1,6-Conjugate addition initiated formal [4+2] annulation of \( p \)-quinone methides with sulfonyl allenols: a unique access to spi-\( \text{ro}[5.5]\)undeca-1,4-dien-3-one scaffolds

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1. **General information**

Unless otherwise specified, all reactions were carried out in oven dried vials or reaction vessels with magnetic stirring under argon atmosphere. Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringe cooled to ambient temperature in a desiccators. All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates. After elution, plate was visualized under UV illumination at 254 nm for UV active materials. Further visualization was achieved by staining 2,4 DNP and charring on a hot gun. Solvents were removed in vacuo and heated with a water bath at 40 °C. Silica gel finer than 200 mesh was used for flash column chromatography. Columns were packed as slurry of silica gel in pet. ether and equilibrated with the appropriate solvent mixture prior to use. The compounds were loaded neat or as a concentrated solution using the appropriate solvent system.

Melting points are uncorrected and recorded using digital Buchi Melting Point Apparatus B-540. $^1$H NMR spectra and $^{13}$C NMR spectra were recorded on Bruker AV 400/500 MHz spectrometers in appropriate solvents using TMS as internal standard or the solvent signals as secondary standards and the chemical shifts are shown in δ scales. Multiplicities of $^1$H NMR signals are designated as s (singlet), d (doublet), dd (doublet of doublet), dt (doublet of triplet), t (triplet), quin (quintet), m (multiplet) etc. High-resolution mass spectrometry (HRMS) was performed on a TOF/Q-TOF mass spectrometer.

1.1 **Preparation of $p$-quinone methides and sulfonyl allenols:**

All solvents and inorganic reagents were obtained from commercial sources and used without purification unless otherwise noted. The $p$-quinone methides and sulfonyl allenols derivatives were prepared following the literature procedures.¹⁻⁵
**Fig. 1** Substituted \(p\)-quinone methides

\[
\begin{array}{cccc}
1a, R = H & 1b, R = Me & 1c, R = iPr & 1d, R = OMe \\
1e, R = Ph & 1f, R = F & 1g, R = Cl & 1h, R = Br \\
1i, R = CF_3 & 1j, R = CN & 1k, R = NO_2 & \\
\end{array}
\]

**Fig. 2** Substituted sulfonyl allenols

\[
\begin{array}{cccc}
2a, R = Me & 2b, R = H & 2c, R = iPr & 2d, R = OMe \\
2e, R = Ph & 2f, R = F & 2g, R = Cl & 2h, R = CF_3 \\
\end{array}
\]

\[
\begin{array}{cccc}
2i, R = Me & 2j, R = Cl & 2k, R = OMe & \\
2l, X = O & 2m, X = S & \\
\end{array}
\]

\[
\begin{array}{cccc}
2p & 2q & 2r & 2s \\
\end{array}
\]
1.2 Optimization studies

Table S1. Optimization of Reaction Conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Base</th>
<th>Solvents</th>
<th>Temp</th>
<th>Yield(^b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd(PPh(_3))(_4)</td>
<td>K(_2)CO(_3)</td>
<td>DMF</td>
<td>rt</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>Pd(PPh(_3))(_4)</td>
<td>K(_2)CO(_3)</td>
<td>DMF</td>
<td>rt</td>
<td>22(^c)</td>
</tr>
<tr>
<td>3</td>
<td>Pd(PPh(_3))(_4)</td>
<td>K(_2)CO(_3)</td>
<td>DMF</td>
<td>55 °C</td>
<td>60</td>
</tr>
<tr>
<td>4</td>
<td>Pd(PPh(_3))(_4)</td>
<td>Na(_2)CO(_3)</td>
<td>DMF</td>
<td>55 °C</td>
<td>NR</td>
</tr>
<tr>
<td>5</td>
<td>Pd(PPh(_3))(_4)</td>
<td>K(_3)PO(_4)</td>
<td>DMF</td>
<td>55 °C</td>
<td>18</td>
</tr>
<tr>
<td>6</td>
<td>Pd(PPh(_3))(_4)</td>
<td>Cs(_2)CO(_3)</td>
<td>DMF</td>
<td>55 °C</td>
<td>28</td>
</tr>
<tr>
<td>7</td>
<td>Pd(PPh(_3))(_4)</td>
<td>K(_2)CO(_3)</td>
<td>THF</td>
<td>55 °C</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>Pd(PPh(_3))(_4)</td>
<td>K(_2)CO(_3)</td>
<td>DMSO</td>
<td>55 °C</td>
<td>NR</td>
</tr>
<tr>
<td>9</td>
<td>Pd(PPh(_3))(_4)</td>
<td>K(_2)CO(_3)</td>
<td>ACN</td>
<td>55 °C</td>
<td>NR</td>
</tr>
<tr>
<td>10</td>
<td>Pd(PPh(_3))(_4)</td>
<td>K(_2)CO(_3)</td>
<td>DMF</td>
<td>55 °C</td>
<td>NR</td>
</tr>
<tr>
<td>11</td>
<td>Pd(_2)(dba)(_3)</td>
<td>K(_2)CO(_3)</td>
<td>DMF</td>
<td>55 °C</td>
<td>NR</td>
</tr>
<tr>
<td>12</td>
<td>Pd(OAc)(_2)</td>
<td>K(_2)CO(_3)</td>
<td>DMF</td>
<td>55 °C</td>
<td>NR</td>
</tr>
<tr>
<td>13</td>
<td>Pd(OAc)(_2)</td>
<td>K(_2)CO(_3)</td>
<td>DMF</td>
<td>55 °C</td>
<td>NR(^d)</td>
</tr>
<tr>
<td>14</td>
<td>Pd(PPh(_3))(_4)</td>
<td>K(_2)CO(_3)</td>
<td>DMF</td>
<td>70 °C</td>
<td>46</td>
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<tr>
<td>15</td>
<td>Pd(PPh(_3))(_4)</td>
<td>K(_2)CO(_3)</td>
<td>DMF</td>
<td>55 °C</td>
<td>82(^e)</td>
</tr>
<tr>
<td>16</td>
<td>Pd(PPh(_3))(_4)</td>
<td>K(_2)CO(_3)</td>
<td>DMF</td>
<td>55 °C</td>
<td>83(^f)</td>
</tr>
<tr>
<td>17</td>
<td>--</td>
<td>K(_2)CO(_3)</td>
<td>DMF</td>
<td>55 °C</td>
<td>NR</td>
</tr>
</tbody>
</table>

