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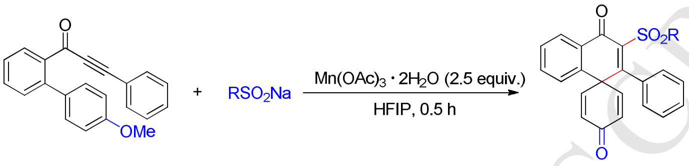

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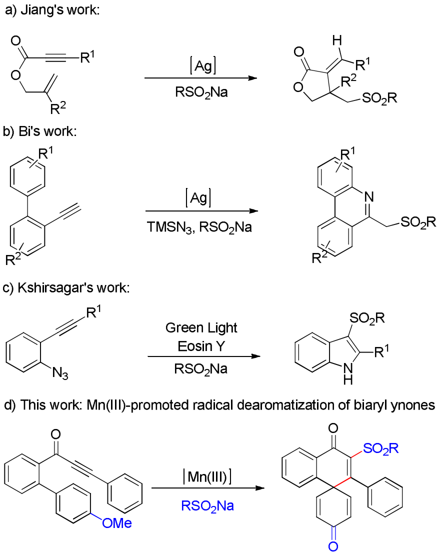
ABSTRACT

A Mn(III)-promoted radical oxidative *ipso*-annulation reaction of biaryl ynones with sodium sulfinates to construct various substituted spiro[5.5]trienones has been explored in this study. This protocol is characterized by mild reaction conditions, good substrates functional group compatibility, cheap and easily prepared $Mn(OAc)_3 \cdot 2H_2O$, and it demonstrates a simple operation.

1. Introduction

Spirocompounds have received considerable attention due to the special properties like conformational transmission, helical structure and photochromismm.[1] Meanwhile, certain spiro-conjugated molecule has been the starting materials for the construction of electroactive molecules which exhibiting nonconventional optoelectronic properties.[2] For example, sprio[5.5]undecatetraenedione has been used to prepare spiro-donors (TFE, BEDT-TTF) and acceptors (TCNQ, DCNOI).[2b] Therefore, the development of efficient methods to synthesize spirocarbocycles is still of high significant.[3] The most frequent strategy for the synthesis of spiro-molecular from readily available aromatic compounds is dearomatization, which mainly involves a 5-*exo-trig* cyclization to build spiro[4.5]decane core structures and their analogues.[4] To the best of our knowledge, research on different functional groups substituted spiro[5.5]trienones has been rarely reported.[5] Thus, a novel and efficient method to construct various important spiro[5.5]trienones is of high desireable.

Sulfones are valuable synthetic intermediates in synthetic chemistry.[6] Meanwhile, it is also very crucial to synthesize the molecules containing sulfone structure motifs because of their applications in material sciences, agrochemicals and pharmaceutical chemistry.[7] Consequently, chemists have spared no efforts to install this valuable functional group into organic molecule.[8] Conventional procedures are likely divided into two modes: the oxidation of the corresponding sulfides[9] and direct C-S bond formation by using benzenesulfonyl hydrazides, arenesulfonic acids and their derivatives.[10] Among them, sodium sulfinates are also used as popular materials to directly synthesize sulfonated compounds, owing to their readily availability, inexpensiveness and high air stability.[11] Especially, radical process by using sodium sulfinates to achieve sulfonylation/cyclization involving alkynes has gained



Scheme 1 The strategies for radical sulfonylation involving alkynes.

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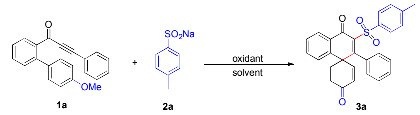
considerable attention. In 2017, Jiang's group reported Ag-catalyzed radical cascade sulfonylation/cyclization of 1,6-enynes with sodium sulfinates (Scheme 1a).[11h] The same year, Bi's group reported that biphenyl acetylene reacted with sodium sulfinates and trimethylsilyl azide (TMSN$_3$) to synthesize 6-methyl sulfonylated phenanthridines via a silver-catalyzed tandem carbon-carbon triple bond hydroazidation, radical sulfonylation and cyclization process (Scheme 1b).[11i] In 2018, Kshirsagar's group described that the visible light initiated radical cascade cyclization reaction for the synthesis of 3-sulfonylindoles from 2-alkynyl-azidoarenes and sodium sulfinates (Scheme 1c).[11j] Based on our ongoing interest in the dearomatization[4f, 4h] and sulfonylation[10f] reactions, we expect to develop a new direct radical oxidative dearomatization of biaryl ynones with sodium sulfinates to form the spiro[5.5]trienones compounds in the presence of manganese(III) acetate (Scheme 1d). This sulfonylation/dearomatization of biaryl ynones could involve the simultaneous formation of C-S, C-C bond and the cleavage of C-O bond in one step and make the formation of quaternary carbon stereocenter. The project provides a simple and efficient approach to obtain a series of sulfonated spiro[5.5]trienones in moderate to excellent yields.

2. Results and discussion

At the beginning of our studies, we chose biaryl ynone **1a** and sodium *p*-toluenesulfinate **2a** as the model substrates to optimize the reaction conditions (Table 1). Initially, the reaction was carried out in the presence of $Mn(OAc)_3\cdot 2H_2O$ (2.0 equiv.) in toluene. Gratifyingly, the expected product **3a** was obtained in 10% yield while a large amount of starting material was recovered (entry 1). The structure of **3a** was unambiguously confirmed by X-ray crystallographic analysis (see the Supporting Information).[12] In order to improve the yield of target product, various oxidants were then screened (entries 2-5). $Mn(OAc)_3\cdot 2H_2O$ was found to be effective oxidant. Next, through the investigation on various solvents, we found that 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) can remarkably improve the yield to 80% (entries 6-11). The cause of such a phenomenon is that radical intermediates could be stabilized by fluorinated solvent.[13] Afterwards, adjusting the loadings of $Mn(OAc)_3\cdot 2H_2O$ to 2.5 equiv. was found to be the best choice and afforded **3a** in 88% yield (entries 12, 12-13). Then, we explored the optimal reaction time and found that it had almost no effect on the yield of product **3a** when the time was shortened to 0.5 h (entries 14-15). Finally, product **3a** can also be obtained 81% yield under argon conditions (Table 1, entry 16). Control reaction demonstrated that $Mn(OAc)_3\cdot 2H_2O$ was essential in this reactivity (entry 17). Eventually, we come up with that the optimized reaction conditions were 0.2 mmol **1a** and 0.4 mmol **2a** with 0.5 mmol $Mn(OAc)_3\cdot 2H_2O$ in the presence of HFIP (2.0 mL) at 25 °C under air for 0.5 h.

