Supplementary Information

Visible-light-enabled spirocyclization of alkynes leading to 3-sulfonyl and 3-sulfenyl azaspiro[4,5]trienones

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1. General information

All commercially available reagent grade chemicals were purchased from Aldrich, Acros, Alfa Aesar and Beijing Ouhe Chemical Company and used as received without further purification unless otherwise stated. All solvents were dried according to standard procedures. $^1$H NMR and $^{13}$C NMR were recorded in CDCl$_3$ on a Bruker Avance III 400 spectrometer with TMS as internal standard (500 MHz $^1$H, 125 MHz $^{13}$C) at room temperature, the chemical shifts (δ) were expressed in ppm and $J$ values were given in Hz. The following abbreviations are used to indicate the multiplicity: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). All first order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted were designated as multiplet (m). Mass analyses and HRMS were obtained on a Finnigan-LCQDECA mass spectrometer and a Bruker Daltonics Bio-TOF-Q mass spectrometer by the ESI method, respectively. Column chromatography was performed on silica gel (200-300 mesh). There is 3.0 cm distance between the reactor and LEDs.

2. Optimization of conditions for the synthesis of 3-sulfenyl azaspiro[4,5]trienone 5a$^a$ (Table S1).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Photocatalyst (mol%)</th>
<th>Solvent</th>
<th>Yield (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Eosin Y (5)</td>
<td>CH$_3$CN</td>
<td>66</td>
</tr>
<tr>
<td>2</td>
<td>Eosin Y (2)</td>
<td>CH$_3$CN</td>
<td>74</td>
</tr>
<tr>
<td>3</td>
<td>Eosin Y (1)</td>
<td>CH$_3$CN</td>
<td>87</td>
</tr>
<tr>
<td>4</td>
<td>Eosin Y (1)</td>
<td>1,4-dioxane</td>
<td>59</td>
</tr>
<tr>
<td>5</td>
<td>Eosin Y (1)</td>
<td>Toluene</td>
<td>32</td>
</tr>
<tr>
<td>6</td>
<td>Eosin Y (1)</td>
<td>CHCl$_3$</td>
<td>58</td>
</tr>
<tr>
<td>7</td>
<td>Eosin Y (1)</td>
<td>Acetone</td>
<td>54</td>
</tr>
<tr>
<td>8</td>
<td>Eosin Y (1)</td>
<td>DCE</td>
<td>58</td>
</tr>
<tr>
<td>9</td>
<td>Eosin Y (1)</td>
<td>DMSO</td>
<td>25</td>
</tr>
<tr>
<td>10</td>
<td>Eosin Y (1)</td>
<td>DME</td>
<td>14</td>
</tr>
<tr>
<td>11</td>
<td>Eosin Y (1)</td>
<td>THF</td>
<td>15</td>
</tr>
<tr>
<td>12</td>
<td>Eosin Y (1)</td>
<td>CH$_3$CN/H$_2$O</td>
<td>52</td>
</tr>
<tr>
<td>13</td>
<td>Eosin Y (1)</td>
<td>H$_2$O</td>
<td>14</td>
</tr>
<tr>
<td>14</td>
<td>Eosin B (1)</td>
<td>CH$_3$CN</td>
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<tr>
<td>15</td>
<td>Rose Bengal (1)</td>
<td>CH$_3$CN</td>
<td>42</td>
</tr>
<tr>
<td>16</td>
<td>Rhodamine B (1)</td>
<td>CH$_3$CN</td>
<td>46</td>
</tr>
</tbody>
</table>
17  Acridine Red (1)       CH\textsubscript{3}CN            33
18  Na\textsubscript{2}-Eosin Y (1)         CH\textsubscript{3}CN    46
19  Ru(bpy)\textsubscript{3}Cl\textsubscript{2}(1)       CH\textsubscript{3}CN    65
20  --                           CH\textsubscript{3}CN    0
21  Eosin Y (1)                   CH\textsubscript{3}CN    0\textsuperscript{c}

\textsuperscript{a} Reaction conditions: \textit{1a} (0.125 mmol), \textit{4a} (0.25 mmol), catalyst (1-5 mol%), Solvent 2 mL, at room temperature, 12h, under air. DME: 1,2-dimethoxyethane; DCE: 1,2-dichloroethane; THF: tetrahydrofuran; \textsuperscript{b} Isolated yields based on \textit{1a}. \textsuperscript{c} Without visible-light irradiation.

3. General procedure

3.1 The procedure for visible-light-induced difunctionalization of alkynes with sulfinic acids leading to 3-sulfonyl azaspiro[4,5]trienones.

\begin{align*}
\text{MeO} & \quad \text{N} \quad \text{O} \\
\text{R}^1 & \quad \text{C} & \quad \text{N} \\
\text{R}^2 & \quad \text{R}^3 & \quad \text{R}^4 & \quad \text{R}^5
\end{align*}

To a solution of sulfinic acid \textit{2} (0.375 mmol) and Na\textsubscript{2}-eosin Y (0.00625 mmol, 5 mol%) in CH\textsubscript{3}CN/H\textsubscript{2}O (\textit{v}\textsubscript{1}/\textit{v}\textsubscript{2}=1/1) 2 mL was added N-(p-methoxyaryl)-propiolamide \textit{1} (0.125 mmol). The reaction vessel was allowed to stir at room temperature under the irradiation of 3W blue LED lamps for 6-24h. After the reaction, the resulting mixture was extracted with EtOAc and the solvent was then removed under vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product \textit{3}.

3.2 The procedure for visible-light-induced difunctionalization of alkynes with thiols leading to 3-sulfenyl azaspiro[4,5]trienones.

\begin{align*}
\text{MeO} & \quad \text{N} \quad \text{O} \\
\text{R}^1 & \quad \text{C} & \quad \text{N} \\
\text{R}^2 & \quad \text{R}^3 & \quad \text{R}^4 & \quad \text{R}^5
\end{align*}

To a solution of thiol \textit{5} (0.25 mmol) and Eosin Y (0.00125 mmol, 1 mol %) in CH\textsubscript{3}CN 2 mL was added N-(p-methoxyaryl)-propiolamide \textit{1} (0.125 mmol). The reaction mixture was open to the air and stirred under the irradiation of 3W blue LED lamps at room temperature for 12h. After completion of the reaction, the solution was concentrated in vacuum. The residue was purified by flash column chromatography using
a mixture of petroleum ether and ethyl acetate as eluent to give the desired product 5.

4. Preliminary mechanistic studies

4.1 N-(p-methoxyaryl)-propiolamide 1a was added independently under the standard conditions.

![Diagram of reaction](image)

To a solution of Na$_2$-Eosin Y (0.00625mmol, 5 mol%) in CH$_3$CN/H$_2$O (v$_1$/v$_2$=1/1) 2 mL was added N-(p-methoxyaryl)-propiolamide 1a (0.125 mmol). The reaction mixture was open to the air and stirred under the irradiation of 3W blue LED lamps at room temperature for 6h. After completion of the reaction, the solution was concentrated in vacuum, none of the desired product 1a’ was detected.

![Diagram of reaction](image)

To a solution of Eosin Y (0.00125mmol, 1 mol %) in CH$_3$CN 2 mL was added N-(p-methoxyaryl)-propiolamide 1a (0.125 mmol). The reaction mixture was open to the air and stirred under the irradiation of 3W blue LED lamps at room temperature for 12h. After completion of the reaction, the solution was concentrated in vacuum, none of the desired product 1a’ was detected.