\(^a\)All reactions were performed using with 0.33 mmol \(1a\), 0.51 mmol \(2\), 0.51 mmol base, 5 mol % Pd(PPh\(_3\))\(_4\), dry DMF (2.0 mL), 12 h; \(^b\)Isolated yields; \(^c\)3.0 equiv. of K\(_2\)CO\(_3\) was employed; \(^d\)20 mol % PPh\(_3\) ligand was employed; \(^e\)10 mol % Pd(PPh\(_3\))\(_4\) catalyst was employed; \(^f\)15 mol% Pd(PPh\(_3\))\(_4\) catalyst was employed.
2 General procedure:

2.1 General procedure for preparation spiro[5.5]undeca-1,4-dien-3-one from p-QMs (3):

\[
\begin{array}{c}
\text{1} \\
\text{R}^5 \text{R}^5 \\
\text{R}^6 \text{R}^6
\end{array}
\begin{array}{c}
\text{2} \\
\text{R}^4 \text{R}^3 \\
\text{R}^1 \text{R}^2
\end{array}
\begin{array}{c}
\text{3} \\
\text{R}^5 \text{R}^6 \\
\text{R}^4 \text{R}^3
\end{array}
\]

\[
Pd(PPh_3)_4, K_2CO_3
\]

DMF, 55 °C, 12 h

To a 5 mL screw-cap vial containing a stir bar were added p-QMs 1 (0.33 mmol, 1.0 equiv), substituted-1-(p-tolyl)-2-tosylpenta-2,3-dien-1-ol 2 (0.51 mmol, 1.5 equiv), Pd(PPh_3)_4 (10 mol%), K_2CO_3 (3.0 equiv) and dry DMF (2 mL). The reaction vial was fitted with a cap, evacuated, and filled with nitrogen and heated at 55 °C for 12 h. The reaction mixture was allowed to warm to ambient temperature. The reaction mixture was diluted with EtOAc and the organic layer was washed with ice cold water (3 X 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure to afford a crude mixture which was purified by column chromatography (silica gel, petroleum ether/EtOAc) to afford the corresponding substituted spiro[5.5]undeca-1,4-dien-3-one 3.

2.2 Procedure for the preparation of intermediate 2aa':

\[
\begin{array}{c}
\text{Ts} \\
\text{Me} \\
\text{Me}
\end{array}
\begin{array}{c}
\text{OH} \\
\text{C} \\
\text{Me}
\end{array}
\begin{array}{c}
\text{Me} \\
\text{Me}
\end{array}
\begin{array}{c}
\text{Ts} \\
\text{Me} \\
\text{Me}
\end{array}
\begin{array}{c}
\text{Me} \\
\text{Me}
\end{array}
\begin{array}{c}
\text{2a} \\
\text{2aa'}
\end{array}
\]

\[
Pd(PPh_3)_4, K_2CO_3
\]

DMF, 55 °C, 12 h

Unstable intermediate, highly reactive 2aa

Stable Form 2aa'

To a 5 mL screw-cap vial containing a stir bar were added 4-methyl-1-(p-tolyl)-2-tosylpenta-2,3-dien-1-ol 2a (0.29 mmol, 1 equiv), Pd(PPh_3)_4 (10 mol%), K_2CO_3 (3.0 equiv) and dry DMF (2 mL). The reaction vial was fitted with a cap, evacuated, and filled with nitrogen and heated at 55 °C for 12 h. The reaction mixture was allowed to warm to ambient temperature. The reaction mixture was diluted with EtOAc and the organic layer was washed with ice cold water (3 X 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure to afford a crude mixture which was purified by column...
chromatography (silica gel, petroleum ether/EtOAc) to afford the corresponding intermediate 2aa’ as 57% yield.

2.3 Control Experiment:

To a seal tube containing a stir bar were added p-QM 1a (33 mmol, 1.0 equiv), 4-methyl-1-(p-tolyl)-2-tosylpent-1-en-3-one 2aa’ (0.51 mmol, 1.5 equiv), K$_2$CO$_3$ (3.0 equiv,) and dry DMF (3 mL). The reaction vial was fitted with a cap, evacuated, and filled with nitrogen and heated at 55 °C for 12 h. The reaction mixture was allowed to warm to ambient temperature. The reaction mixture was diluted with EtOAc and work up with cold H$_2$O (3 X 10 mL). After completion of the work up, EtOAc was evaporated on rotary evaporator and purified by flash silica gel column using a gradient of ethyl acetate / petroleum ether to afford corresponding 2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-11-phenyl-7-(p-tolyl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one 3a in 79%.