Table 1

Optimization of reaction conditions[a]



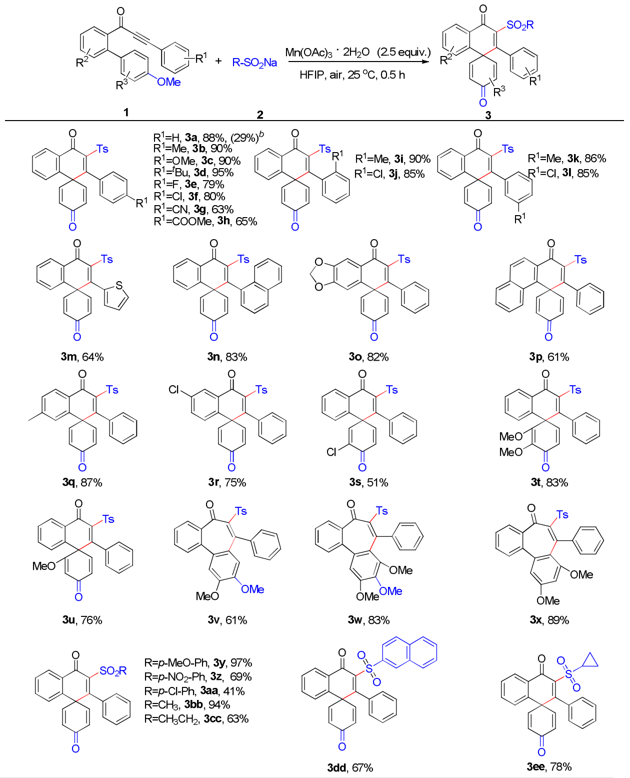
Entry	Oxidant (equiv.)	Solvent	Time (h)	Yield[b] (%)
1	$Mn(OAc)_3\cdot 2H_2O$ (2.0)	Toluene	12	10
2	$K_2S_2O_8$ (2.0)	Toluene	12	n.d.
3	TBHP (2.0)	Toluene	12	n.d.
4	$Mn(OAc)_2\cdot 4H_2O$ (2.0)	Toluene	12	n.d.
5	$PhI(OAc)_2$ (2.0)	Toluene	12	trace
6	$Mn(OAc)_3\cdot 2H_2O$ (2.0)	DCE	12	25
7	$Mn(OAc)_3\cdot 2H_2O$ (2.0)	1,4-dioxane	12	40
8	$Mn(OAc)_3\cdot 2H_2O$ (2.0)	CH_3CH_2OH	12	19
9	$Mn(OAc)_3\cdot 2H_2O$ (2.0)	CH_3COOH	12	15
10	$Mn(OAc)_3\cdot 2H_2O$ (2.0)	CH_3CN	12	trace
11	$Mn(OAc)_3\cdot 2H_2O$ (2.0)	HFIP	12	80
12	$Mn(OAc)_3\cdot 2H_2O$ (2.5)	HFIP	12	88
13	$Mn(OAc)_3\cdot 2H_2O$ (3.0)	HFIP	12	85
14	$Mn(OAc)_3\cdot 2H_2O$ (2.5)	HFIP	3	88
15	**$Mn(OAc)_3\cdot 2H_2O$ (2.5)**	**HFIP**	**0.5**	**88**
16[c]	$Mn(OAc)_3\cdot 2H_2O$ (2.5)	HFIP	0.5	81
17	-	HFIP	0.5	n.d.

[a] Reactions were carried out under the following conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), oxidant and solvent (2 mL), 25 °C under air. [b] Isolated yields. [c] Under argon. DCE = 1,2-dichloroethane; HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol.

With the optimized conditions in hand, we further explored the scope and limitation of this radical sulfonylation/dearomatization reaction between biaryl ynones **1** and sodium sulfinates **2** (Table 2). Initially, the electronic effect of substituent groups on aromatic ring (R^1 group) connected with the triple bond was investigated. Electron-donating groups and halogen groups were proved to be competent candidates in this transformation and they afforded the corresponding products (**3a-f, 3i-l**) in good yields. In particular, the product bearing *para-tert*-butyl group gave excellent yield (**3d**, 95% yield). **3g** and **3h** were obtained in moderate yields when the *para*-position of aromatic ring was occupied by -CN, or -COOMe. When distal position of the alkynone triple bond was replaced with thienyl and naphthyl, the spiroannular dearomatization reaction also proceeded well, and afforded corresponding products in 64% and 83% yields (**3m**, **3n**). Soon after, the study on the aryl group (R^2 group) which attaches to the carbonyl moiety was carried out. Both electron-donating and withdrawing groups (**3o-3r**) also worked well in the optimized conditions. Next, *p*-methoxyl-substituted aryl group (R^3 group) was examined. The introduction of chlorine group in the *ortho*-position to the -OMe produced the spiro compound **3s** in 51% yield. With the incorporation of single methoxyl group at *meta*-position or two methoxyl group at *ortho*- and *meta*-positions to the -OMe, we produced the corresponding dearomatized compounds **3u** in 76% or **3t** in 83% yield. But the *ortho*-position of the -OMe was substituted by single methoxyl group, which formed 9,10-dimethoxy-7-phenyl-6-tosyl-5*H*-dibenzo[*a*,*c*][7]annulen-5-one **3v** in 61% yield. The structure was unambiguously determined by X-ray crystallographic analysis (see the Supporting Information).[12] The substrate whose two methoxyl groups were placed in the *ortho*-positions of the -OMe, also gave the seven-membered ring product **3w** in 83% yield. Substrate having two meta-methoxy groups was also conducted under the standard conditions and furnished the seven-membered ring product **3x** in 89% yield. For the formation of spiro products and seven-membered ring products was due to the influence of electronic effects on the phenyl directly attached to the methoxyl. Then 1-(4'-hydroxy-[1,1'-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one was tested under optimized reaction conditions , and gave product **3a** in 29% yield. *Ortho*- and *meta*-methoxy substituted biaryl ynones were also conducted under the standard reaction conditions, regrettably, we could not obtain the desired products. Finally, sodium sulfinates were investigated. Various sulfonate

Table 2

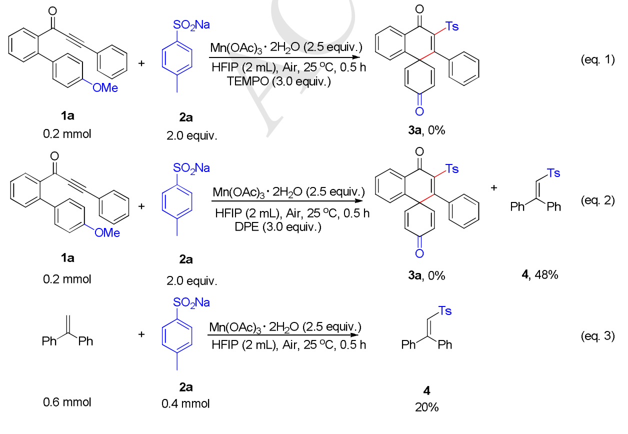
Substrate scope for the reaction^a



^{a}Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (0.5 mmol), HFIP (2.0 mL), 25 °C, air, 0.5 h. Isolated yields are shown. ^{b}1-(4'-hydroxy-[1,1'-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one reacted with **2a** under optimized reaction condition.

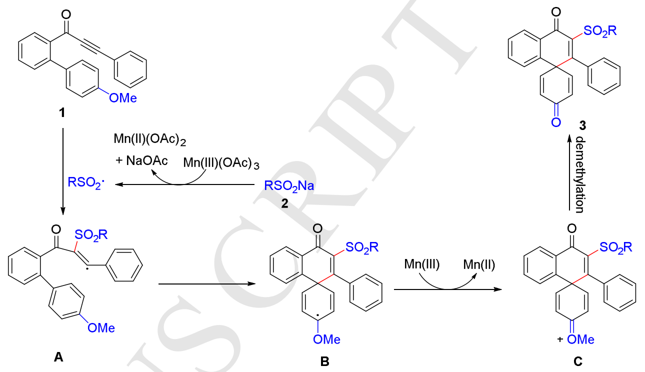
salts reacted with **1a** respectively under the optimized conditions, which gave corresponding spiro compounds (**3y-3ee**) in moderate to excellent yields.

