6H), 0.88 (dd, J = 6.8, 1.6 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 185.2, 157.5, 148.9, 148.4, 146.3, 144.4, 138.0, 136.2, 132.3, 131.7, 130.8, 129.2, 128.6, 126.5, 121.6, 120.4, 110.7, 55.4, 27.5, 27.1, 23.6, 22.2, 21.9, 21.7. HRMS (ESI-TOF): m/z calcd for $C_{27}H_{30}NaO_4S$, 473.1762; found $[M + Na]^+$, 473.1755.

*4-(((4-Chlorophenyl)sulfonyl)(2-methoxyphenyl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one (**3an**).* Yellow solid. Isolated yield: 75% (106 mg) (eluent: petroleum ether/EtOAc = 30:1). Mp: 183−184 °C. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.51 (d, J = 2.4 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.43−7.34 (m, 3H), 7.24 (dd, J = 7.2, 1.6 Hz, 1H), 7.03 (t, J = 7.6 Hz, 1H), 6.75 (d, J = 8.4 Hz, 1H), 6.38 (d, J = 2.8 Hz, 1H), 3.52 (s, 3H), 3.20−3.12 (m, 1H), 3.03−2.95 (m, 1H), 1.20 (t, J = 6.4 Hz, 6H), 0.88 (dd, J = 6.8, 2.0 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 185.1, 157.3, 149.3, 148.8, 144.9, 140.1, 139.1, 136.7, 132.5, 132.0, 130.5, 130.1, 128.7, 126.1, 121.1, 120.6, 110.6, 55.3, 27.5, 27.1, 22.2, 21.9, 21.7. HRMS (ESI-TOF): m/z calcd for $C_{26}H_{27}ClNaO_4S$, 493.1216; found $[M + Na]^+$, 493.1218.

*2,6-Diisopropyl-4-((2-methoxyphenyl)((4-methoxyphenyl)-sulfonyl)methylene)cyclohexa-2,5-dien-1-one (**3ao**).* Yellow solid. Isolated yield: 85% (119 mg) (eluent: petroleum ether/EtOAc = 30:1). Mp: 170−171 °C. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.56 (d, J = 2.8 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.38 (t, J = 7.2 Hz, 1H), 7.19 (d, J = 7.2 Hz, 1H), 7.00 (t, J = 7.2 Hz, 1H), 6.85 (d, J = 8.4 Hz, 2H), 6.76 (d, J = 8.4 Hz, 1H), 6.39 (d, J = 2.8 Hz, 1H), 3.83 (s, 3H), 3.54 (s, 3H), 3.20−3.12 (m, 1H), 3.02−2.94 (m, 1H), 1.20 (t, J = 6.4 Hz, 6H), 0.88 (d, J = 6.8 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 185.2, 163.6, 157.4, 148.9, 148.3, 146.5, 135.8, 132.3, 132.2, 131.6, 130.9, 130.8, 126.5, 121.7, 120.4, 113.7, 110.6, 55.8, 55.4, 27.5, 27.1, 22.2, 22.0, 21.7. HRMS (ESI-TOF): m/z calcd for $C_{27}H_{30}NaO_5S$, 489.1712; found [M + Na], 489.1710.

*4-(((4-(tert-Butyl)phenyl)sulfonyl)(2-methoxyphenyl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one (**3ap**).* Yellow solid. Isolated yield: 82% (121 mg) (eluent: petroleum ether/EtOAc = 30:1). Mp: 173−174 °C. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.52 (d, J = 2.4 Hz, 1H), 7.69 (d, J = 8.8 Hz, 2H), 7.48−7.42 (m, 3H), 7.26 (dd, J = 7.2, 1.2 Hz, 1H), 7.06 (t, J = 7.6 Hz, 1H), 6.80 (d, J = 8.0 Hz, 1H), 6.45 (d, J = 2.4 Hz, 1H), 3.56 (s, 3H), 3.22−3.15 (m, 1H), 3.06−2.99 (m, 1H), 1.35 (s, 9H), 1.22 (d, J = 3.2 Hz, 3H), 1.21 (d, J = 3.2 Hz, 3H), 0.93 (d, J = 2.4 Hz, 3H), 0.92 (d, J = 2.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 185.2, 157.5, 157.4, 148.9, 148.4, 146.4, 137.9, 136.1, 132.4, 131.6, 130.8, 128.4, 126.6, 125.5, 121.6, 120.4, 110.6, 55.3, 35.3, 31.1, 27.4, 27.1, 22.2, 22.0, 21.7. HRMS (ESI-TOF): m/z calcd for $C_{30}H_{36}NaO_4S$, 515.2232; found $[M + Na]^+$, 515.2236.