4.2 The addition of TEMPO in the model reaction systems.

![Diagram of reaction](image)

To a solution of 4-methylbenzenesulfinic acid 2a (0.375 mmol), TEMPO (0.375 mmol), and Na$_2$-Eosin Y (0.00625mmol, 5 mol%) in CH$_3$CN/H$_2$O (v$_1$/v$_2$=1/1) 2 mL was added N-(p-methoxyaryl)-propiolamide 1 (0.125 mmol) (0.125 mmol). The reaction
mixture was open to air and stirred under the irradiation of 3W blue LED lamps at room temperature for 6h. After completion of the reaction, the solution was concentrated in vacuum, none of desired product 3a was detected.

To a solution of 4-methylbenzenethiol 2a (0.25 mmol), TEMPO (0.25 mmol), and Eosin Y (0.001 mmol, 1 mol %) in CH$_3$CN 2 mL was added N-($p$-methoxyaryl)-propiolamide 1 (0.125 mmol) (0.125 mmol). The reaction mixture was open to the air and stirred under the irradiation of 3W blue LED lamps at room temperature for 12h. After completion of the reaction, the solution was concentrated in vacuum, TEMPO-trapped thyl radical complex (p-MePhS–TEMPO) was also detected by LC-MS experiment and none of desired product 5a was obtained.
4.3 Investigation of mechanism by ESR

Electron spin resonance (ESR) spectra were recorded with a JEOL JES FA200 (X-band). The sample was bubbled with Ar for over 20 min, then small amount of the sample was transferred to a flat cell, and ESR spectra were recorded under different conditions.

(1)

Mixture of Na$_2$-eosin Y (2.5 mM), 4-methylbenzenesulfinic acid 2a (50 mM), and DMPO (100 mM) in CH$_3$CN/H$_2$O was transferred to a capillary, and the ESR spectra were recorded under different conditions (Figure S1.). A very weak radical signal was trapped without irradiation of visible light. Notably, when the reaction mixture of 2a was irradiated with visible light (1 min and 3 min), a distinct signal of a trapped radical was observed, suggesting the involvement of a sulfonyl radical in the transformation. These results indicated that photocatalysis plays an essential role in the formation of the sulfonyl radical.
Figure S1. ESR spectra of mixture of Na$_2$-eosin Y (2.5 mM), 4-methylbenzenesulfinic acid 2a (50 mM), and DMPO (100 mM) in CH$_3$CN/H$_2$O under different conditions. ESR conditions: frequency (9.43 GHz), power (1 mW), modulation width (0.1 mT), center field (336.7 mT), sweep width (10 mT), sweep time (1 min), time constant (0.1 s).

Mixture of Eosin Y (0.25mM), 4-methylbenzenethiol 4a (25mM), and DMPO (50 mM) in CH$_3$CN was transferred to a flat cell, and the ESR spectra were recorded under different conditions (Figure S2). No radical was trapped without irradiation of visible light. Notably, when the reaction mixture of 4a was irradiated with visible light (1 min and 3 min), a distinct signal of a trapped radical was observed, suggesting the involvement of a thiol radical in the transformation. These results indicated that photocatalysis plays an essential role in the formation of the thiol radical.
**Figure S2.** ESR spectra of mixture of Eosin Y (0.25 mM), 4-methylbenzenethiol 4a (25 mM), and DMPO (50 mM) in CH$_3$CN under different conditions. ESR conditions: frequency (9.43 GHz), power (1 mW), modulation width (0.1 mT), center field (336.7 mT), sweep width (10 mT), sweep time (1 min), time constant (0.1 s).

### 4.3 The UV-visible spectroscopy and Fluorescence quenching studies for the synthesis of 3-sulfonyl azaspiro[4,5]trienone (Stern–Volmer Studies)

UV-visible spectroscopy of reaction solution was recorded on a SHIMADZU UV-3600 UV-visible spectrophotometer. The sample was prepared by mixing N-(4-methoxyphenyl)-N-methyl-3-phenylpropiolamide 1a with solvent CH$_3$CN (M[N-(4-methoxyphenyl)-N-methyl-3-phenylpropiolamide] = 1.25×10$^{-2}$ mol/L in a light path quartz UV cuvette. The absorption was collected and the result was listed in Figure S3.
Figure S3. UV–vis spectra of 1a.

UV-visible spectroscopy of reaction solution was recorded on a SHIMADZU UV-3600 UV-visible spectrophotometer. The sample was prepared by mixing 4-methylbenzenesulfinic acid 2a with solvent CH$_3$CN (M[4-methylbenzenesulfinic acid] = 3.75×10$^{-2}$ mol/L in a light path quartz UV cuvette. The absorption was collected and the result was listed in Figure S4.

Figure S4. UV–vis spectra of the 2a.

The fluorescence emission intensities were recorded on a Fluormax-4600 spectrofluorimeter. The excitation wavelength was fixed at 530 nm, and the emission wavelength was measured at 549 nm (emission maximum). The samples were prepared by mixing N-(4-methoxyphenyl)-N-methyl-3-phenylpropiolamide 1a in CH$_3$CN (total volume = 0.1 mL) in a light path quartz fluorescence cuvette. The concentration of N-(4-methoxyphenyl)-N-methyl-3-phenylpropiolamide 1a stock solution is 1.25×10$^{-2}$ mol/L in CH$_3$CN. Then the emission intensity was collected and the result was presented in Figure S5.
Figure S5. Fluorescence spectra of 1a

The fluorescence emission intensities were recorded on a Fluormax-4600 spespectrofluorimeter. The excitation wavelength was fixed at 530nm, and the emission wavelength was measured at 549 nm (emission maximum). The samples were prepared by mixing 4-methylbenzenesulfonic acid 2a in CH\(_3\)CN (total volume = 0.1 mL) in a light path quartz fluorescence cuvette. The concentration of 4-methylbenzene sulfonic acid stock solution is 3.75×10\(^{-2}\)mol/L in CH\(_3\)CN. The concentration of 4-methylbenzenesulfonic acid 2a stock solution is 3.75×10\(^{-2}\)mol/L in CH\(_3\)CN. Then, the emission intensity was collected and the result was presented in Figure S6.

![Fluorescence spectra of 1a](image)

Figure S6 Fluorescence spectra of 2a.

UV-visible spectroscopy of reaction solution was recorded on a SHIMADZU UV-3600 UV-visible spectrophotometer. The sample was prepared by mixing Na\(_2\)-EosinY, N-(4-methoxyphenyl)-N-methyl-3-phenylpropiolamide 1a and 4-methylbenzenesulfinic acid 2a with solvent CH\(_3\)CN/H\(_2\)O (V\(_1\)/V\(_2\)=1:1) (M[Na\(_2\)-EosinY] = 6.25×10\(^{-4}\)mol/L, M[N-(4-methoxyphenyl)-N-methyl-3-phenylpropiolamide] = 1.25×10\(^{-2}\)mol/L, M[4-methylbenzenesulfinic acid] = 3.75×10\(^{-2}\)mol/L in a light path quartz UV cuvette. The UV-visible spectroscopy indicated that the maximum absorption wavelength of reaction solution was found to be 530 nm. The absorption was collected and the result was listed in Figure S7.
Figure S7. UV–vis spectra of the reaction mixture.