To gain more insight into the pathway of the reaction, some control experiments were conducted (Scheme 2). When 3.0 equiv. of TEMPO (2,2,6,6-tetramethylpiperindine-1-oxyl) was added as radical scavenger to the standard conditions, the radical sulfonylation/dearomatization reaction was completely suppressed (eq. 1). **3a** couldn't be obtained while vinyl sulfone **4** was isolated in 48% yield when another radical scavenger DPE (1,1-diphenylethylene) was applied in the standard conditions (eq. 2). Moreover, in the absence of substrate **1a**, vinyl sulfone **4** could also be received in 20% yield (eq. 3). These results indicated that the spiroannular dearomatization reaction might involve a radical addition pathway.



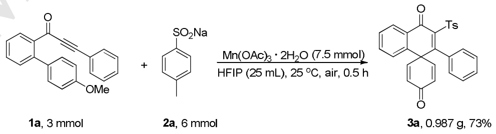
Scheme 2 Mechanistic studies.

Based on above experiments, a plausible mechanism was proposed in Scheme 3. First, sulfonyl radical was generated in situ from sodium sulfinate **2** oxidized by Mn(III) salt. Subsequently, sulfonyl radical added to more electron-rich alpha position of the conjugated alkynone **1** formed vinyl radical intermediate **A**. Intermediate **A** then underwent a 6-*exo-trig* cyclization to form the dearomatization intermediate **B**, which oxidized by Mn(III) salt to generate the oxocarbenium ion **C**. Demethylation of intermediate **C** furnished the desired sulfonylated spiro[5.5]trienones product **3**.



Scheme 3 Proposed mechanism of the reaction.

To investigate the preparative practicality of this novel method, a gram scale reaction of **1a** was performed under standard conditions (scheme 4). The product **3a** could be successfully obtained in 73% yield (0.987g) from 3 mmol **1a** and 6 mmol **2a** under optimized conditions.



Scheme 4 Gram-scale reaction.

3. Conclusions

In summary, we have developed a novel Mn(III)-promoted sulfonyl radical addition/dearomative spirocyclization reaction between biaryl ynones and sodium sulfinates. This method obtained sulfonyl substituted spiro[5.5]trienones in moderate to excellent yields with the construction of C-S, C-C bond and the cleavage of C-O bond in one step. Based on the advantages of simple operation and mild reaction conditions, we believe that this project is significant for the synthesis of sulfonyl substituted spirocyclic. Meanwhile, we expect this sulfonyl substituted spirocyclic could be found in the natural products and it is useful for pharmaceuticals and material electrochemistry in the future.

4. Experimental section

4.1. General

All reagents were purchased from commercial suppliers and used without further purification. Column chromatography was carried out on silica gel (200-300 mesh). ^{1}H NMR spectra were recorded on 400 MHz in $CDCl_3$, ^{13}C NMR spectra were recorded on 100 MHz in $CDCl_3$ and ^{19}F NMR spectra were recorded on 376 MHz in $CDCl_3$. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as internal standard. IR spectra were recorded on FT-IR spectrometer and only major peaks are reported in cm^{-1}. High-resolution mass spectral analysis (HRMS) date were measured on a Bruker Apex II. All products were characterized by HRMS. Copies of the ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra are provided in the Supporting Information. The substrates **1** were prepared according to literature procedure.[5a, 14]

4.2. General Procedure for Synthesis of 3

In a 10 mL dried tube, substrates **1** (0.2 mmol, 1.0 equiv.), sodium sulfinates **2** (0.4 mmol, 2.0 equiv.), Mn(OAc)$_3$·2H$_2$O (0.5 mmol, 2.5 equiv.) and HFIP (2.0 mL) were added. The reaction mixture was stirred at 25 ^{o}C for 0.5 h under air. After the reaction was completed, the reaction mixture was concentrated in vacuo and the residue was purified by column chromatography (silica gel, appropriate mixture of petroleum ether/ethyl acetate/dichloromethane = 3:1:1) to afford products **3**.

4.3. Characterization data of Products:

*4.3.1. 2’-phenyl-3’-tosyl-4’H-spiro[cyclohexane-1,1’-naphthalene]-2,5-diene-4,4’-dione (**3a**):* 79.6 mg, 88% yield; yellow solid, melting point 268-270 °C; ^{1}H NMR (400 MHz, CDCl$_3$,δ, ppm): 8.15 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.59-7.55 (m, 1H), 7.51-7.47 (m, 1H), 7.39-7.29 (m, 5H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 6.8 Hz, 1H), 6.68 (d, *J* = 10.0 Hz, 2H), 6.31 (d, *J* = 10.0 Hz, 2H), 2.41 (s, 3H), ^{13}C NMR (100 MHz, CDCl$_3$, δ, ppm): 178.7, 162.0, 146.7, 144.5, 140.2, 138.3, 137.0, 134.0, 133.7, 130.9, 130.3, 129.2, 129.0, 128.1, 127.8, 127.1, 52.7, 21.6. IR (neat, cm^{-1}): 2956, 1657, 1622, 1596, 1453, 1318, 1154, 856, 762, 716. HRMS (ESI) (*m/z*): calcd for C$_{28}$H$_{20}$O$_4$S ([M+H]$^+$), 453.1155; found 453.1159.

*4.3.2. 2’-(p-tolyl)-3’-tosyl-4’H-spiro[cyclohexane-1,1’-naphthalene]-2,5-diene-4,4’-dione (**3b**):* 84.0 mg, 90% yield; grey solid, melting point 200-202 °C; ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 8.14 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.58-7.53 (m, 1H), 7.50-7.46 (m, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.67 (d, *J* = 10.0 Hz, 2H), 6.32 (d, *J* = 10.0 Hz, 2H), 2.40 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, δ, ppm): 184.2, 178.7, 162.5, 146.9, 144.3, 140.2, 139.2, 138.4, 137.0, 133.9, 130.8, 130.2, 129.2, 128.8, 128.0, 127.8, 126.9, 52.8, 21.6, 21.3. IR (neat, cm^{-1}): 2957, 1659, 1621, 1596, 1451, 1324, 1159, 857, 812, 760. HRMS (ESI) (m/z): calcd for C$_{29}$H$_{22}$O$_4$S ([M+H]$^+$), 467.1312; found 467.1316.

*4.3.3. 2’-(4-methoxyphenyl)-3’-tosyl-4’H-spiro[cyclohexane-1,1’-naphthalene]-2,5-diene-4,4’-dione (**3c**):* 87.4 mg, 90% yield; brown solid, melting point 230-232 °C; ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 8.14 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.58-7.54 (m, 1H), 7.50-7.46 (m, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.23-7.21 (m, 1H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 10.0 Hz, 2H), 6.35 (d, *J* = 10.0 Hz, 2H), 3.81 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, δ, ppm): 184.2, 178.8, 162.4, 160.3, 147.1, 144.4, 140.4, 138.5, 137.0, 134.0, 130.8, 130.3, 129.2, 128.8, 128.5, 128.0, 127.8, 126.0, 112.7, 55.1, 53.0, 21.6. IR (neat, cm^{-1}): 2954, 1657, 1622, 1597, 1450, 1308, 1249, 1160, 1031, 758. HRMS (ESI) (*m/z*): calcd for C$_{29}$H$_{22}$O$_5$S ([M+H]$^+$), 483.1261; found 483.1267.