*4-((2-(Allyloxy)phenyl)(phenylsulfonyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (**4a**).* Yellow solid. Isolated yield: 86% (127 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 94−95 °C. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.55 (d, J = 2.4 Hz, 1H), 7.79 (d, J = 0.8 Hz, 1H), 7.77 (d, J = 1.2 Hz, 1H), 7.59−7.54 (m, 1H), 7.43 (d, J = 8.4 Hz, 2H), 7.41−7.37 (m, 1H), 7.33−7.30 (m, 1H), 7.06 (td, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 1H), 6.78 (d, J = 8.4 Hz, 1H), 6.52 (d, J = 2.4 Hz, 1H), 5.93−5.80 (m, 1H), 5.27−5.22 (m, 1H), 5.22−5.19 (m, 1H), 4.41−4.34 (m, 1H), 4.28−4.21 (m, 1H), 1.38 (s, 9H), 1.10 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.3, 156.3, 151.0, 150.6, 145.1, 141.0, 136.7, 133.2, 132.6, 132.4, 131.5, 130.9, 128.5, 128.4, 126.5, 121.6, 120.5, 117.1, 111.7, 68.6, 36.0, 35.5, 29.7, 29.3. HRMS (ESI-TOF): m/z calcd for $C_{30}H_{34}NaO_4S^+$, 513.2075; found $[M + Na]^+$, 513.2087.

*4-((2-(Allyloxy)phenyl)(tosyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (**4b**).* Yellow solid. Isolated yield: 85% (129 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 137−138 °C. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.56 (d, J = 2.4 Hz, 1H), 7.66 (d, J = 8.0 Hz, 2H), 7.43−7.38 (m, 1H), 7.28 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.06 (t, J = 7.2 Hz, 1H),

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6.81 (d, J = 8.4 Hz, 1H), 6.51 (d, J = 2.8 Hz, 1H), 5.92−5.82 (m, 1H), 5.24 (dd, J_1 = 11.2 Hz, J_2 = 1.6 Hz, 1H), 5.22−5.19 (m, 1H), 4.43−4.37 (m, 1H), 4.31−4.25 (m, 1H), 2.43 (s, 3H), 1.38 (s, 9H), 1.10 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.3, 156.4, 150.9, 150.4, 145.6, 144.2, 138.1, 136.4, 132.6, 132.3, 131.4, 131.0, 129.1, 128.4, 126.6, 121.8, 120.5, 117.0, 111.8, 68.7, 36.0, 35.4, 29.7, 29.3, 21.6. HRMS (ESI-TOF): m/z calcd for $C_{31}H_{36}NaO_4S^+$, 527.2232; found $[M + Na]^+$, 527.2220.

*4-((2-(Allyloxy)phenyl)((4-fluorophenyl)sulfonyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (**4c**).* Yellow solid. Isolated yield: 81% (124 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 107−108 °C. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.59 (d, J = 2.4 Hz, 1H), 7.78−7.23 (m, 2H), 7.42−7.38 (m, 1H), 7.33 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.11−7.05 (m, 3H), 6.77 (d, J = 8.0 Hz, 1H), 6.49 (d, J = 2.4 Hz, 1H), 5.91−5.81 (m, 1H), 5.24 (dd, J_1 = 4 Hz, J_2 = 1.6 Hz, 1H), 5.21 (dd, J_1 = 3.2 Hz, J_2 = 1.6 Hz, 1H), 4.40−4.34 (m, 1H), 4.26−4.21 (m, 1H), 1.39 (s, 9H), 1.10 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.2, 156.1, 151.2, 150.8, 144.5, 136.7, 132.4 (d, J_{C-F} = 2.1 Hz), 131.4 (d, J_{C-F} = 9.5 Hz), 131.3, 130.8, 126.3, 121.4, 120.6, 117.2, 115.6 (d, J_{C-F} = 22.4 Hz), 111.6, 68.5, 36.1, 35.5, 29.7, 29.3. HRMS (ESI-TOF): m/z calcd for $C_{30}H_{33}FNaO_4S^+$, 531.1981; found $[M + Na]^+$, 531.1969.