2.4 Procedure for the preparation 1-Cyclohexyl-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-4,4-dimethyl-5-phenyl-2-tosylpent-1-en-3-one (4):

To a 5 mL screw-cap vial containing a stir bar were added p-QM 1a (0.33 mmol, 1.0 equiv), 1-Cyclohexyl-4-methyl-2-tosylpenta-2,3-dien-1-ol 2s (0.51 mmol, 1.5 equiv), Pd(PPh$_3$)$_4$ (10 mol%), K$_2$CO$_3$ (3.0 equiv) and dry DMF (2 mL). The reaction vial was fitted with a cap, evacuated, and filled with nitrogen and heated at 55 °C for 12 h. The reaction mixture was allowed to warm to ambient temperature. The reaction mixture was diluted with EtOAc and the organic layer was washed with ice cold water (3 X 10 mL). After completion of the work up, EtOAc was evaporated on rotary evaporator and purified by flash silica gel column using a gradient of ethyl acetate / petroleum ether to afford corresponding 4 as 76% yield.
2.5 Procedure for preparation 2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-11-phenyl-7-(p-tolyl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3a):

\[ \begin{align*}
\text{To a seal tube containing a stir bar were added } & p-QM \ 1a \ (3.3 \ \text{mmol, 1.0 equiv}), \ 4\text{-methyl-1-(p-tolyl)-2-tosylpenta-2,3-dien-1-ol} \ 2a \ (5.1 \ \text{mmol, 1.5 equiv)}, \ Pd(PPh_3)_4 \ (10 \ \text{mol%}), \ K_2CO_3 \ (3.0 \ \text{equiv}), \text{ and dry DMF (30 mL). The reaction vial was fitted with a cap, evacuated, and filled with nitrogen and heated at 55 °C for 12 h. The reaction mixture was allowed to warm to ambient temperature. The reaction mixture was diluted with EtOAc and work up with cold H}_2\text{O (3 X 25 mL). After completion of the work up, EtOAc was evaporated on rotary evaporator and purified by flash silica gel column using a gradient of ethyl acetate / petroleum ether to afford corresponding 2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-11-phenyl-7-(p-tolyl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one 3a in 79 % yield.} 
\end{align*} \]

2.6 Procedure for product transformations.

2.6.1 Procedure for the Synthesis of 5:

\[ \begin{align*}
\text{To a 5 mL screw-cap vial containing a stir bar were added 2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-11-phenyl-7-(p-tolyl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one 3a (0.33 mmol, 1 equiv.), DCM (2.0 mL) and trifluoroacetic acid (0.5 ml). The reaction vial was fitted with a cap, evacuated, and filled with nitrogen and heated at 60 °C for 3 h. The reaction mixture was allowed to warm to ambient temperature. The reaction mixture was diluted with DCM and work up with ice cold H}_2\text{O (3 X 10 mL). After completion of the work up, DCM was evaporated on rotary evaporator and purified by flash silica gel column using a gradient of ethyl acetate /} 
\end{align*} \]
petroleum ether to afford corresponding 2,4-di-tert-butyl-8,8-dimethyl-7-phenyl-11-(p-tolyl)-10-tosylspiro[5.5]undeca-1,4-diene-3,9-dione 5 in 95% yield.

2.6.2 Procedure for Synthesis of 6:

To the solution of 3a (0.15 mmol, 1 equiv.) in EtOH (5 mL) was added palladium on carbon (10 mg, 10 wt %) in hydrogenation reactor and the reaction mixture was stirred under hydrogen (300 psi) with 75 °C for 12 h. After the completion of the reaction (indicated by TLC), the catalyst was filtered over a plug of Celite bed (EtOAc eluent) and the solvent was evaporated under reduced pressure to afford the corresponding product 2,4-di-tert-butyl-9-hydroxy-8,8-dimethyl-7-phenyl-11-(p-tolyl)-10-tosylspiro[5.5]undeca-1,4-dien-3-one 6 in 99% yield.

3. Characterization data:
All reactions were performed on 100 mg scale of p-Quinone Methides.

2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-11-phenyl-7-(p-tolyl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3a):

White Solid, 178 mg, 82 % yield; mp = 180-182 °C; Rf = 0.6 (Pet. ether/Ethyl acetate- 90:10); 1H NMR (500 MHz, CDCl3) δ = 11.25 (s, 1 H), 7.64 - 7.58 (d, J = 8.0 Hz, 2 H), 7.25 - 7.20 (d, J = 8.0 Hz, 2 H), 7.14 - 7.02 (m, 5 H), 6.98 (s, 1 H), 6.95 (s, 1 H), 6.91 (d, J = 2.7 Hz, 1 H), 6.76 (d, J = 7.6 Hz, 2 H), 5.25 (d, J = 2.7 Hz, 1 H), 3.40 (s, 1 H), 3.23 (s, 1 H), 2.40 (s, 3 H), 2.34 (s, 3 H), 1.41 (s, 3 H), 1.28 (s, 3 H), 1.13 (s, 9 H), 0.66 (s, 9 H); 13C NMR (125 MHz, CDCl3) δ =185.7, 169.5, 147.6, 145.6, 145.4, 144.5, 141.4, 137.4, 137.0, 136.9, 135.7, 131.9, 131.5, 129.9, 128.7, 128.6, 128.5, 128.4, 127.6, 127.4, 127.1, 127.0, 105.1, 53.5, 50.6, 44.5, 40.5, 35.0, 34.3, 29.0, 28.6, 28.3, 22.7, 21.5, 21.0; HRMS (ESI-TOF) m/z: [M+H]+ calcd for C41H39O4S 637.3346, found 637.3344.
2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-7,11-di-p-tolyl-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3b):