*4.3.4. 2’-(4-(tert-butyl)phenyl)-3’-tosyl-4’H-spiro[cyclohexane-1,1’-naphthalene]-2,5-diene-4,4’-dione (**3d**):* 97.0 mg, 95% yield; yellow solid, melting point 200-202 °C; ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 8.14 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.58-7.54 (m, 1H), 7.50-7.46 (m, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.22-7.20 (m, 1H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 10.0 Hz, 2H), 6.31 (d, *J* = 10.0 Hz, 2H), 2.41 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, CDCl$_3$, δ, ppm): 184.2, 178.8, 162.6, 152.4, 147.0, 144.3, 140.2, 138.5, 137.1, 134.0, 130.9, 130.7, 130.3, 129.2, 128.8, 128.0, 127.8, 126.8, 124.0, 52.8, 34.7, 31.2, 21.6. IR (neat, cm^{-1}): 2960, 2902, 1623, 1597, 1452, 1309, 1159, 857, 814, 759. HRMS (ESI) (*m/z*): calcd for C$_{32}$H$_{28}$O$_4$S ([M+H]$^+$), 509.1781; found 509.1787.

*4.3.5. 2’-(4-fluorophenyl)-3’-tosyl-4’H-spiro[cyclohexane-1,1’-naphthalene]-2,5-diene-4,4’-dione (**3e**):* 74.0 mg, 79% yield; yellow solid, melting point 260-262 °C; ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 8.14 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.60-7.56 (m, 1H), 7.51-7.47 (m, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.15-7.11 (m, 2H), 7.03 (t, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 10.0 Hz, 2H), 6.34 (d, *J* = 10.0 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, δ, ppm): 183.8, 178.5, 164.2, 161.3 (d, *J* = 87.0 Hz), 146.6, 144.6, 140.7, 138.2, 136.9, 134.1, 131.0, 130.1, 129.5 (d, *J* = 3.0 Hz), 129.3, 129.1, 128.8, 128.0, 127.9, 114.4 (d, *J* = 22.0 Hz), 52.6, 21.6. ^{19}F NMR (376 MHz, CDCl$_3$, δ, ppm): -111.1. IR (neat, cm^{-1}): 2955, 1663, 1623, 1597, 1451, 1313, 1227, 1154, 847, 766. HRMS (ESI) (*m/z*): calcd for C$_{28}$H$_{19}$FO$_4$S ([M+H]$^+$), 471.1061; found 471.1069.

*4.3.6. 2’-(4-chlorophenyl)-3’-tosyl-4’H-spiro[cyclohexane-1,1’-naphthalene]-2,5-diene-4,4-dione (**3f**):* 78.2 mg, 80% yield; brown solid, melting point 222-224 °C; ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 8.15 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.60-7.56 (m, 1H), 7.52-7.48 (m, 1H), 7.33-7.30 (m, 4H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.66 (d, *J* = 10.0 Hz, 2H), 6.35 (d, *J* = 10.0 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, δ, ppm): 183.8, 178.5, 160.6, 146.5, 144.7, 140.7, 138.2, 136.9, 135.5, 134.2, 132.1, 131.1, 130.2, 129.4, 129.3, 129.0, 128.5, 128.1, 127.9, 127.6, 52.5, 21.6. IR (neat, cm^{-1}): 2958, 1658, 1622, 1597, 1487, 1451, 1309, 1159, 858, 758. HRMS (ESI) (*m/z*): calcd for C$_{28}$H$_{19}$ClO$_4$S ([M+H]$^+$), 487.0765; found 487.0768.

*4.3.7. 4-(4,4-dioxo-3’-tosyl-4’H-spiro[cyclohexane-1,1’-naphthalene]-2,5-dien-2’-yl)benzonitrile (**3g**):* 60.0 mg, 63% yield; yellow solid, melting point 152-154 °C; ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 8.16 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.62-7.58 (m, 1H), 7.54-7.50 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.23-7.21 (m, 1H), 6.67 (d, *J* = 10.0 Hz, 2H), 6.36 (d, *J* = 10.0 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, δ, ppm): 183.4, 178.2, 159.1, 146.0, 145.1, 140.7, 138.3, 137.7, 136.7, 134.4, 131.4, 130.9, 130.0, 129.6, 129.5, 129.0, 128.2, 128.1, 127.9, 118.0, 113.2, 52.1, 21.7. IR (neat, cm^{-1}): 2954, 2229, 1659, 1619, 1596, 1452, 1314, 1154, 849, 729. HRMS (ESI) (*m/z*): calcd for C$_{29}$H$_{19}$NO$_4$S ([M+H]$^+$), 478.1108; found 478.1109.

*4.3.8. Methyl 4-(4,4’-dioxo-3’-tosyl-4’H-spiro[cyclohexane-1,1’-naphthalene]-2,5-dien-2’-yl)benzoate (**3h**):* 66.5 mg, 65% yield; brown solid, melting point 260-262 °C; ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 8.15 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.60-7.56 (m, 1H), 7.52-7.48 (m, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.24-7.21 (m, 3H), 6.69 (d, *J* = 10.0 Hz, 2H), 6.32 (d, *J* = 10.0 Hz, 2H), 3.91 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, δ, ppm): 183.6, 178.4, 166.1, 160.6, 146.3, 144.8, 140.3, 138.2, 137.9, 136.8, 134.2, 131.1, 130.6, 130.1, 129.4, 129.3, 129.0, 128.2, 128.1, 127.8, 127.3, 52.3, 52.2, 21.6. IR (neat, cm^{-1}): 2953, 1729, 1658, 1597, 1452, 1307, 1272, 1160, 862, 717. HRMS (ESI) (*m/z*): calcd for $C_{30}H_{22}O_6S$ ([M+H]$^+$), 511.1210; found 511.1217.

*4.3.9. 2’-(o-tolyl)-3’-tosyl-4’H-spiro[cyclohexane-1,1’-naphthalene]-2,5-diene-4,4’-dione (**3i**):* 83.5 mg, 90% yield; yellow solid, melting point 260-262 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.16-8.14 (m, 1H), 7.86 (d, J = 8.4 Hz, 2H), 7.59-7.54 (m, 1H), 7.52-7.48 (m, 1H), 7.30-7.27 (m, 3H), 7.22 (t, J = 8.0 Hz, 2H), 7.12 (t, J = 7.6 Hz, 1H), 6.89 (d, J = 7.6 Hz, 1H), 6.85 (dd, J = 10.0 Hz, J = 3.2 Hz, 1H), 6.48 (dd, J = 9.6 Hz, J = 2.8 Hz, 1H), 6.34 (dd, J = 10.0 Hz, J = 1.6 Hz, 1H), 6.24 (dd, J = 10.0 Hz, J = 1.6 Hz, 1H), 2.41 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 183.9, 178.7, 162.4, 147.6, 145.4, 144.5, 140.4, 138.3, 137.6, 135.1, 134.0, 133.0, 131.1, 130.6, 130.4, 129.9, 129.3, 129.2, 129.1, 128.9, 128.0, 127.3, 125.4, 124.1, 53.5, 21.6, 21.2. IR (neat, cm^{-1}): 2959, 1658, 1622, 1596, 1452, 1308, 1155, 858, 820, 760. HRMS (ESI) (*m/z*): calcd for $C_{29}H_{22}O_4S$ ([M+H]$^+$), 467.1312; found 467.1317.