The fluorescence emission intensity of reaction solution was recorded on a Fluoromax-4600 spectrofluorimeter. The excitation wavelength was fixed at 530nm, and the emission wavelength was measured at 549 nm. The sample was prepared by mixing Na₂-EosinY, N-(4-methoxyphenyl)-N-methyl-3-phenylpropionamide 1a, 4-methylbenzenesulfinic acid 2a with solvent CH₃CN/H₂O (V₁/V₂=1:1) (M[Na₂-EosinY] = 6.25x10⁻⁶mol/L, M[N-(4-methoxyphenyl)-N-methyl-3-phenylpropionamide] = 1.25x10⁻⁴mol/L, M[4-methylbenzenesulfinic acid] = 3.75x10⁻⁴mol/L) in a light path quartz fluorescence cuvette. The emission intensity was collected and the result was listed in Figure S8.

Figure S8. Fluorescence spectra of the reaction mixture.
The fluorescence emission intensities were recorded on a Fluormax-4600 spectrophotometer. The excitation wavelength was fixed at 530 nm, and the emission wavelength was measured at 549 nm (emission maximum). The samples were prepared by mixing Na₂-EosinY (6.25×10⁻⁶ mol/L) and different amounts of 4-methylbenzene-sulfinic acid 2a in CH₃CN (total volume = 0.1 mL) in a light path quartz fluorescence cuvette. The concentration of 4-methylbenzene sulfinic acid stock solution is 3.75×10⁻⁸ mol/L in CH₃CN. For each quenching experiment, 0.1 mL of 4-methylbenzenesulfinic acid 2a stock solution was titrated to a mixed solution of Na₂-EosinY (0.1 mL, in a total volume = 1.0 mL). Then the emission intensity was collected and the results were presented in Figure S9.

**Figure S9.** Quenching of Na₂-EosinY fluorescence emission in the presence of 4-methylbenzenesulfinic acid 2a

An indeed fluorescence quenching phenomenon of Na₂-EosinY under various concentrations of 4-methylbenzenesulfinic acid 2a was demonstrated in a curve of [I₀/I] vs C [4-methylbenzenesulfinic acid], as shown in Figure S10 (Stern-Volmer plots).
The fluorescence emission intensities were recorded on a Fluormax-4600 spectrophotometer. The excitation wavelength was fixed at 530nm, and the emission wavelength was measured at 549nm (emission maximum). The samples were prepared by mixing Na<sub>2</sub>-EosinY (6.25×10<sup>-6</sup>mol/L) and different amount of N-(4-methoxyphenyl)-N-methyl-3-phenylpropionamide 1a in CH<sub>3</sub>CN (total volume = 0.1 mL) in a light path quartz fluorescence cuvette. The concentration of N-(4-methoxyphenyl)-N-methyl-3-phenylpropionamide 1a stock solution is 1.25×10<sup>-8</sup>mol/L in CH<sub>3</sub>CN. For each quenching experiment, 0.1mL of alkynes stock solution was titrated to a mixed solution of Na<sub>2</sub>-EosinY (0.1mL, in a total volume = 1.0 mL). Then the emission intensity was collected and the results were presented in Figure S11. An fluorescence quenching phenomenon of Na<sub>2</sub>-EosinY under various concentrations of alkyne 1a was shown in Figure S12 (Stern-Volmer plots).

![Figure S10. Stern-volmer plots](image)

**Figure S10.** Stern-volmer plots

![Figure S11. Quenching of Na<sub>2</sub>-EosinY fluorescence emission in the presence of alkyne 1a](image)

**Figure S11.** Quenching of Na<sub>2</sub>-EosinY fluorescence emission in the presence of alkyne 1a

![Figure S12. Stern-volmer plots.](image)

**Figure S12.** Stern-volmer plots.

4.4 The UV-visible spectroscopy and Fluorescence quenching studies for the
synthesis of 3-sulfenyl azaspiro[4,5]trienone (Stern–Volmer Studies)

UV-visible spectroscopy of reaction solution was recorded on a SHIMADZU UV-3600 UV-visible spectrophotometer. The sample was prepared by mixing of Eosin Y, N-(4-methoxyphenyl)-N-methyl-3-phenylpropioamide 1a and thiophenol 4a with solvent (CH$_3$CN) (M[EosinY] = 1.25×10$^{-5}$mol/L, M[alkynes] = 1.25×10$^{-3}$mol/L, M[thiophenol] = 2.5×10$^{-3}$mol/L in a light path quartz UV cuvette. The UV-visible spectroscopy indicated that the maximum absorption wavelength of reaction solution was found to be 530 nm. The absorption was collected and the result was listed in Figure S13.

![Figure S13. UV–vis spectra of the reaction mixture.](image)

The fluorescence emission intensity of reaction solution was recorded on a Fluoromax-4600 spectrofluorimeter. The excitation wavelength was fixed at 500nm, and the emission wavelength was measured at 558 nm. The sample was prepared by mixing EosinY, alkynes, thiophenol with solvent (CH$_3$CN) (M[EosinY] = 1.25×10$^{-6}$mol/L, M[alkyne] = 1.25×10$^{-4}$mol/L, M[thiophenol] = 2.5×10$^{-4}$mol) in a light path quartz fluorescence cuvette. The emission intensity was collected and the result was listed in Figure S14.

![Figure S14. Fluorescence spectra of the reaction mixture.](image)
Figure S14. Fluorescence spectra of the reaction mixture

The fluorescence emission intensities were recorded on a Fluormax-4600 spectrofluorimeter. The excitation wavelength was fixed at 500 nm, and the emission wavelength was measured at 558 nm (emission maximum). The samples were prepared by mixing Eosin Y (1.25×10⁻⁶ mol/L) and different amounts of Thiophenol in CH₂CN (total volume = 0.1 mL) in a light path quartz fluorescence cuvette. The concentration of Thiophenol stock solution is 2.5×10⁻⁸ mol/L in CH₂CN. For each quenching experiment, 0.1 mL of Thiophenol stock solution was titrated to a mixed solution of Eosin Y (0.1 mL, in a total volume = 1.0 mL). Then the emission intensity was collected and the results were presented in Figure S15.

Figure S15. Quenching of Eosin Y fluorescence emission in the presence of thiophenol 4a.

An indeed fluorescence quenching phenomenon of Eosin Y under various concentrations of thiophenol was demonstrated in a curve of [I₀/I] vs C[Thiophenol], as shown in Figure S16 (Stern-Volmer plots).
Figure S16. Stern-volmer plots.

The fluorescence emission intensities were recorded on a Fluormax-4600 spectrophotometer. The excitation wavelength was fixed at 500 nm, and the emission wavelength was measured at 557 nm (emission maximum). The samples were prepared by mixing Eosin Y (1.25×10⁻⁶ mol/L) and different amounts of styrene in CH₂CN (total volume = 0.1 mL) in a light path quartz fluorescence cuvette. The concentration of alkynes stock solution is 1.25×10⁻⁸ mol/L in CH₂CN. For each quenching experiment, 0.1 mL of alkynes stock solution was titrated to a mixed solution of Eosin Y (0.1 mL, in a total volume = 1.0 mL). Then the emission intensity was collected and the results were presented in Figure S17. An fluorescence quenching phenomenon of EosinY under various concentrations of alkynes was shown in Figure S18 (Stern-Volmer plots).

Figure S17. Quenching of Eosin Y fluorescence emission in the presence of alkyne 1a.