Yellow Solid, 156 mg, 74 % yield; mp = 206-207 °C; Rf = 0.6 (Pet. ether/Ethyl acetate- 90:10); 1H NMR (400 MHz, CDCl3) δ = 11.24 (s, 1 H), 7.64 - 7.58 (d, J = 8.4 Hz, 2 H), 7.25 - 7.20 (d, J = 7.6 Hz, 2 H), 7.14 - 7.01 (d, 3 H), 6.87 (d, J = 3.1 Hz, 2 H), 6.84 - 6.72 (m, 3 H), 6.62 (s, 1 H), 5.25 (d, J = 3.1 Hz, 1 H), 3.38 (s, 1 H), 3.17 (s, 1 H), 2.40 (s, 3 H), 2.34 (s, 3 H), 2.18 (s, 3 H), 1.40 (s, 3 H), 1.27 (s, 3 H), 1.12 (s, 9 H), 0.66 (s, 9 H); 13C NMR (100 MHz, CDCl3) δ = 185.8, 169.6, 147.5, 145.8, 145.2, 144.5, 141.5, 137.4, 137.0, 136.8, 135.8, 133.7, 131.8, 131.5, 129.9, 128.7, 128.6, 128.3, 128.0, 127.74, 127.70, 127.3, 105.1, 53.1, 50.5, 44.5, 40.5, 34.9, 34.4, 29.0, 28.6, 28.3, 22.7, 21.5, 21.1, 20.8; HRMS (ESI-TOF) m/z: [M+H]+ calcd for C42H51O4S 651.3503, found 651.3502.

2,4-Di-tert-butyl-9-hydroxy-11-(4-isopropylphenyl)-10,10-dimethyl-7-(p-tolyl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3c):

White Solid, 146 mg, 73 % yield; mp = 193-194 °C; Rf = 0.7 (Pet. ether/Ethyl acetate- 90:10); 1H NMR (400 MHz, CDCl3) δ = 11.24 (s, 1 H), 7.66 - 7.56 (m, J = 8.2 Hz, 2 H), 7.25 - 7.19 (m, J = 7.8 Hz, 2 H), 7.15 - 7.09 (m, 1 H), 7.09 - 7.00 (m, 2 H), 6.94 - 6.87 (m, 1 H), 6.87 (d, J = 2.7 Hz, 1 H), 6.83 (br. s., 2 H), 6.76 (d, J = 7.3 Hz, 1 H), 6.63 (d, J = 6.4 Hz, 1 H), 5.23 (d, J = 3.2 Hz, 1 H), 3.38 (s, 1 H), 3.18 (s, 1 H), 2.73 (spt, J = 6.9 Hz, 1 H), 2.40 (s, 3 H), 2.34 (s, 3 H), 1.41 (s, 3 H), 1.28 (s, 3 H), 1.12 (s, 9 H), 1.09 (d, J = 6.9 Hz, 6 H), 0.64 (s, 9 H); 13C NMR (100 MHz, CDCl3) δ = 185.8, 169.7, 147.8, 147.5, 145.7, 145.2, 144.5, 141.5, 137.4, 136.9, 135.8, 134.0, 131.9, 131.5, 129.9, 128.7, 128.6, 128.5 128.4, 127.4, 125.4, 125.1, 105.0, 53.2, 50.4, 44.5, 40.5, 34.9, 34.3, 33.6, 29.0, 28.6, 28.3, 23.9, 22.7, 21.5, 21.1; HRMS (ESI-TOF) m/z: [M+H]+ calcd for C44H55O4S 679.3816, found 679.3820.

2,4-Di-tert-butyl-9-hydroxy-11-(4-methoxyphenyl)-10,10-dimethyl-7-(p-tolyl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3d):

White Solid, 147 mg, 72 % yield; mp = 164-165 °C; Rf = 0.6 (Pet. ether/Ethyl acetate- 90:10); 1H NMR (400 MHz, CDCl3) δ = 11.24 (s, 1 H), 7.63 - 7.58 (m, 2 H), 7.25 - 7.20 (m, J = 8.2 Hz, 2 H), 7.13 - 7.02 (m, 3 H), 6.87 (d, J = 3.2 Hz, 1 H), 6.84 (br. s., 1 H), 6.76 (d, J = 7.3 Hz, 1 H),
6.71 - 6.63 (m, 1 H), 6.63 - 6.57 (m, 1 H), 6.57 - 6.48 (m, 1 H), 5.26 (d, \( J = 2.7 \) Hz, 1 H), 3.67 (s, 3 H), 3.38 (s, 1 H), 3.17 (s, 1 H), 2.40 (s, 3 H), 2.34 (s, 3 H), 1.39 (s, 3 H), 1.25 (s, 3 H), 1.12 (s, 9 H), 0.69 (s, 9 H); \(^{13}\text{C} \text{NMR (100 MHz, CDCl}_3\)) \( \delta = 185.8, 169.6, 158.7, 147.6, 145.9, 145.3, 144.5, 141.5, 137.4, 135.8, 133.0, 131.5, 129.9, 129.4, 129.3, 129.0, 128.7, 128.6, 128.4, 127.4, 125.3, 105.1, 55.2, 52.6, 50.6, 44.6, 40.6, 35.0, 34.4, 29.0, 28.7, 28.3, 22.6, 21.5, 21.1; HRMS (ESI-TOF) m/z: [M+H]\(^+\) calcd for C\(_{42}\)H\(_{51}\)O\(_5\)S 667.3452, found 667.3445.