*4.3.10. 2’-(2-chlorophenyl)-3’-tosyl-4’H-spiro[cyclohexane-1,1’-naphthalene]-2,5-diene-4,4’-dione (**3j**):* 82.9 mg, 85% yield; brown solid, melting point 274-276 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.14 (dd, J = 7.6 Hz, J = 0.8 Hz, 1H), 7.98 (d, J = 8.4 Hz, 2H), 7.60-7.56 (m, 1H), 7.52-7.48 (m, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.35-7.29 (m, 3H), 7.26-7.22 (m, 2H), 7.18 (dd, J = 10.0 Hz, J = 3.2 Hz, 1H), 7.08 (dd, J = 7.6 Hz, J = 1.2 Hz, 1H), 6.53 (dd, J = 10.0 Hz, J = 3.2 Hz, 1H), 6.38 (dd, J = 9.6 Hz, J = 1.6 Hz, 1H), 6.31 (dd, J = 10.0 Hz, J = 1.6 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 183.9, 178.3, 158.7, 147.2, 145.6, 144.6, 141.0, 138.1, 137.5, 134.2, 132.4, 131.9, 131.3, 130.8, 130.4, 130.2, 129.3, 129.2, 128.2, 128.1, 127.5, 125.5, 53.2, 21.6. IR (neat, cm^{-1}): 2957, 1659, 1622, 1598, 1452, 1308, 1156, 857, 780, 758. HRMS (ESI) (*m/z*): calcd for $C_{28}H_{19}ClO_4S$ ([M+H]$^+$), 487.0765; found 487.0769.

*4.3.11. 2’-(m-tolyl)-3’-tosyl-4’H-spiro[cyclohexane-1,1’-naphthalene]-2,5-diene-4,4’-dione (**3k**):* 80.6 mg, 86% yield; yellow solid, melting point 236-238 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.15 (dd, J = 7.6 Hz, J = 0.8 Hz, 1H), 7.85 (d, J = 8.0 Hz, 2H), 7.58-7.54 (m, 1H), 7.50-7.46 (m, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.23-7.16 (m, 3H), 6.94 (d, J = 7.2 Hz, 1H), 6.89 (s, 1H), 6.69-6.65 (m, 2H), 6.32-6.29 (m, 2H), 2.40 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 184.0, 178.7, 162.3, 146.8, 144.3, 140.0, 138.3, 136.9, 136.5, 133.9, 133.6, 130.7, 130.5, 130.2, 129.9, 129.1, 127.9, 127.7, 127.5, 126.9, 124.1, 52.6, 21.5, 21.3. IR (neat, cm^{-1}): 2950, 1659, 1620, 1596, 1451, 1309, 1156, 864, 808, 758. HRMS (ESI) (*m/z*): calcd for $C_{29}H_{22}O_4S$ ([M+H]$^+$), 467.1312; found 467.1316.

*4.3.12. 2’-(3-chlorophenyl)-3’-tosyl-4’H-spiro[cyclohexane-1,1’-naphthalene]-2,5-diene-4,4’-dione (**3l**):* 81.2 mg, 84% yield; yellow solid, melting point 236-238 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.15 (dd, J = 8.0 Hz, J = 1.2 Hz, 1H), 7.85 (d, J = 8.0 Hz, 2H), 7.60-7.56 (m, 1H), 7.52-7.48 (m, 1H), 7.36-7.26 (m, 4H), 7.22 (d, J = 7.6 Hz, 1H), 7.07-7.05 (m, 2H), 6.70-6.65 (m, 2H), 6.36-6.32 (m, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 183.7, 178.4, 159.8, 146.4, 146.3, 144.7, 140.6, 137.9, 136.7, 135.1, 134.2, 133.0, 131.0, 130.0, 129.3, 129.2, 128.9, 128.4, 128.0, 127.8, 127.1, 125.6, 52.3, 21.6. IR (neat, cm^{-1}): 2954, 1661, 1626, 1596, 1452, 1306, 1156, 857, 790, 763. HRMS (ESI) (*m/z*): calcd for $C_{28}H_{19}ClO_4S$ ([M+H]$^+$), 487.0765; found 487.0770.

*4.3.13. 2’-(thiophen-2-yl)-3’-tosyl-4’H-spiro[cyclohexane-1,1’-naphthalene]-2,5-diene-4,4’-dione (**3m**):* 58.0 mg, 64% yield; grey solid, melting point 210-212 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.10 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.59-7.55 (m, 1H), 7.49-7.45 (m, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 7.6 Hz, 1H), 7.15 (d, J = 2.8 Hz, 1H), 7.06-7.04 (m, 1H), 6.65 (d, J = 10.0 Hz, 2H), 6.44 (d, J = 9.6 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 184.4, 178.4, 155.5, 146.5, 144.4, 142.0, 138.5, 136.8, 134.2, 133.3, 131.4, 131.0, 130.1, 129.3, 129.2, 128.9, 128.1, 126.8, 52.6, 21.7. IR (neat, cm^{-1}): 2956, 1659, 1622, 1596, 1452, 1307, 1153, 856, 757, 705. HRMS (ESI) (*m/z*): calcd for $C_{26}H_{18}O_4S_2$ ([M+H]$^+$), 459.0719; found 459.0724.

*4.3.14. 2’-(naphthalene-1-yl)-3’-tosyl-4’H-spiro[cyclohexane-1,1’-naphthalene]-2,5-diene-4,4’-dione (**3n**):* 83.4 mg, 83% yield, yellow solid, melting point 226-228 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.21 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.86-7.82 (m, 2H), 7.75 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 8.0 Hz, 1H), 7.55-7.51 (m, 2H), 7.49-7.47 (m, 1H), 7.45-7.42 (m, 1H), 7.40-7.36 (m, 1H), 7.22-7.19 (m, 3H), 7.15-7.13 (m, 1H), 6.76 (dd, J = 10.0 Hz, J = 3.2 Hz, 1H), 6.58 (dd, J = 9.6 Hz, J = 3.2 Hz, 1H), 6.36 (dd, J = 9.6 Hz, J = 1.6 Hz, 1H), 5.83 (dd, J = 10.4 Hz, J = 1.6 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 183.9, 178.7, 161.5, 147.9, 146.3, 144.7, 142.1, 138.0, 137.9, 134.2, 132.8, 131.1, 131.0, 130.7, 129.7, 129.5, 129.3, 129.2, 128.3, 127.5, 126.6, 126.1, 125.1, 123.9, 53.7, 21.7. IR (neat, cm^{-1}): 2955, 1665, 1625, 1596, 1451, 1305, 1157, 857, 806, 739. HRMS (ESI) (*m/z*): calcd for $C_{32}H_{22}O_4S$ ([M+H]$^+$), 503.1312; found 503.1317.