Figure S18. Stern-volmer plots.
5. Characterization data of products 3a-5r

1-methyl-4-phenyl-3-tosyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3a). Compound 3a was obtained in 76% yield according to the general procedure (6h). White solid; mp 273.2-274.6 °C. ¹H NMR (CDCl₃, 500 MHz, ppm): δ 7.93 (d, J = 8.3 Hz, 2H), 7.44 (t, J = 7.5 Hz, 1H), 7.39-7.33 (m, 4H), 7.15 (d, J = 7.2 Hz, 2H), 6.43 (s, 4H), 2.83 (s, 3H), 2.44 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 183.1, 163.6, 161.5, 145.6, 142.3, 137.0, 136.2, 134.3, 130.3, 129.7, 129.3, 128.6, 128.0, 127.8, 68.2, 26.4, 21.8; HRMS calc. for C₂₃H₁₉NO₄SNa (M+Na)⁺, 428.0932; found, 428.0935.

1-methyl-4-phenyl-3-(phenylsulfonyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3b). Compound 3b was obtained in 60% yield according to the general procedure (8h). White solid; mp 215.7-217.0 °C. ¹H NMR (CDCl₃, 500 MHz, ppm): δ 8.05 (d, J = 8.1 Hz, 2H), 7.66 (d, J = 7.5 Hz, 1H), 7.55 (t, J = 8.1 Hz, 2H), 7.44 (t, J = 8.5 Hz, 1H), 7.38 (t, J = 7.8 Hz, 2H), 7.15 (d, J = 7.1 Hz, 2H), 6.44 (s, 2H), 2.83 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 183.1, 163.5, 162.1, 142.2, 139.2, 136.7, 134.4, 130.4, 129.2, 129.1, 128.6, 128.0, 127.8, 68.3, 26.4; HRMS calc. for C₂₂H₁₇NO₄SNa (M+Na)⁺, 414.0776, found, 414.0777.

3-(4-chlorophenylsulfonyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3c). Compound 3c was obtained in 55% yield according to the general procedure (10 h). Yellow solid; mp 267.9-268.6 °C. ¹H NMR (CDCl₃, 500 MHz, ppm): δ 7.99 (d, J = 8.7 Hz, 2H), 7.52 (d, J = 8.7 Hz, 2H), 7.46 (t, J = 7.5 Hz, 1H), 7.39 (t, J = 7.9 Hz, 2H), 7.15 (d, J = 7.1 Hz, 2H), 6.47-6.42 (m, 4H), 2.84 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 183.0, 163.4, 162.4, 142.0, 141.3, 137.5, 136.4, 134.5, 130.8, 130.6, 129.4, 128.4,
3-(4-bromophenylsulfonyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3d), Compound 3d was obtained in 85% yield according to the general procedure (12h). Yellow solid; mp 274.4-275.2 °C. 1H NMR (CDCl$_3$, 500 MHz, ppm):$^\delta$ 7.91 (d, $J = 8.7$ Hz, 2H), 7.69 (d, $J = 8.7$ Hz, 2H), 7.46 (t, $J = 7.5$ Hz, 1H), 7.39 (t, $J = 7.9$ Hz, 2H), 7.14 (d, $J = 7.1$ Hz, 2H), 6.47-6.42 (m, 4H), 2.84 (s, 3H); 13C NMR (CDCl$_3$, 125 MHz, ppm):$^\delta$ 182.9, 163.4, 162.5, 142.0, 138.1, 136.3, 134.5, 132.4, 130.8, 130.6, 130.1, 128.4, 128.1, 127.8, 68.4, 26.4; HRMS calc. for C$_{22}$H$_{16}^{35}$ClNO$_4$SNa (M+Na)$^+$, 448.0386; found, 448.0384.

![Diagram of 3d](image)

1-methyl-4-phenyl-3-(4-(trifluoromethyl)phenylsulfonyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3e), Compound 3e was obtained in 81% yield according to the general procedure (6h). Yellow solid; mp 254.7-255.5 °C. 1H NMR (CDCl$_3$, 500 MHz, ppm):$^\delta$ 8.19 (d, $J = 8.2$ Hz, 2H), 7.81 (d, $J = 8.4$ Hz, 2H), 7.47 (t, $J = 7.5$ Hz, 1H), 7.40 (t, $J = 7.9$ Hz, 2H), 7.16 (d, $J = 7.4$ Hz, 2H), 6.48-6.42 (m, 4H), 2.84 (s, 3H); 13C NMR (CDCl$_3$, 125 MHz, ppm):$^\delta$ 182.9, 163.3 (d, $J = 6.8$ Hz), 142.6, 141.8, 136.0, 135.7, 134.5, 130.7, 129.9, 128.2, 128.1, 127.8, 126.2 (q, $J = 3.7$ Hz), 123.1 (d, $J = 271.6$ Hz), 68.5, 26.4; HRMS calc. for C$_{23}$H$_{16}F$_3NO$_4$SNa (M+Na)$^+$, 482.0650; found, 482.0655.

![Diagram of 3e](image)

1-methyl-4-phenyl-3-(2-(trifluoromethyl)phenylsulfonyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3f), Compound 3f was obtained in 80% yield according to the general procedure (8h). White solid; mp 219.6-220.9 °C. 1H NMR (CDCl$_3$, 500 MHz, ppm):$^\delta$
8.52 (d, J = 7.4 Hz, 1H), 7.82-7.78 (m, 3H), 7.44 (t, J = 7.5 Hz, 1H), 7.38 (t, J = 7.9 Hz, 2H), 7.30 (d, J = 7.3 Hz, 2H), 6.51-6.45 (m, 4H), 2.79 (s, 3H); 13C NMR (CDCl₃, 125 MHz, ppm): δ 183.2, 162.3, 161.4, 142.2, 137.4, 136.0, 134.4, 134.2, 132.2, 130.8, 128.7 (d, J = 33.3 Hz), 128.3, 128.1, 128.1, 128.0 (q, J = 6.0 Hz), 122.9 (d, J = 272.9 Hz), 68.0, 26.2; HRMS calc. for C₂₃H₁₆F₃NO₄SNa (M+Na)+, 482.0650; found, 482.0653.

1-methyl-4-phenyl-3-(trifluoromethylsulfonyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3g), Compound 3g was obtained in 37% yield according to the general procedure (24h). White solid; mp 198.7-200.4 °C. 1H NMR (CDCl₃, 500 MHz, ppm): δ 7.41-7.38 (m, 5H), 6.54-6.49 (m, 4H), 2.95 (s, 3H); 13C NMR (CDCl₃, 125 MHz, ppm): δ 183.7, 165.8, 151.3, 144.1, 133.5, 130.3, 130.2, 128.8, 127.8, 119.9, 68.3, 26.7; HRMS calc. for C₁₇H₁₂F₃NO₄SNa (M+Na)+, 406.0337; found, 406.0341.

1-methyl-4-p-tolyl-3-tosyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3h), Compound 3h was obtained in 52% yield according to the general procedure (6h). Yellow solid; mp 213.5-215.1 °C. 1H NMR (CDCl₃, 500 MHz, ppm): δ 7.93 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 7.07 (d, J = 8.2 Hz, 2H), 6.45-6.40 (m, 4H), 2.81 (s, 3H), 2.44 (s, 3H), 2.37 (s, 3H); 13C NMR (CDCl₃, 125 MHz, ppm): δ 183.2, 163.7, 161.9, 145.5, 142.5, 140.8, 136.5, 136.3, 134.2, 129.7, 129.3, 128.7, 127.8, 125.7, 68.2, 26.3, 21.8, 21.5; HRMS calc. for C₂₄H₂₁NO₄SNa (M+Na)+, 442.1089; found, 442.1091.