11-([1,1'-biphenyl]-4-yl)-2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-7-(p-tolyl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3e):

![Structure Image]

White Solid, 128 mg, 67 % yield; mp = 160-162 °C; \( R_f = 0.5 \) (Pet. ether/Ethyl acetate- 90:10); \(^1\text{H} \text{NMR (400 MHz, CDCl}_3\)) \( \delta = 11.27 \) (s, 1 H), 7.63 (d, \( J = 8.2 \) Hz, 2 H), 7.46 - 7.41 (m, 2 H), 7.40 - 7.35 (m, 2 H), 7.33 - 7.27 (m, 2 H), 7.26 - 7.20 (m, 3 H), 7.16 - 7.12 (m, 1 H), 7.11 - 7.05 (m, 2 H), 7.01 (d, \( J = 7.3 \) Hz, 1 H), 6.91 (d, \( J = 3.2 \) Hz, 1 H), 6.86 - 6.74 (m, 2 H), 5.29 (d, \( J = 2.7 \) Hz, 1 H), 3.42 (s, 1 H), 3.27 (s, 1 H), 2.41 (s, 3 H), 2.35 (s, 3 H), 1.46 (s, 3 H), 1.33 (s, 3 H), 1.15 (s, 10 H), 0.66 (s, 9 H); \(^{13}\text{C} \text{NMR (100 MHz, CDCl}_3\)) \( \delta = 185.7, 169.4, 147.7, 145.4, 144.5, 141.4, 140.6, 140.2, 137.3, 137.0, 136.0, 135.7, 132.4, 131.5, 129.9, 128.8, 128.6, 128.4, 127.4, 127.2, 126.9, 126.2, 125.8, 105.1, 53.3, 50.5, 44.5, 40.5, 35.0, 34.4, 29.0, 28.6, 28.38 22.7, 21.5, 21.1; HRMS (ESI-TOF) m/z: [M+H]\(^+\) calcd for C\(_{47}\)H\(_{53}\)O\(_3\)S 713.3659, found 713.3657.

2,4-Di-tert-butyl-11-(4-fluorophenyl)-9-hydroxy-10,10-dimethyl-7-(p-tolyl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3f):

![Structure Image]

White solid, 163 mg, 78 % yield; mp = 186-188 °C; \( R_f = 0.7 \) (Pet. ether/Ethyl acetate- 90:10); \(^1\text{H} \text{NMR (400 MHz, CDCl}_3\)) \( \delta = 11.25 \) (s, 1 H), 7.64 - 7.55 (d, \( J = 8.4 \) Hz, 2 H), 7.25 - 7.18 (d, \( J = 8.4 \) Hz, 2 H), 7.11 - 7.02 (m, 3 H), 6.91 (s, 1 H), 6.88 (d, \( J = 3.1 \) Hz, 1 H), 6.73 (s, 2 H), 6.77 (s, 2 H), 5.24 (d, \( J = 3.1 \) Hz, 1 H), 3.39 (s, 1 H), 3.22 (s, 1 H), 2.40 (s, 3 H), 2.34 (s, 3 H), 1.39 (s, 3 H), 1.24 (s, 3 H), 1.12 (s, 9 H), 0.69 (s, 9 H); \(^{13}\text{C} \text{NMR (100 MHz, CDCl}_3\)) \( \delta = 185.5, 169.2, 163.2, 160.8, 147.9, 145.5, 144.6, 141.1, 137.2, 135.6, 133.3, 132.7, 131.5, 129.9, 128.7, 128.3, 127.4, 114.2, 105.2, 52.7, 50.6, 44.4, 40.4, 35.0, 34.4, 29.0, 28.7, 28.3, 22.5, 21.5, 21.1; \(^{19}\text{F} \text{NMR (376 MHz, CDCl}_3\)) \( \delta = -115.3; \) HRMS (ESI-TOF) m/z: [M+H]\(^+\) calcd for C\(_{41}\)H\(_{48}\)O\(_4\)FS 655.3252, found 655.3251.
2,4-Di-tert-butyl-11-(4-chlorophenyl)-9-hydroxy-10,10-dimethyl-7-(p-tolyl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3g):

White solid, 161 mg, 79 % yield; mp = 226-227 °C; Rf = 0.7 (Pet. ether/Ethyl acetate- 90:10); 1H NMR (400 MHz, CDCl3) δ = 11.25 (s, 1 H), 7.63 - 7.56 (m, J = 8.3 Hz, 2 H), 7.24 - 7.19 (m, J = 8.1 Hz, 2 H), 7.11 - 7.03 (m, 4 H), 7.03 - 6.95 (m, 1 H), 6.95 - 6.84 (m, 2 H), 6.76 (d, J = 7.3 Hz, 1 H), 6.73 - 6.61 (m, 1 H), 5.23 (d, J = 3.2 Hz, 1 H), 3.40 (s, 1 H), 3.20 (s, 1 H), 2.40 (s, 3 H), 2.34 (s, 3 H), 1.39 (s, 3 H), 1.24 (s, 3 H), 1.12 (s, 9 H), 0.70 (s, 9 H); 13C NMR (100 MHz, CDCl3) δ = 185.5, 169.0, 147.9, 145.7, 145.2, 144.6, 141.0, 137.3, 137.1, 135.5, 135.5, 133.2, 129.9, 129.6, 128.7, 128.7, 128.3, 127.6, 127.4, 127.3, 127.2, 105.2, 52.9, 50.5, 44.4, 40.4, 35.0, 34.5, 29.0, 28.6, 28.3, 22.6, 21.5, 21.0; HRMS (ESI-TOF) m/z: [M+H]+ calcd for C41H48O4ClS  671.2956, found 671.2946.