*4.3.15. 6’-phenyl-7’-tosyl-8’H-spiro[cyclohexane-1,5’-naphtho[2,3-d][1,3]dioxole]-2,5-diene-4,8’-dione (**3o**):* 81.6 mg, 82% yield; brown solid, melting point 282-284 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.86 (d, J = 8.4 Hz, 2H), 7.52 (s, 1H), 7.39-7.29 (m, 5H), 7.12 (d, J = 7.2 Hz, 2H), 6.63 (d, J = 10.0 Hz, 2H), 6.58 (s, 1H), 6.31 (d, J = 10.0 Hz, 2H), 6.05 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 183.9, 177.2, 161.1, 152.9, 149.1, 146.8, 144.4, 139.8, 138.4, 133.7, 133.6, 130.9, 129.2, 129.1, 128.8, 127.1, 127.0, 125.8, 106.8, 106.3, 102.4, 52.7, 21.6. IR (neat, cm^{-1}): 2921, 1664, 1626, 1595, 1479, 1322, 1282, 1160, 1029, 873. HRMS (ESI) (*m/z*): calcd for $C_{29}H_{20}O_6S$ ([M+H]$^+$), 497.1053; found 497.1058.

*4.3.16. 3’-phenyl-2-tosyl-1’H-spiro[cyclohexane-1,4’-phenanthrene]-2,5-diene-1’,4-dione (**3p**):* 61.0 mg, 61% yield; brown solid, melting point 304-306 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.27 (d, J = 8.8 Hz, 1H), 8.13 (d, J = 8.8 Hz, 1H), 8.00 (d, J = 8.8 Hz, 1H), 7.91-7.86 (m, 3H), 7.60 (t, J = 7.2 Hz, 1H), 7.44-7.38 (m, 2H), 7.34-7.29 (m, 4H), 7.06 (d, J = 7.6 Hz, 2H), 6.77 (d, J = 10.0 Hz, 2H), 6.51 (d, J = 10.0 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 183.3, 179.1, 160.5, 147.1, 144.5, 141.2, 138.4, 136.3, 135.3, 133.6, 131.2, 131.0, 130.4, 130.0, 129.4, 129.2, 129.0, 128.7, 127.2, 125.9, 125.8, 122.7, 53.4, 21.6. IR (neat, cm^{-1}): 2952, 1654, 1621, 1597, 1463, 1319, 1159, 806, 766, 702. HRMS (ESI) (*m/z*): calcd for $C_{32}H_{22}O_4S$ ([M+H]$^+$), 503.1312; found 503.1317.

*4.3.17. 7’-methyl-2’-phenyl-3’-tosyl-4’H-spiro[cyclohexane-1,1’-naphthalene]-2,5-diene-4,4’-dione (**3q**):* 81.3 mg, 87% yield; brown solid, melting point 241-243 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.04 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.4 Hz, 2H), 7.38-7.28 (m, 6H), 7.13 (d, J = 7.2 Hz, 2H), 6.97 (s, 1H), 6.66 (d, J = 10.0 Hz, 2H), 6.31 (d, J = 10.0 Hz, 2H), 2.41 (s, 3H), 2.35(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 184.2, 178.5, 161.6, 146.9, 145.3, 144.4, 140.1, 138.4, 137.0, 133.7, 130.8, 130.3, 129.2, 129.1, 128.9, 128.1, 127.9, 127.1, 127.0, 52.6, 21.8, 21.6. IR (neat, cm^{-1}): 2956, 1658, 1621, 1570, 1442, 1306, 1156, 868, 781, 702. HRMS (ESI) (*m/z*): calcd for $C_{29}H_{22}O_4S$ ($[M+H]^+$), 467.1312; found 467.1318.

*4.3.18. 6'-chloro-2'-phenyl-3'-tosyl-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (**3r**):* 72.5 mg, 75% yield; yellow solid, melting point 246-248 °C; ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 8.09 (d, *J* = 2.4 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.50 (dd, *J* = 8.4 Hz, *J* = 2.4 Hz, 1H), 7.39-7.28 (m, 5H), 7.17-7.11 (m, 3H), 6.65 (d, *J* = 10.0 Hz, 2H), 6.31 (d, *J* = 10.0 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, δ, ppm): 183.7, 177.6, 162.2, 146.2, 144.7, 140.1, 138.1, 135.8, 135.4, 134.1, 133.4, 131.5, 131.1, 129.6, 129.3, 128.9, 127.6, 127.1, 127.0, 52.3, 21.6. IR (neat, cm^{-1}): 2955, 1661, 1623, 1592, 1410, 1326, 1160, 865, 730, 701. HRMS (ESI) (*m/z*): calcd for $C_{28}H_{19}ClO_4S$ ($[M+H]^+$), 487.0765; found 487.0770.

*4.3.19. 3-chloro-2'-phenyl-3'-tosyl-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (**3s**):* 50.0 mg, 51% yield; brown solid, melting point 224-226 °C; ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 8.16 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.62-7.57 (m, 1H), 7.54-7.50 (m, 1H), 7.40-7.37 (m, 2H), 7.36-7.34 (m, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.22-7.20 (m, 1H), 7.12-7.09 (m, 2H), 6.87 (d, *J* = 2.8 Hz, 1H), 6.70 (dd, *J* = 10.0 Hz, *J* = 3.2 Hz, 1H), 6.36 (d, *J* = 10.0 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, δ, ppm): 178.4, 177.1, 160.7, 147.0, 144.7, 142.3, 140.4, 138.1, 136.0, 135.3, 134.3, 133.2, 130.1, 129.9, 129.6, 129.4, 129.3, 129.0, 128.3, 127.7, 127.3, 127.2, 127.1, 126.7, 54.3, 21.6. IR (neat, cm^{-1}): 2964, 1666, 1595, 1453, 1305, 1157, 836, 767, 703, 690. HRMS (ESI) (*m/z*): calcd for $C_{28}H_{19}ClO_4S$ ($[M+H]^+$), 487.0765; found 487.0771.

*4.3.20. 2,3-dimethoxy-2'-phenyl-3'-tosyl-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (**3t**):* 84.7 mg, 83% yield; brown solid, melting point 212-214 °C; ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 8.12 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.57-7.53 (m, 1H), 7.49-7.45 (m, 1H), 7.39-7.37 (m, 2H), 7.34-7.23 (m, 4H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 6.33 (d, *J* = 9.6 Hz, 1H), 6.27 (d, *J* = 9.6 Hz, 1H), 3.80 (s, 3H), 3.42 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, δ, ppm): 183.5, 178.8, 162.0, 158.7, 144.2, 141.4, 140.6, 140.1, 138.5, 137.8, 133.9, 133.3, 130.7, 129.8, 129.1, 128.9, 128.6, 127.7, 127.3, 127.1, 126.9, 126.4, 61.1, 60.5, 57.0, 21.5. IR (neat, cm^{-1}): 2876, 1657, 1602, 1447, 1320, 1255, 1155, 1031, 767, 704. HRMS (ESI) (*m/z*): calcd for $C_{30}H_{24}O_6S$ ($[M+H]^+$), 513.1366; found 513.1371.