*4-((2-(Allyloxy)phenyl)((4-chlorophenyl)sulfonyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (**4d**).* Yellow solid. Isolated yield: 78% (123 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 90−91 °C. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.57 (d, J = 2.4 Hz, 1H), 7.70−7.65 (m, 2H), 7.44−7.36 (m, 3H), 7.33 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H), 6.78 (d, J = 8.4 Hz, 1H), 6.50 (d, J = 2.4 Hz, 1H), 5.90−5.80 (m, 1H), 5.24 (s, 1H), 5.21 (dd, J_1 = 6.4 Hz, J_2 = 1.6 Hz, 1H), 4.40−4.34 (m, 1H), 4.26−4.20 (m, 1H), 1.39 (s, 9H), 1.10 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.2, 156.1, 151.3, 150.9, 144.2, 140.0, 139.2, 137.0, 132.5, 132.4, 131.7, 130.8, 129.9, 128.7, 126.3, 121.3, 120.6, 117.2, 111.6, 68.6, 36.1, 35.5, 29.7, 29.3. HRMS (ESI-TOF): m/z calcd for $C_{30}H_{33}ClNaO_4S^+$, 547.1686; found $[M + Na]^+$, 547.1675.

*4-((2-(Allyloxy)-5-methylphenyl)(phenylsulfonyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (**4e**).* Yellow solid. Isolated yield: 84% (127 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 88−89 °C. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.52 (d, J = 2.8 Hz, 1H), 7.80 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 8.0 Hz, 2H), 7.18 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.13 (d, J = 1.8 Hz, 1H), 6.68 (d, J = 8.4 Hz, 1H), 6.54 (d, J = 2.0 Hz, 1H), 5.90−5.80 (m, 1H), 5.21 (dd, J_1 = 9.6 Hz, J_2 = 1.6 Hz, 1H), 5.18 (d, J = 1.2 Hz, 1H), 4.34 (dd, J_1 = 13.6 Hz, J_2 = 4.8 Hz, 1H), 4.22 (dd, J_1 = 13.2 Hz, J_2 = 4.4 Hz, 1H), 2.36 (s, 3H), 1.36 (s, 9H), 1.11 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.4, 154.2, 150.6, 141.2, 133.2, 132.9, 131.9, 131.1, 129.8, 128.5, 126.7, 121.3, 117.0, 111.6, 68.7, 36.1, 35.5, 29.8, 29.4, 20.5. HRMS (ESI-TOF): m/z calcd for $C_{31}H_{36}NaO_4S^+$, 527.2232; found $[M + Na]^+$, 527.2218.

*4-((2-(Allyloxy)-5-methylphenyl)(tosyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (**4f**).* Yellow solid. Isolated yield: 86% (134 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 145−146 °C. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.53 (d, J = 2.8 Hz, 1H), 7.68 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 7.19 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.10 (d, J = 2.0 Hz, 1H), 6.70 (d, J = 8.4 Hz, 1H), 6.54 (d, J = 2.8 Hz, 1H), 5.90−5.80 (m, 1H), 5.21 (dd, J_1 = 9.2 Hz, J_2 = 1.6 Hz, 1H), 5.17 (d, J = 1.2 Hz, 1H), 4.39−4.33 (m, 1H), 4.27−4.22 (m, 1H), 2.43 (s, 3H), 2.36 (s, 3H), 1.37 (s, 9H), 1.11 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.3, 154.3, 150.8, 150.4, 145.8, 144.2, 138.4, 136.4, 132.9, 132.8, 131.8, 131.2, 129.7, 129.1, 128.5, 126.7, 121.5, 116.9, 111.7, 68.8, 36.1, 35.5, 29.8, 29.4, 21.7, 20.5. HRMS (ESI-TOF): m/z calcd for $C_{32}H_{38}NaO_4S^+$, 541.2389; found $[M + Na]^+$, 541.2373.

*4-((2-(Allyloxy)-5-methylphenyl)((4-fluorophenyl)sulfonyl)-methylene)-2,6-di-tert-utylcyclohexa-2,5-dien-1-one (**4g**).* Yellow solid. Isolated yield: 79% (124 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 108−109 °C. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.56 (d, J = 2.4 Hz, 1H), 7.81−7.74 (m, 2H), 7.19 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.15 (d, J = 2.0 Hz, 1H), 7.11−7.05 (m, 2H), 6.66 (d, J = 8.4 Hz, 1H), 6.51 (d, J = 2.8 Hz, 1H), 5.88−5.79 (m, 1H), 5.22 (s, 1H), 5.20−5.16 (m, 1H), 4.36−4.30 (m, 1H), 4.23−4.17 (m, 1H), 2.37 (s, 3H), 1.38 (s, 9H), 1.11 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.2, 165.5 (d, J_{C-F} = 253.5 Hz), 154.0, 151.1, 150.8, 144.7, 136.7, 132.8, 132.7, 132.1, 131.4 (d, J_{C-F} = 9.4 Hz), 131.0, 130.0, 126.4, 121.1, 117.0, 115.6 (d, J_{C-F} = 22.4 Hz), 111.5, 68.6, 36.1, 35.5, 29.7, 29.4, 20.5. HRMS (ESI-TOF): m/z calcd for $C_{31}H_{35}FNaO_4S^+$, 545.2138; found $[M + Na]^+$, 545.2127.