1-methyl-4-m-tolyl-3-tosyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3i), Compound 3i was obtained in 60% yield according to the general procedure (20h). Yellow solid; mp 266.7-268.4 °C. 1H NMR (CDCl₃, 400 MHz, ppm): δ 7.92 (d, J = 8.3 Hz, 2H), 7.34 (d, J
= 8.1 Hz, 2H), 7.25-7.22 (m, 2H), 6.94-6.91 (m, 2H), 6.45-6.40 (m, 4H), 2.82 (s, 3H), 2.44 (s, 3H), 2.35 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): δ 183.2, 163.7, 161.8, 145.5, 142.4, 137.6, 136.7, 136.3, 134.2, 131.2, 130.0, 129.3, 128.6, 128.4, 127.8, 124.8, 68.2, 26.3, 21.8, 21.4; HRMS calc. for C$_{24}$H$_{21}$NO$_4$SNa (M+Na)$^+$, 442.1089; found, 442.1091.

**4-(4-methoxyphenyl)-1-methyl-3-tosyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3j),**

Compound 3j was obtained in 81% yield according to the general procedure (6h). White solid; mp 216.5-218.3 °C. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): δ 7.94 (d, $J = 8.3$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.19 (d, $J = 8.9$ Hz, 2H), 6.88 (d, $J = 8.9$ Hz, 2H), 6.48-6.40 (m, 4H), 3.83 (s, 3H), 2.80 (s, 3H), 2.44 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): δ 183.3, 163.8, 161.5, 161.4, 145.4, 142.8, 136.4, 135.9, 134.1, 129.8, 129.7, 129.3, 120.7, 113.6, 68.1, 55.3, 26.2, 21.8; HRMS calc. for C$_{24}$H$_{21}$NO$_4$SNa (M+Na)$^+$, 458.1038; found, 458.1037.

**3-(4-bromophenylsulfonyl)-4-(4-methoxyphenyl)-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3k),**

Compound 3k was obtained in 53% yield according to the general procedure (10h). White solid; mp 223.0-224.1 °C. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): δ 7.92 (d, $J = 8.7$ Hz, 2H), 7.68 (d, $J = 8.7$ Hz, 2H), 7.19 (d, $J = 8.9$ Hz, 2H), 6.89 (d, $J = 8.3$ Hz, 2H), 6.48 (d, $J = 10.3$ Hz, 2H), 6.41 (d, $J = 10.3$ Hz, 2H), 3.83 (s, 3H), 2.80 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): δ 183.1, 163.6, 162.4, 161.6, 142.5, 138.2, 135.2, 134.2, 132.3, 130.9, 130.0, 129.8, 120.5, 113.7, 68.2, 55.3, 26.2; HRMS calc. for C$_{23}$H$_{18}$BrNO$_5$SNa (M+Na)$^+$, 521.9987; found, 521.9989.
4-(4-fluorophenyl)-1-methyl-3-tosyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3l), Compound 3l was obtained in 61% yield according to the general procedure (6h). White solid; mp 267.8-268.1 °C. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): δ 7.92 (d, $J = 8.3$ Hz, 2H), 7.35 (d, $J = 8.1$ Hz, 2H), 7.19-7.16 (m, 2H), 7.08 (t, $J = 8.5$ Hz, 2H), 6.46 (t, $J = 8.2$ Hz, 2H), 6.42 (t, $J = 8.6$ Hz, 2H), 2.82 (s, 3H), 2.45 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): δ 182.9, 163.8 (d, $J = 250.5$ Hz), 163.4, 160.3, 145.8, 142.2, 137.3, 136.0, 134.5, 130.1 (d, $J = 8.6$ Hz), 129.8, 129.3, 124.5 (d, $J = 3.6$ Hz), 115.5 (d, $J = 22.0$ Hz), 68.2, 26.4, 21.8; HRMS calc. for C$_{23}$H$_{18}$FNO$_4$SNa (M+Na)$^+$, 446.0838; found, 446.0839.

4-(4-chlorophenyl)-1-methyl-3-tosyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3m), Compound 3m was obtained in 53% yield according to the general procedure (6h). Yellow solid; mp 231.2-232.7 °C. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): δ 7.92 (d, $J = 8.4$ Hz, 2H), 7.37-7.34 (m, 4H), 7.11 (d, $J = 8.6$ Hz, 2H), 6.47-6.40 (m, 4H), 2.82 (s, 3H), 2.45 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): δ 182.9, 163.3, 160.1, 145.8, 142.1, 137.5, 136.8, 135.9, 134.5, 129.8, 129.3, 128.5, 127.0, 68.1, 26.4, 21.8; HRMS calc. for C$_{23}$H$_{18}$ClNO$_4$SNa (M+Na)$^+$, 462.0543; found, 462.0544.

4-(4-bromophenyl)-1-methyl-3-tosyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3n), Compound 3n was obtained in 49% yield according to the general procedure (7h). Yellow solid; mp 258.1-259.4 °C. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): δ 7.91 (d, $J = 8.1$ Hz, 2H), 7.51 (d, $J = 8.3$ Hz, 2H), 7.35 (d, $J = 8.1$ Hz, 2H), 7.04 (d, $J = 8.4$ Hz, 2H), 6.46 (d, $J = 10.1$ Hz, 2H), 6.40 (d, $J = 10.1$ Hz, 2H), 2.82 (s, 3H), 2.45 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): δ 182.8, 163.3, 160.0, 145.8, 142.0, 137.5, 135.9, 134.6, 131.4, 129.8, 129.4, 129.4, 127.5, 125.2, 68.0, 26.4, 21.8; HRMS calc. for C$_{23}$H$_{18}$BrNO$_4$SNa (M+Na)$^+$, 506.0038; found, 506.0041.
1,4-dimethyl-3-tosyl-1-azaspiro[4.5]dec-3,6,9-triene-2,8-dione, Compound 3o was obtained in 25% yield according to the general procedure (24h). White solid; mp 231.2-232.4 °C. 1H NMR (CDCl₃, 500 MHz, ppm): δ 8.01 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 6.61 (d, J = 10.0 Hz, 2H), 6.29 (d, J = 10.1 Hz, 2H), 2.77 (s, 3H), 2.45 (s, 3H), 2.31 (s, 3H); 13C NMR (CDCl₃, 125 MHz, ppm): δ 183.3, 163.8, 161.2, 145.6, 143.4, 136.4, 135.6, 134.5, 129.8, 129.0, 68.2, 26.3, 21.8, 12.1; HRMS calc. for C₁₈H₁₇NO₄SNa (M+Na)⁺, 366.0776; found, 366.0779.

1,6-dimethyl-4-phenyl-3-tosyl-1-azaspiro[4.5]dec-3,6,9-triene-2,8-dione (3p), Compound 3p was obtained in 80% yield according to the general procedure (10h). Yellow solid; mp 219.1-220.7 °C. 1H NMR (CDCl₃, 500 MHz, ppm): δ 7.92 (d, J = 8.3 Hz, 2H), 7.45 (t, J = 8.4 Hz, 1H), 7.37 (t, J = 8.0 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 7.2 Hz, 2H), 6.44-6.31 (m, 3H), 2.73 (s, 3H), 2.44 (s, 3H), 1.73 (s, 3H); 13C NMR (CDCl₃, 125 MHz, ppm): δ 183.8, 164.0, 161.7, 150.7, 145.5, 142.4, 137.4, 136.3, 133.9, 133.0, 130.7, 129.7, 129.2, 128.4, 128.1, 127.8, 70.5, 26.0, 21.8, 17.7; HRMS calc. for C₂₄H₂₁NO₄SNa (M+Na)⁺, 442.1089; found, 442.1092.