*4.3.21. 2-methoxy-2'-phenyl-3'-tosyl-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (**3u**):* 73.0 mg, 76% yield; brown solid, melting point 241-243 °C; ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 8.12 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.56-7.52 (m, 1H), 7.49-7.45 (m, 1H), 7.37-7.28 (m, 5H), 7.16 (t, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 7.2 Hz, 1H), 6.39 (d, *J* = 9.6 Hz, 1H), 6.28 (dd, *J* = 9.6 Hz, *J* = 1.2 Hz, 1H), 5.55 (d, *J* = 0.8 Hz, 1H), 3.54 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, δ, ppm): 186.5, 178.9, 171.9, 161.8, 144.3, 142.3, 140.8, 138.5, 137.7, 134.0, 133.2, 130.5, 129.5, 129.1, 129.0, 128.7, 127.7, 127.3, 126.9, 126.8, 126.7, 105.5, 56.0, 55.2, 21.5. IR (neat, cm^{-1}): 2968, 1670, 1628, 1595, 1453, 1309, 1223, 1161, 855, 798. HRMS (ESI) (*m/z*): calcd for $C_{29}H_{22}O_5S$ ($[M+H]^+$), 483.1261; found 483.1264.

*4.3.22. 9,10-dimethoxy-7-phenyl-6-tosyl-5H-dibenzo[a,c][7]annulen-5-one (**3v**):* 60.3 mg, 61% yield; yellow solid, melting point 184-186 °C; ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 7.78 (d, *J* = 8.0 Hz, 1H), 7.68-7.64 (m, 1H), 7.49 (t, *J* = 7.6 Hz 2H), 7.44 (d, *J* = 8.0 Hz, 2H) 7.39-7.32 (m, 3H), 7.17 (s, 1H), 7.12 (d, *J* = 6.0 Hz, 3H), 6.60 (s, 1H), 6.34 (s, 1H), 3.95 (s, 3H), 3.50 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, δ, ppm): 193.3, 150.1, 149.1, 147.8, 143.9, 143.8, 141.1, 138.7, 137.4, 135.1, 132.5, 131.2, 129.0, 128.9, 128.6, 128.3, 128.2, 127.6, 125.2, 114.6, 112.9, 56.0, 55.5, 21.5. IR (neat, cm^{-1}): 2969, 1668, 1596, 1538, 1484, 1356, 1266, 1152, 1030, 775. HRMS (ESI) (*m/z*): calcd for $C_{30}H_{24}O_5S$ ($[M+H]^+$), 497.1417; found 497.1426.

*4.3.23. 8,9,10-trimethoxy-7-phenyl-6-tosyl-5H-dibenzo[a,c][7]annulen-5-one (**3w**):* 87.8 mg, 83% yield; yellow solid, melting point 112-114 °C; ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 7.82 (d, *J* = 7.6 Hz, 1H), 7.69-7.65 (m, 1H), 7.53 (d, *J* = 4.4 Hz, 2H), 7.22-7.13 (m, 3H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.84 (s, 1H), 3.91 (s, 3H), 3.69 (s, 3H), 2.92 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, δ, ppm): 193.2, 154.6, 153.1, 146.4, 144.9, 143.4, 142.5, 141.7, 138.7, 138.0, 135.7, 134.5, 131.1, 128.8, 128.3, 128.2, 127.7, 127.6, 127.0, 125.3, 122.5, 108.4, 60.4, 59.3, 56.0, 21.3. IR (neat, cm^{-1}): 2940, 1709, 1588, 1493, 1345, 1259, 1145, 1034, 771, 706. HRMS (ESI) (*m/z*): calcd for $C_{31}H_{26}O_6S$ ($[M+H]^+$), 527.1523; found 527.1534.

*4.3.24. 8,10-dimethoxy-7-phenyl-6-tosyl-5H-dibenzo[a,c][7]annulen-5-one (**3x**):* 88.1 mg, 89% yield, yellow solid, melting point 83-85 °C; ^{1}H NMR (400 MHz, CDCl$_3$,δ, ppm): 7.85 (d, *J* = 8.0 Hz, 1H), 7.68-7.64 (m, 1H), 7.53-7.52 (m, 2H), 7.19-7.02 (m, 5H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.69 (d, *J* = 2.4 Hz, 1H), 6.29 (d, *J* = 2.4 Hz, 1H), 3.80 (s, 3H), 3.16 (s, 3H), 2.26 (s, 3H), ^{13}C NMR (100 MHz, CDCl$_3$, δ, ppm): 193.3, 161.1, 160.5, 146.7, 144.7, 143.3, 141.9, 140.0, 138.5, 138.0, 135.6, 131.0, 128.7, 128.5, 128.0, 127.8, 127.5, 126.5, 125.1, 117.9, 106.6, 99.3, 55.4, 55.3, 21.3. IR (neat, cm^{-1}): 2938, 1708, 1600, 1557, 1456, 1316, 1207, 1144, 1023, 737. HRMS (ESI) (*m/z*): calcd for $C_{30}H_{24}O_5S$ ($[M+H]^+$), 497.1417; found 497.1422.

*4.3.25. 3'-((4-methoxyphenyl)sulfonyl)-2'-phenyl-4'H-spiro[cyclohexa[2,5]diene-1,1'-naphthalene]-4,4'-dione (**3y**):* 90.9 mg, 97% yield; yellow solid, melting point 218-220 °C; ^{1}H NMR (400 MHz, CDCl$_3$,δ, ppm): 8.18 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.60-7.56 (m, 1H), 7.53-7.49 (m, 1H), 7.40-7.38 (m, 1H), 7.37-7.33 (m, 2H), 7.22 (dd, *J* = 7.6 Hz, *J* = 0.4 Hz, 1H), 7.13-7.11 (m, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 10.0 Hz, 2H), 6.32 (d, *J* = 10.0 Hz, 2H), 3.87 (s, 3H), ^{13}C NMR (100 MHz, CDCl$_3$, δ, ppm): 184.2, 178.9, 163.6, 161.6, 146.8, 140.4, 136.9, 134.1, 133.8, 132.5, 131.5, 130.9, 130.3, 129.3, 129.2, 128.1, 127.9, 127.1, 127.0, 113.8, 55.6, 52.6. IR (neat, cm^{-1}): 1657, 1619, 1593, 1495, 1310, 1263, 1156, 1020, 860, 760. HRMS (ESI) (*m/z*): calcd for $C_{28}H_{20}O_5S$ ($[M+H]^+$), 469.1104; found 469.1110.

*4.3.26. 3'-((4-nitrophenyl)sulfonyl)-2'-phenyl-4'H-spiro[cyclohexa[2,5]diene-1,1'-naphthalene]-4,4'-dione (**3z**):* 66.2 mg, 69% yield, white solid, melting point 220-222 °C; ^{1}H NMR (400 MHz, CDCl$_3$,δ, ppm): 8.32 (d, *J* = 8.8 Hz, 2H), 8.16 (d, *J* = 8.8 Hz, 2H), 8.11 (d, *J* = 6.8 Hz, 1H), 7.64-7.60 (m, 1H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.46-7.42 (m, 1H), 7.40-7.36 (m, 2H), 7.26 (d, *J* = 8.8 Hz, 1H), 7.18 (d, *J* = 6.8 Hz, 2H), 6.72 (d, *J* = 10.0 Hz, 2H), 6.37 (d, *J* = 10.0 Hz, 2H), ^{13}C NMR (100 MHz, CDCl$_3$, δ, ppm): 183.8, 178.5, 164.2, 150.3, 146.9, 146.1, 139.1, 137.2, 134.5, 133.0, 131.2, 130.0, 129.7, 129.5, 128.0, 127.3, 126.9, 123.8, 52.8. IR (neat, cm^{-1}): 3098, 1664, 1625, 1600, 1529, 1450, 1302, 1160, 769, 684. HRMS (ESI) (*m/z*): calcd for $C_{27}H_{17}NO_6S$ ($[M+H]^+$), 484.0849; found 484.0856.