*4-((2-(Allyloxy)-5-chlorophenyl)(tosyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (**4h**).* Yellow solid. Isolated yield: 73% (118 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 152−153 °C. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.54 (d, J = 2.4 Hz, 1H), 7.70−7.64 (m, 2H), 7.36 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H), 7.29−7.24 (m, 3H), 6.76 (d, J = 8.8 Hz, 1H), 6.47 (d, J = 2.4 Hz, 1H), 5.88−5.78 (m, 1H), 5.23 (dd, J_1 = 3.6 Hz, J_2 = 1.6 Hz, 1H), 5.22−5.18 (m, 1H), 4.41−4.35 (m, 1H), 4.31−4.25 (m, 1H), 2.44 (s, 3H), 1.37 (s, 9H), 1.12 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.2, 155.1, 151.4, 150.9, 144.6, 143.7, 137.9, 136.9, 132.2, 131.9, 131.1, 130.5, 129.4, 128.5, 126.4, 125.5, 123.4, 117.4, 113.1, 69.2, 36.1, 35.6, 29.7, 29.4, 21.7. HRMS (ESI-TOF): m/z calcd for $C_{31}H_{35}ClNaO_4S^+$, 561.1842; found $[M + Na]^+$, 561.1830.

*2,6-Di-tert-butyl-4-((2-(phenylethynyl)phenyl)(phenylsulfonyl)-methylene)cyclohexa-2,5-dien-1-one (**4i**).* Yellow solid. Isolated yield: 76% (122 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 140−141 °C. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.76 (d, J = 2.4 Hz, 1H), 7.74 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 7.6 Hz, 1H), 7.50−7.42 (m, 4H), 7.33 (s, 1H), 7.31−7.28 (m, 2H), 7.25 (t, J = 7.6 Hz, 2H), 7.07 (d, J = 7.2 Hz, 2H), 6.58 (d, J = 2.4 Hz, 1H), 1.43 (s, 9H), 1.06 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.2, 151.5, 151.4, 145.6, 140.4, 137.6, 135.0, 133.6, 131.9, 131.4, 131.3, 129.8, 128.8, 128.7, 128.4, 128.3, 128.0, 126.6, 125.3, 122.5, 94.4, 87.4, 36.3, 35.6, 29.8, 29.3. HRMS (ESI-TOF): m/z calcd for $C_{35}H_{34}NaO_3S^+$, 557.2126; found $[M + Na]^+$, 557.2139.

*2,6-Di-tert-butyl-4-((2-((4-chlorophenyl)ethynyl)phenyl)-(phenylsulfonyl)methylene)cyclohexa-2,5-dien-1-one (**4j**).* Yellow solid. Isolated yield: 72% (123 mg) (eluent: petroleum ether/EtOAc = 20:1). Mp: 149−150 °C. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.74 (d, J = 2.8 Hz, 1H), 7.74 (d, J = 7.6 Hz, 2H), 7.63 (d, J = 7.6 Hz, 1H), 7.52−7.43 (m, 4H), 7.35−7.31 (m, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 6.55 (d, J = 2.4 Hz, 1H), 1.43 (s, 9H), 1.06 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.2, 151.5, 151.4, 145.6, 140.5, 137.6, 135.0, 134.8, 133.6, 132.6, 131.9, 131.5, 131.2, 129.8, 128.9, 128.7, 128.4, 128.3, 126.5, 125.0, 121.0, 93.0, 88.3, 36.3, 35.6, 29.9, 29.3. HRMS (ESI-TOF): m/z calcd for $C_{35}H_{33}ClNaO_3S^+$, 591.1737; found $[M + Na]^+$, 591.1729.

*2,6-Di-tert-butyl-4-((phenylsulfonyl)methyl)phenol (**5**).* White solid. Mp: 110−112 °C. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.63 (d, J = 8.0 Hz, 3H), 7.48 (t, J = 7.6 Hz, 2H), 6.80 (s, 2H), 5.31 (s, 1H), 4.27 (s, 2H), 1.37 (s, 18H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 154.3, 137.9, 136.1, 133.4, 128.9, 128.7, 127.7, 118.8, 63.2, 34.2, 30.1.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c01213.

^1H and $^{13}C\{^1H\}$ NMR spectra for all products and X-ray crystallographic data (PDF)

Accession Codes

CCDC 1980583−1980584 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre,

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Notes

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