11-(4-bromophenyl)-2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-7-(p-tolyl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3h):

Yellow Solid, 159 mg, 83 % yield; mp = 228-230 °C; Rf = 0.7 (Pet. ether/Ethyl acetate- 90:10); 1H NMR (400 MHz, CDCl3) δ = 11.25 (s, 1 H), 7.60 (d, J = 7.6 Hz, 2 H), 7.22 (d, J = 8.4 Hz, 3 H), 7.14 (d, J = 7.6 Hz, 1 H), 7.10 - 7.02 (m, 3 H), 6.86 (d, J = 3.1 Hz, 1 H), 6.83 (d, J = 7.6 Hz, 1 H), 6.76 (d, J = 7.6 Hz, 1 H), 6.68 - 6.57 (d, 1 H), 5.23 (d, J = 3.1 Hz, 1 H), 3.40 (s, 1 H), 3.18 (s, 1 H), 2.40 (s, 3 H), 2.34 (s, 3 H), 1.39 (s, 3 H), 1.24 (s, 3 H), 1.12 (s, 9 H), 0.70 (s, 9 H); 13C NMR (100 MHz, CDCl3) δ = 185.5, 169.0, 148.0, 145.7, 145.2, 144.6, 141.0, 137.2, 137.1, 136.0, 135.5, 133.5, 131.5, 130.7, 130.6, 130.2, 129.9, 128.8, 128.7, 128.2, 127.4, 121.3, 105.2, 53.0, 50.5, 44.3, 40.3, 35.0, 34.5, 29.0, 28.6, 28.3, 22.6, 21.5, 21.1; HRMS (ESI-TOF) m/z: [M+Na]+ calcd for C41H47O4BrNaS 739.2250, found 739.2253.

2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-7-(p-tolyl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3i):

White solid, 145 mg, 83 % yield; mp = 215-216 °C; Rf = 0.8 (Pet. ether/Ethyl acetate- 90:10); 1H NMR (400 MHz, CDCl3) δ = 11.27 (s, 1 H), 7.60 (d, J = 8.3 Hz, 2 H), 7.41 - 7.32 (m, 1 H), 7.25 (br. s., 1 H), 7.23 (s, 2 H), 7.14 - 7.01 (m, 4 H), 6.95 - 6.84 (m, 2 H), 6.76 (d, J = 8.1 Hz, 1 H), 5.22 (d, J = 2.9 Hz, 1 H), 3.43 (s, 1 H), 3.30 (s, 1 H), 2.40 (s, 3 H), 2.35 (s,
3 H), 1.41 (s, 3 H), 1.27 (s, 3 H), 1.14 (s, 9 H), 0.64 (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 185.4, 168.8, 148.1, 146.5, 146.0, 144.8, 144.6, 141.2, 140.9, 137.2, 135.4, 132.1, 132.0, 131.5, 131.5, 129.9, 129.8, 128.8, 128.7, 128.3, 127.4, 105.3, 53.5, 50.5, 44.3, 40.4, 35.1, 34.4, 29.0, 28.6, 28.3 22.6, 21.5, 21.1; $^{19}$F NMR (376 MHz, CDCl$_3$) δ = -62.7; HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for C$_{42}$H$_{48}$O$_4$F$_3$S 705.3220, found 705.3210.

4-(8,10-Di-tert-butyl-3-hydroxy-2,2-dimethyl-9-oxo-5-(p-toly)-4-tosylspiro[5.5]undeca-3,7,10-trien-1-yl)benzonitrile (3j):

White solid, 169 mg, 82 % yield; mp = 219-220 °C; $R_f$ = 0.5 (Pet. ether/Ethyl acetate- 90:10); $^1$H NMR (400 MHz, CDCl$_3$) δ = 11.27 (s, 1 H), 7.68 - 7.53 (d, $J$ = 7.9 Hz, 2 H), 7.40 - 7.31 (d, 2 H), 7.25 - 7.15 (d, $J$ = 7.9 Hz, 2 H), 7.06 (m, 4 H), 6.89 (d, $J$ = 2.4 Hz, 2 H), 6.76 (d, $J$ = 7.3 Hz, 1 H), 5.20 (d, $J$ = 2.4 Hz, 1 H), 3.43 (s, 1 H), 3.29 (s, 1 H), 2.39 (s, 3 H), 2.34 (s, 3 H), 1.40 (s, 3 H), 1.24 (s, 3 H), 1.13 (s, 9 H), 0.67 (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 185.2, 168.5, 148.3, 146.3, 144.7, 144.5, 142.7, 140.7, 137.3, 137.2, 135.2, 132.5, 131.5,130.7, 130.6, 129.9, 129.2, 128.8, 128.7, 128.2, 127.4, 118.3, 111.2, 105.4, 53.7, 50.6, 44.2, 40.4, 35.1, 34.5, 29.0, 28.6, 28.3, 22.6, 21.5, 21.0; HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for C$_{42}$H$_{48}$O$_4$NS 662.3299, found 662.3295.