7-methoxy-1-methyl-4-phenyl-3-(phenylsulfonyl)-1-azaspiro[4.5]dec-3,6,9-triene-2,8-dione (3q), Compound 3q was obtained in 64% yield according to the general procedure (8h). Yellow solid; mp 238.1-239.8 °C. 1H NMR (CDCl₃, 500 MHz, ppm): δ 8.06 (t, J = 7.3 Hz, 2H), 7.66 (d, J = 7.4 Hz, 1H), 7.55 (t, J = 8.1 Hz, 2H), 7.42 (d, J = 7.5 Hz, 1H), 7.37 (t, J = 7.8 Hz, 2H), 7.12 (t, J = 7.2 Hz, 2H), 6.42 (s, 2H), 5.28 (s, 1H), 3.66 (s, 3H), 2.82 (s, 3H); 13C NMR (CDCl₃, 125 MHz, ppm): δ 178.7, 163.3, 163.2, 154.6,
7-chloro-1-methyl-4-phenyl-3-(2-(trifluoromethyl)phenylsulfonyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3q), Compound 3r was obtained in 71% yield according to the general procedure (10h). White solid; mp 196.7-198.5 °C. \(^1\)H NMR (CDCl\(_3\), 500 MHz, ppm): \(\delta\) 8.50 (d, \(J = 7.2\) Hz, 1H), 7.83-7.79 (m, 3H), 7.46 (t, \(J = 7.5\) Hz, 1H), 7.39 (t, \(J = 7.9\) Hz, 2H), 7.27-7.25 (m, 2H), 6.66 (d, \(J = 2.8\) Hz, 1H), 6.56-6.51 (m, 2H), 2.81 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz, ppm): \(\delta\) 176.4, 162.9, 160.5, 142.9, 137.9, 137.8, 136.7 (d, \(J = 119.6\) Hz), 134.3 (d, \(J = 16.7\) Hz), 133.3, 132.2, 131.0, 128.8, 128.7 (d, \(J = 33.2\) Hz), 128.3, 128.0, 127.9, 122.9 (d, \(J = 272.9\) Hz), 69.7, 26.4; HRMS calc. for C\(_{23}\)H\(_{19}\)NO\(_5\)SNa (M+Na\(^+\)), 444.0882; found, 444.0883.

4-phenyl-3-tosyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3s), Compound 3r was obtained in 24% yield according to the general procedure (24h). Grey oil. \(^1\)H NMR (CDCl\(_3\), 500 MHz, ppm): \(\delta\) 7.87 (d, \(J = 8.3\) Hz, 2H), 7.44 (t, \(J = 7.4\) Hz, 1H), 7.37 (t, \(J = 7.8\) Hz, 2H), 7.32 (d, \(J = 8.2\) Hz, 2H), 7.11 (d, \(J = 7.4\) Hz, 2H), 6.56 (s, 1H), 6.55 (d, \(J = 10.0\) Hz, 2H), 6.31 (d, \(J = 10.0\) Hz, 2H), 2.44 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz, ppm): \(\delta\) 183.2, 165.5, 164.6, 145.6, 142.5, 136.3, 136.3, 132.6, 130.4, 129.8, 129.2, 128.4, 128.0, 127.8, 64.0, 21.8; HRMS calc. for C\(_{22}\)H\(_{17}\)NO\(_4\)SNa (M+Na\(^+\)), 414.0770; found, 414.0764.

Characterization data of products 5a-5q
1-methyl-4-phenyl-3-(p-tolylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

Compound 5a was obtained in 87% yield according to the general procedure (12h). Yellow solid; mp 159.3-160.2 °C. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): δ 7.31-7.28 (m, 1H), 7.25-7.20 (m, 2H), 7.23-7.19 (m, 4H), 6.99 (d, $J = 8.0$ Hz, 2H), 6.51 (d, $J = 10.2$ Hz, 2H), 6.45 (d, $J = 10.3$ Hz, 2H), 2.88 (s, 3H), 2.26 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125MHz, ppm): δ 184.0, 167.8, 151.7, 145.3, 137.8, 133.1, 132.8, 131.7, 130.8, 129.7, 129.5, 128.3, 128.2, 127.7, 67.7, 26.3, 21.1; HRMS calc. for C$_{23}$H$_{19}$NO$_2$SNa (M+Na)$^+$, 396.1034; found, 396.1036.

![Diagram of 1-methyl-4-phenyl-3-(p-tolylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione](image)

1-methyl-4-p-tolyl-3-(p-tolylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

Compound 5b was obtained in 69% yield according to the general procedure (12h). Yellow solid; mp 183.9-184.5 °C. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): δ 7.21 (d, $J = 7.9$ Hz, 2H), 7.15 (d, $J = 7.9$ Hz, 2H), 7.07 (d, $J = 7.9$ Hz, 2H), 7.00 (d, $J = 7.9$ Hz, 2H), 6.51 (d, $J = 10.1$ Hz, 2H), 6.46 (d, $J = 10.1$ Hz, 2H), 2.86 (s, 3H), 2.31 (s, 3H), 2.27 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125MHz, ppm): δ 184.1, 167.8, 151.7, 145.3, 137.8, 133.1, 132.8, 131.7, 130.8, 129.7, 129.5, 128.3, 128.2, 127.7, 67.7, 26.3, 21.1; HRMS calc. for C$_{24}$H$_{21}$NO$_2$SNa (M+Na)$^+$, 410.1191; found, 410.1195.

![Diagram of 1-methyl-4-p-tolyl-3-(p-tolylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione](image)

4-(4-methoxyphenyl)-1-methyl-3-(p-tolylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

Compound 5c was obtained in 65% yield according to the general procedure (12h). Yellow solid; mp 145.1-145.9 °C. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): δ 7.28 (t, $J = 8.6$ Hz, 2H), 7.21 (d, $J = 7.9$ Hz, 2H), 7.02 (d, $J = 7.8$ Hz, 2H), 6.78 (d, $J = 8.6$ Hz, 2H), 6.51 (d, $J = 10.2$ Hz, 2H), 6.48 (d, $J = 10.2$ Hz, 2H), 3.78 (s, 3H), 2.86 (s, 3H), 2.28 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): δ 184.1, 167.9, 160.7, 152.2, 145.7, 137.6, 133.0, 132.0, 131.5, 129.7, 129.0, 128.1, 128.0, 127.8, 67.6, 26.2, 21.3, 21.1; HRMS calc. for C$_{26}$H$_{23}$NO$_2$SNa (M+Na)$^+$, 440.1191; found, 440.1195.
4-(4-fluorophenyl)-1-methyl-3-(p-tolylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione, Compound 5d was obtained in 70% yield according to the general procedure (12h). Yellow solid; mp 144.4-145.7 °C. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 7.18 (d, $J$ = 7.9 Hz, 4H), 6.98 (d, $J$ = 7.9 Hz, 2H), 6.91 (t, $J$ = 8.5 Hz, 2H), 6.50 (d, $J$ = 10.1 Hz, 2H), 6.50 (d, $J$ = 10.1 Hz, 2H), 2.88 (s, 3H), 2.27 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 183.8, 167.7, 163.1 (d, $J$ = 249.4 Hz), 149.7, 145.2, 138.1, 133.3, 133.2, 131.9, 130.2 (d, $J$ = 33.5 Hz), 129.7, 127.2, 126.7 (d, $J$ = 13.7 Hz), 115.5 (d, $J$ = 21.7 Hz), 67.7, 26.3, 21.1; HRMS calc. for C$_{23}$H$_{18}$FNO$_2$SNa (M+Na)$^+$, 414.0940; found, 414.0937.