*4.3.27. 3'-((4-chlorophenyl)sulfonyl)-2'-phenyl-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (**3aa**):* 38.9 mg, 41% yield; brown solid, melting point 288-290 °C; ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.15 (dd, *J* = 7.6 Hz, *J* = 0.8 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.61-7.57 (m, 1H), 7.53-7.51 (m, 1H), 7.49-7.48 (m, 1H), 7.47-7.46 (m, 1H), 7.43-7.39 (m, 1H), 7.37-7.33 (m, 2H), 7.24-7.22 (m, 1H), 7.14-7.11 (m, 2H), 6.67 (d, *J* = 10.0 Hz, 2H), 6.33 (d, *J* = 10.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 183.9, 178.7, 162.9, 146.5, 140.3, 139.9, 139.8, 137.1, 134.3, 133.5, 131.1, 130.5, 130.1, 129.5, 129.4, 129.0, 128.1, 127.9, 127.2, 127.0, 52.8. IR (neat, cm^{-1}): 1658, 1623, 1597, 1454, 1317, 1154, 1086, 788, 764, 715. HRMS (ESI) (*m/z*): calcd for $C_{27}H_{17}ClO_4S$ ($[M+H]^+$), 473.0609; found 473.0614.

*4.3.28. 3'-(methylsulfonyl)-2'-phenyl-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (**3bb**):* 70.4 mg, 94% yield; white solid, melting point 276-278 °C; ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.31 (dd, J = 7.6 Hz, J = 0.8 Hz, 1H), 7.67-7.63 (m, 1H), 7.61-7.57 (m, 1H), 7.40-7.36 (m, 1H), 7.33-7.29 (m, 3H), 7.10 (d, J = 7.2 Hz, 2H), 6.70 (d, J = 10.0 Hz, 2H), 6.36 (d, J = 10.0 Hz, 2H), 3.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 184.0, 179.7, 162.5, 146.5, 139.7, 137.4, 134.5, 133.3, 131.1, 130.0, 129.5, 128.2, 128.1, 127.3, 127.0, 52.6, 45.8. IR (neat, cm^{-1}): 2956, 2869, 1665, 1601, 1455, 1306, 1150, 854, 751, 721. HRMS (ESI) (m/z): calcd for $C_{22}H_{16}O_4S$ ($[M+H]^+$), 377.0842; found 377.0846.

*4.3.29. 3'-(ethylsulfonyl)-2'-phenyl-4'H-spiro[cyclohexa[2,5]diene-1,1'-naphthalene]-4,4'-dione (**3cc**):* 49.1 mg, 63% yield, yellow solid, melting point 285-287 °C; ^1H NMR (400 MHz, $CDCl_3$,δ, ppm): 8.30 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.67-7.63 (m, 1H), 7.61-7.57 (m, 1H), 7.39-7.35 (m, 1H), 7.32-7.29 (m, 3H), 7.09-7.07 (m, 2H), 6.71 (d, *J* = 10.0 Hz, 2H), 6.35 (d, *J* = 10.0 Hz, 2H), 3.54 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 184.1, 179.8, 163.8, 146.6, 137.5, 137.3, 134.5, 133.2, 131.0, 129.9, 129.5, 129.3, 128.2, 128.0, 127.1, 126.9, 52.7, 51.2, 6.9. IR (neat, cm^{-1}): 3043, 1666, 1624, 1596, 1452, 1311, 1145, 857, 798, 757. HRMS (ESI) (*m/z*): calcd for $C_{23}H_{18}O_4S$ ($[M+H]^+$), 391.0999; found 391.1003.

*4.3.30. 3'-(naphthalen-2-ylsulfonyl)-2'-phenyl-4'H-spiro[cyclohexa[2,5]diene-1,1'-naphthalene]-4,4'-dione (**3dd**):* 65.2 mg, 67% yield; white solid, melting point 254-256 °C; ^1H NMR (400 MHz, $CDCl_3$,δ, ppm): 8.55 (s, 1H), 8.14 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 8.01-7.94 (m, 3H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.68-7.61 (m, 2H), 7.60-7.56 (m, 1H), 7.51-7.47 (m, 1H), 7.45-7.36 (m, 3H), 7.23-7.21 (m, 1H), 7.19-7.17 (m, 2H), 6.70 (d, *J* = 10.0 Hz, 2H), 6.34 (d, *J* = 10.0 Hz, 2H), ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 184.1, 178.8, 162.4, 146.7, 140.2, 138.0, 136.9, 135.2, 134.2, 133.6, 131.9, 131.0, 130.2, 129.6, 129.4, 129.3, 129.2, 128.7, 128.1, 127.9, 127.4, 127.2, 127.1, 123.5, 52.7. IR (neat, cm^{-1}): 3049, 1657, 1619, 1452, 1325, 1160, 1128, 1069, 762, 712. HRMS (ESI) (*m/z*): calcd for $C_{31}H_{20}O_4S$ ($[M+H]^+$), 489.1155; found 489.1161.

*4.3.31. 3'-(cyclopropylsulfonyl)-2'-phenyl-4'H-spiro[cyclohexa[2,5]diene-1,1'-naphthalene]-4,4'-dione (**3ee**):* 62.6 mg, 78% yield, white solid, melting point 276-278 °C; ^1H NMR (400 MHz, $CDCl_3$,δ, ppm): 8.31 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.67-7.63 (m, 1H), 7.61-7.57 (m, 1H), 7.37-7.33 (m, 1H), 7.30-7.27 (m, 3H), 7.08-7.05 (m, 2H), 6.73 (dd, *J* = 10.0 Hz, 2H), 6.34 (dd, *J* = 10.0 Hz, 2H), 3.41-3.35 (m, 1H), 1.17-1.13 (m, 2H), 1.03-0.97 (m, 2H), ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 184.0, 179.7, 161.0, 146.7, 139.0, 137.2, 134.3, 133.4, 130.8, 130.0, 129.3, 129.1, 128.0, 126.9, 52.4, 32.8, 5.7. IR (neat, cm^{-1}): 3052, 1663, 1623, 1595, 1454, 1319, 1151, 887, 729, 709. HRMS (ESI) (*m/z*): calcd for $C_{24}H_{18}O_4S$ ($[M+H]^+$), 403.0999; found 403.1002.

*4.3.32. (2-tosylethene-1,1-diyl)dibenzene (**4**):* ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.47 (d, J = 8.0 Hz, 2H), 7.39-7.34 (m, 2H), 7.31-7.27 (m, 4H), 7.21-7.19 (m, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.10-7.08 (m, 2H), 6.99 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 154.6, 143.7, 139.2, 138.6, 135.5, 130.2, 129.7, 129.3, 128.9, 128.8, 128.5, 128.2, 127.8, 127.7, 21.5. HRMS (ESI) (m/z): calcd for $C_{21}H_{18}O_2S$ ($[M+H]^+$), 335.1100; found 335.1100.

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