2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-11-(4-nitrophenyl)-7-(p-toly)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3k):

White solid, 138 mg, 69 % yield; mp = 206-207 °C; $R_f$ = 0.5 (Pet. ether/Ethyl acetate- 90:10); $^1$H NMR (400 MHz, CDCl$_3$) δ = 11.28 (s, 1 H), 7.97 (d, $J$ = 7.3 Hz, 1 H), 7.88 (d, $J$ = 8.2 Hz, 1 H), 7.62 - 7.57 (m, $J$ = 8.2 Hz, 2 H), 7.24 - 7.20 (m, $J$ = 7.8 Hz, 2 H), 7.15 (d, $J$ = 7.8 Hz, 1 H), 7.09 - 7.04 (m, 3 H), 6.97 (d, $J$ = 7.8 Hz, 1 H), 6.91 (d, $J$ = 2.7 Hz, 1 H), 6.76 (d, $J$ = 7.8 Hz, 1 H), 5.22 (d, $J$ = 3.2 Hz, 1 H), 3.44 (s, 1 H), 3.37 (s, 1 H), 2.44 (s, 9 H), 2.40 (s, 3 H), 2.34 (s, 3 H), 1.41 (s, 3 H), 1.25 (s, 3 H), 1.14 (s, 9 H), 0.65 (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 185.2, 168.4, 148.5, 147.0, 146.3, 144.9, 144.7, 144.4, 140.6, 137.4, 137.1, 135.1, 132.7, 131.5, 129.9, 129.1, 128.9, 128.8, 128.2, 127.4, 122.1, 122.1, 105.4, 53.4, 50.6, 44.2, 40.3, 35.1, 34.5, 29.0, 28.6, 28.4, 22.6, 21.5, 21.1; HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for C$_{41}$H$_{48}$O$_6$NS 682.3197, found 682.3187.
11-(2-bromophenyl)-2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-7-(p-tolyl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3l):

White solid, 107 mg, 56 % yield; mp = 188-189 °C; Rf = 0.5 (Pet. ether/Ethyl acetate- 90:10); 1H NMR (400 MHz, CDCl3) δ = 11.26 (s, 1 H), 7.59 (d, J = 8.5 Hz, 2 H), 7.46 - 7.38 (m, 1 H), 7.24 - 7.14 (m, 3 H), 7.08 - 6.99 (m, 3 H), 6.98 - 6.90 (m, 2 H), 6.86 (d, J = 3.1 Hz, 1 H), 6.75 (d, J = 7.3 Hz, 1 H), 5.37 (d, J = 3.1 Hz, 1 H), 4.24 (s, 1 H), 3.44 (s, 1 H), 2.40 (s, 3 H), 2.33 (s, 3 H), 1.42 (s, 3 H), 1.35 (s, 3 H), 1.13 (s, 9 H), 0.65 (s, 9 H); 13C NMR (100 MHz, CDCl3) δ = 185.5, 169.0, 148.1, 146.0, 144.5, 144.3, 140.8, 137.5, 137.0, 136.2, 135.4, 132.9, 131.4, 130.8, 129.8, 128.8, 128.7, 128.5, 127.5, 127.4, 125.8, 105.4, 50.4, 49.4, 45.8, 41.5, 35.0, 34.4, 29.1, 28.7, 28.0 23.3, 22.6, 21.5; HRMS (ESI-TOF) m/z: [M+Na]+ calcd for C41H47O4SiBrNaS 739.2250, found 739.2248.

2,4-Di-tert-butyl-9-hydroxy-11-(3-methoxyphenyl)-10,10-dimethyl-7-(p-tolyl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3m):

White solid, 131 mg, 64 % yield; dr = 54:46 mp = 116-117 °C; Rf = 0.6 (Pet. ether/Ethyl acetate- 90:10); 1H NMR (400 MHz, CDCl3) δ = 11.25 (s, 1.90 H), 7.59 (d, J = 7.6 Hz, 3.87 H), 7.21 (d, J = 7.6 Hz, 3.96 H), 7.05 (t, J = 7.8 Hz, 5.97 H), 7.01 - 6.92 (m, 2.44 H), 6.90 (d, J = 9.0 Hz, 1.55 H), 6.76 (d, J = 6.8 Hz, 1.87 H), 6.70 - 6.61 (m, 1.94 H), 6.52 (d, J = 7.6 Hz, 0.85 H), 6.48 (s, 1 H), 6.35 (d, J = 7.6 Hz, 1 H), 6.31 (s, 0.78 H), 5.27 (d, J = 2.9 Hz, 1.91H), 3.68 (s, 2.72 H), 3.56 (s, 3 H), 3.40 (s, 1.92 H), 3.26 (s, 1 H), 3.15 (s, 0.84 H), 2.39 (s, 5.79 H), 2.34 (s, 5.90 H), 1.42 (s, 5.81 H), 1.28 (br. s., 6.24 H), 1.13 (s, 17.53 H), 0.69 (s, 17.45 H); 13C NMR (100 MHz, CDCl3) δ = 185.8, 185.7, 169.6, 169.4, 158.9, 158.7, 147.6, 147.5, 145.6, 145.4, 145.3, 144.5, 141.9, 141.3, 138.4, 137.3, 137.0, 135.5, 131.4, 129.8, 129.7, 129.2, 129.0, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.3, 124.4, 121.2, 119.0, 114.5, 113.1, 110.7, 105.1, 55.4, 55.2, 53.6, 53.0, 50.9, 50.6, 44.4, 41.7, 40.5, 34.9, 34.4, 29.1, 29.0, 28.6, 28.3, 22.7, 22.4, 21.6, 21.5, 21.0; HRMS (ESI-TOF) m/z: [M+H]+ calcd for C42H51O5S 667.3452, found 667.3444.