4-(4-chlorophenyl)-1-methyl-3-(p-tolylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione, Compound 5e was obtained in 57% yield according to the general procedure (12h). Yellow oil; $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 7.10 (d, $J$ = 7.6 Hz, 4H), 7.01 (d, $J$ = 8.3 Hz, 2H), 6.90 (d, $J$ = 7.9 Hz, 2H), 6.42 (d, $J$ = 10.0 Hz, 2H), 6.38 (d, $J$ = 10.1 Hz, 2H), 2.81 (s, 3H), 2.20 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 182.7, 166.5, 147.7, 144.0, 137.3, 134.5, 132.8, 132.2, 131.2, 128.7, 128.5, 128.0, 127.5, 125.7, 66.6, 25.3, 20.1; HRMS calc. for C$_{23}$H$_{18}$ClNO$_2$SNa (M+Na)$^+$, 430.0644; found, 430.0649.

4-(4-bromophenyl)-1-methyl-3-(p-tolylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione, Compound 5f was obtained in 53% yield according to the general procedure (12h).
Yellow oil; $^1$H NMR (CDCl$_3$, 500 MHz, ppm): δ 7.32 (d, $J$ = 8.4 Hz, 2H), 7.16 (d, $J$ = 8.0 Hz, 2H), 7.00 (d, $J$ = 8.4 Hz, 2H), 6.96 (d, $J$ = 7.9 Hz, 2H), 6.48 (d, $J$ = 10.2 Hz, 2H), 6.45 (d, $J$ = 10.2 Hz, 2H), 2.88 (s, 3H), 2.28 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): δ 183.7, 167.5, 148.5, 145.0, 138.4, 133.9, 133.3, 132.3, 131.4, 129.8, 129.7, 129.5, 126.6, 123.8, 67.6, 26.3, 21.2; HRMS calc. for C$_{23}$H$_{18}$BrNO$_2$SNa (M+Na)$^+$, 474.0139; found, 474.0141.

7-chloro-1-methyl-4-phenyl-3-(p-tolylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione, Compound 5g was obtained in 71% yield according to the general procedure (12h). Yellow solid; mp 169.8-171.6 °C. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): δ 7.30 (t, $J$ = 7.1 Hz, 1H), 7.24 (d, $J$ = 7.3 Hz, 2H), 7.19 (d, $J$ = 8.0 Hz, 2H), 7.13 (d, $J$ = 7.5 Hz, 2H), 6.97 (d, $J$ = 7.8 Hz, 2H), 6.72 (d, $J$ = 2.2 Hz, 1H), 6.55-6.49 (m, 2H), 2.90 (s, 3H), 2.26 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): δ 177.2, 167.4, 150.0, 145.9, 141.0, 138.1, 136.3, 133.5, 132.2, 132.0, 130.2, 129.7, 129.6, 128.4, 128.2, 127.1, 69.5, 26.5, 21.1; HRMS calc. for C$_{23}$H$_{18}^{35}$ClNO$_2$SNa (M+Na)$^+$, 430.0644; found, 430.0641.

(R)-7-methoxy-1-methyl-4-phenyl-3-(p-tolylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione, Compound 5h was obtained in 58% yield according to the general procedure (12h). Yellow oil. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): δ 7.29 (t, $J$ = 7.2 Hz, 1H), 7.25-7.21 (m, 2H), 7.18 (d, $J$ = 7.5 Hz, 2H), 6.99 (d, $J$ = 7.9 Hz, 2H), 6.52-6.44 (m, 2H), 5.35 (d, $J$ = 2.1 Hz, 1H), 3.66 (s, 3H), 2.87 (s, 3H), 2.27 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): δ 179.5, 167.5, 153.8, 152.9, 146.0, 137.8, 132.3, 132.1, 131.8, 130.9, 129.7, 129.5, 128.3, 128.2, 127.8, 111.4, 69.1, 55.5, 26.0, 21.1; HRMS calc. for C$_{24}$H$_{21}$NO$_3$SNa (M+Na)$^+$, 426.1140; found, 426.1147.
(S)-1,6-dimethyl-4-phenyl-3-(p-tolylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione, Compound 5i was obtained in 87% yield according to the general procedure (12h).
Yellow oil. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 7.34-7.32 (m, 1H), 7.29-7.25 (m, 4H), 7.23 (d, $J = 8.0$ Hz, 2H), 7.02 (d, $J = 7.9$ Hz, 2H), 6.49 (s, 2H), 6.37 (s, 1H), 2.79 (s, 3H), 2.29 (s, 3H), 1.78 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 184.7, 168.1, 153.5, 152.1, 145.5, 137.8, 133.0, 132.6, 132.0, 131.5, 130.6, 129.8, 128.4, 128.1, 127.9, 69.7, 25.8, 21.1,17.9; HRMS calc. for C$_{24}$H$_{21}$NO$_2$SNa (M+Na)$^+$, 410.1191; found, 410.1196.

6-methoxy-1-methyl-4-phenyl-3-(p-tolylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione, Compound 5j was obtained in 68% yield according to the general procedure (12h).
Yellow oil. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 7.30-7.22 (m, 3H), 7.19-7.14 (m, 4H), 6.99 (d, $J = 8.0$ Hz, 2H), 6.40-6.37 (dd, $J_1 = 1.3$ Hz, $J_2 = 9.8$ Hz, 1H), 6.30 (d, $J = 9.8$ Hz, 1H), 5.76 (d, $J = 1.1$ Hz, 1H), 3.74 (s, 3H), 2.78 (s, 3H), 2.26 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 186.2, 168.7, 168.5, 152.8, 141.0, 137.3, 132.4, 132.2, 130.8, 130.6, 129.7, 129.5, 128.5, 128.3, 128.0, 106.2, 69.0, 56.3, 26.0, 21.1; HRMS calc. for C$_{24}$H$_{21}$NO$_3$SNa (M+Na)$^+$, 426.1140; found, 426.1146.

1-methyl-4-phenyl-3-(phenylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione, Compound 5k was obtained in 56% yield according to the general procedure (12h).
Yellow oil. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 7.29-7.23 (m, 7H), 7.20-7.17 (m, 3H), 6.53 (d, $J = 10.0$ Hz, 2H), 6.47 (d, $J = 10.1$ Hz, 2H), 2.89 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 183.9, 167.7, 152.8, 145.1, 133.2, 132.2, 131.7, 131.0, 130.7, 129.7, 128.9,
128.3, 128.1, 127.5, 67.7, 26.3; HRMS calc. for C_{22}H_{17}NO_2SNa (M+Na)^+, 382.0878; found, 382.0879.

![Chemical Structure](image)

**3-(4-methoxyphenylthio)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione**, Compound 5l was obtained in 50% yield according to the general procedure (12h). Yellow solid; mp 156.3-157.6 °C. ^1^H NMR (CDCl\textsubscript{3}, 500 MHz, ppm): δ 7.28-7.27 (m, 2H), 7.24-7.22 (m, 3H), 7.17-7.15 (m, 2H), 6.69 (d, J = 8.9 Hz, 2H), 6.49 (d, J = 10.3 Hz, 2H), 6.43 (d, J = 10.2 Hz, 2H), 3.74 (s, 3H), 2.87 (s, 3H); ^13^C NMR (CDCl\textsubscript{3}, 125 MHz, ppm): δ 184.0, 167.9, 159.8, 150.2, 145.3, 134.6, 133.5, 133.1, 130.7, 129.4, 128.3, 128.2, 121.1, 114.5, 67.7, 55.3, 26.3; HRMS calc. for C_{23}H_{19}NO_3SNa (M+Na)^+, 412.0983; found, 412.0985.

![Chemical Structure](image)

**3-(4-fluorophenylthio)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione**, Compound 5m was obtained in 62% yield according to the general procedure (12h). Yellow solid; mp 126.7-127.6 °C. ^1^H NMR (CDCl\textsubscript{3}, 500 MHz, ppm): δ 7.31-7.30 (m, 3H), 7.24 (d, J = 7.4 Hz, 2H), 7.17 (d, J = 7.5 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 6.51 (d, J = 10.0 Hz, 2H), 6.45 (d, J = 10.3 Hz, 2H), 2.88 (s, 3H); ^13^C NMR (CDCl\textsubscript{3}, 125 MHz, ppm): δ 183.9, 167.6, 162.5, 151.6, 145.0, 134.2 (d, J = 8.3 Hz), 133.2, 132.7, 130.5, 129.7, 128.3, 128.2, 126.1 (d, J = 3.3 Hz), 116.1 (d, J = 22.0 Hz), 67.7, 26.3; HRMS calc. for C_{22}H_{16}FNO_2SNa (M+Na)^+, 400.0783; found, 400.0788.

![Chemical Structure](image)
3-(4-chlorophenylthio)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione,
Compound 5n was obtained in 71% yield according to the general procedure (12h).
Yellow solid; mp 180.7-181.3 °C. 

\[ ^1H \text{ NMR (CDCl}_3, 500 \text{ MHz, ppm): } \delta 7.35-7.32 \text{ (m, 1H), 7.29-7.26 (m, 2H), 7.24-7.19 (m, 4H), 7.15 (d, } J = 8.7 \text{ Hz, 2H), 6.52-6.46 (m, 4H), 2.89 (s, 3H); } ^{13}C \text{ NMR (CDCl}_3, 125 \text{ MHz, ppm): } \delta 183.8, 167.5, 152.9, 144.9, 133.9, 133.3, 132.7, 132.0, 130.5, 130.0, 129.9, 129.1, 128.4, 128.1, 67.8, 26.3; \] 

HRMS calc. for C\textsubscript{22}H\textsubscript{16}\text{^35ClNO}_2\text{SNa (M+Na)}^+, 416.0488; found, 416.0489.

3-(3-chlorophenylthio)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione,
Compound 5o was obtained in 54% yield according to the general procedure (12h).
Yellow solid; mp 187.9-189.3 °C. 

\[ ^1H \text{ NMR (CDCl}_3, 500 \text{ MHz, ppm): } \delta 7.33-7.27 \text{ (m, 1H), 7.28-7.25 (m, 2H), 7.22-7.17 (m, 4H), 7.13-7.11 (m, 2H), 6.53 (d, } J = 10.3 \text{ Hz, 2H), 6.48 (d, } J = 10.3 \text{ Hz, 2H), 2.91 (s, 3H); } ^{13}C \text{ NMR (CDCl}_3, 125 \text{ MHz, ppm): } \delta 183.8, 167.4, 153.4, 144.8, 134.6, 133.5, 133.3, 131.5, 130.7, 130.4, 129.9, 129.0, 128.4, 128.0, 127.7, 67.9, 26.4; \] 

HRMS calc. for C\textsubscript{22}H\textsubscript{16}\text{^35ClNO}_2\text{SNa (M+Na)}^+, 416.0488; found, 416.0486.

3-(2-chlorophenylthio)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione,
Compound 5p was obtained in 53% yield according to the general procedure (12h).
Yellow solid; mp 138.4-140.0 °C. 

\[ ^1H \text{ NMR (CDCl}_3, 500 \text{ MHz, ppm): } \delta 7.32-7.30 \text{ (m, 1H), 7.27-7.26 (m, 1H), 7.25-7.21 (m, 5H), 7.12-7.07 (m, 2H), 6.53 (d, } J = 10.2 \text{ Hz, 2H), 6.46 (d, } J = 10.2 \text{ Hz, 2H), 2.90 (s, 3H); } ^{13}C \text{ NMR (CDCl}_3, 125 \text{ MHz, ppm): } \delta 184.0, 167.4, 152.0, 145.1, 135.8, 133.2, 131.1, 130.5, 130.2, 130.0, 129.7, 129.0, 128.3, 127.9, 127.0, 67.9, 26.3; \] 

HRMS calc. for C\textsubscript{22}H\textsubscript{16}\text{^35ClNO}_2\text{SNa (M+Na)}^+, 416.0488; found, 416.0489.
**1-methyl-3-(naphthalen-2-ylthio)-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione**, Compound 5q was obtained in 60% yield according to the general procedure (12h). Yellow solid; mp 153.4-154.0 °C. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 7.79 (d, $J = 1.5$ Hz, 1H), 7.74-7.72 (m, 1H), 7.68-7.66 (m, 1H), 7.63 (d, $J = 8.6$ Hz, 1H), 7.45-7.43 (m, 2H), 7.34-7.32 (m, 1H), 7.23-7.16 (m, 5H), 6.54 (d, $J = 10.2$ Hz, 2H), 6.46 (d, $J = 10.2$ Hz, 2H), 2.89 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 183.9, 167.8, 152.5, 145.1, 133.4, 133.2, 132.5, 132.4, 130.7, 130.6, 130.0, 128.7, 128.6, 128.4, 128.2, 128.1, 127.7, 127.5, 126.5, 126.4, 67.8, 26.3; HRMS calc. for C$_{26}$H$_{19}$NO$_2$SNa (M+Na)$^+$, 432.1034; found, 432.1037.

**1-methyl-4-phenyl-3-(phenylselanyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione**, Compound 5r was obtained in 63% yield according to the general procedure (12h). White solid; mp:128.1-129.4. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 7.31 (d, $J = 7.3$ Hz, 2H), 7.18 (t, $J = 7.4$ Hz, 1H), 7.13-7.08 (m, 3H), 7.05-7.01 (m, 4H), 6.43 (d, $J = 10.2$ Hz, 2H), 6.35 (d, $J = 10.2$ Hz, 2H), 2.83 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 182.9, 167.8, 153.1, 144.0, 132.9, 132.1, 130.2, 129.2, 128.4, 128.0, 127.2, 127.0, 126.9, 126.1, 68.0, 25.4; HRMS calc. for C$_{22}$H$_{17}$NO$_2$SeNa (M+Na)$^+$, 430.0322; found, 430.0318.
6. Copies of NMR spectra for 3a–5r

3a

\[
\text{\begin{center}
\includegraphics[width=\textwidth]{nmr_spectrum_3a.png}
\end{center}}
\]
3d

S34
3e
3m

S43
3n
3q
5d
5e

S54
S55
$\text{5h}$
5m
$\text{Ph}$

$\text{C}_6\text{H}_4\text{p-F}$

$\text{O}$

$\text{N}$

$\text{O}$

$\text{S}$

$\text{C}_6\text{H}_4\text{p-F}$

$\text{O}$

$\text{N}$

$\text{O}$

$\text{S}$

$\text{C}_6\text{H}_4\text{p-F}$
5r