2,4-Di-tert-butyl-11-(3-fluorophenyl)-9-hydroxy-10,10-dimethyl-7-(p-tolyl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3n):

White solid, 141 mg, 67 % yield; dr = 58:42; mp = 223-224 °C; Rf = 0.6 (Pet. ether/Ethyl acetate- 90:10); 1H NMR (400 MHz, CDCl3) δ = 11.26 (s, 1.76
H), 7.60 (d, J = 7.6 Hz, 3.59 H), 7.22 (d, J = 7.6 Hz, 3.58 H), 7.13 - 7.01 - 6.97 (m, 7.30 H), 6.87 (m, 1.89 H), 6.85 - 6.81 (m, 1.55 H), 6.81 - 6.73 (m, 2.49 H), 6.68 (d, J = 10.5 Hz, 1.34 H), 6.61 - 6.53 (m, 1 H), 6.53 - 6.41 (m, 0.70 H), 5.25 (br. s., 1.79 H), 3.39 (br. s., 1.77 H), 3.25 (s, 1 H), 3.18 (s, 0.73 H), 2.40 (s, 5.42 H), 2.34 (s, 5.38 H), 1.42 (s, 5.43 H), 1.27 (s, 5.50 H), 1.13 (s, 16.18 H), 0.69 (s, 16.14 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 185.5, 169.1, 145.8, 145.7, 145.1, 144.6, 144.6, 140.8, 139.5, 139.4, 137.3, 137.2, 135.5, 135.4, 131.5, 131.5, 131.5, 129.9, 128.8, 128.7, 128.2, 127.4, 105.2, 50.6, 44.4, 40.4, 35.0, 34.4, 29.0, 28.7, 28.4, 22.7, 21.5, 21.1; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta = -113.6, -114.3\); HRMS (ESI-TOF) m/z: [M+H]\(^+\) calcld for C\(_{41}\)H\(_{40}\)O\(_4\)ClNaS 693.2776, found 693.2780.

2,4-Di-tert-butyl-11-(3-chlorophenyl)-9-hydroxy-10,10-dimethyl-7-(p-tolyl)-8-tosylspiro

[5.5]undeca-1,4,8-trien-3-one (3o):

![Diagram of the molecule](image)

White solid, 161 mg, 79 % yield; dr = 57:43; mp = 190-191 \(^\circ\)C; \(R_f = 0.6\) (Pet. ether/Ethyl acetate- 90:10); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 11.26\) (s, 1.70 H), 7.60 (m, 3.51 H), 7.23 (m, J = 7.3 Hz, 3.55 H), 7.14 - 7.01 (m, 7.83 H), 7.01 - 6.91 (m, 2.20 H), 6.87 (m, 2.70 H), 6.76 (d, J = 6.9 Hz, 2.48 H), 6.65 (d, J = 7.3 Hz, 1 H), 5.25 (br. s., 0.73 H), 5.21 (br. s., 1 H), 3.41 (s, 0.75 H), 3.39 (s, 1 H), 3.21 (s, 1 H), 3.16 (s, 0.76 H), 2.40 (s, 5.18 H), 2.34 (s, 5.19 H), 1.42 (s, 5.40 H), 1.26 (s, 5.54 H), 1.19 - 1.09 (m, 15.78 H), 0.69 (s, 15.71 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 185.5, 169.0, 148.2, 147.9, 145.8, 145.1, 145.0, 144.6, 141.0, 140.8, 139.0, 137.2, 135.5, 133.5, 133.3, 131.5, 129.9, 128.7, 128.7, 128.6, 128.2, 127.4, 127.2, 126.7, 105.1, 53.4, 53.0, 50.5, 44.3, 40.3, 35.0, 34.4, 29.0, 28.7, 28.4, 22.6, 22.4, 21.5, 21.1; HRMS (ESI-TOF) m/z: [M+Na]\(^+\) calcld for C\(_{41}\)H\(_{47}\)O\(_4\)ClNaS 693.2776, found 693.2780.

2,4-Di-tert-butyl-11-(2,4-dichlorophenyl)-9-hydroxy-10,10-dimethyl-7-(p-tolyl)-8-tosylspiro

[5.5]undeca-1,4,8-trien-3-one (3p):

![Diagram of the molecule](image)

White solid, 121 mg, 62 % yield; mp = 115-117 \(^\circ\)C; \(R_f = 0.6\) (Pet. ether/Ethyl acetate- 90:10); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 11.26\) (s, 1 H), 7.61 - 7.55 (m, J = 8.3 Hz, 2 H), 7.25 (d, J = 2.2 Hz, 1 H), 7.22 - 7.17 (m, J = 7.8 Hz, 2 H), 7.12 (d, J = 6.8 Hz, 1 H), 7.04 (d, J = 8.1 Hz, 2 H), 6.95 (d, J = 8.8 Hz, 1 H), 6.90 (dd, J = 2.2, 8.8 Hz, 1 H), 6.84 (d, J = 2.9 Hz, 1 H), 6.75 (d, J = 7.1 Hz, 1 H), 5.29 (d, J = 2.9 Hz, 1 H), 4.22 (s, 1 H), 3.45 (s, 1 H), 2.40 (s, 3 H), 2.33 (s, 3 H), 1.38 (s, 3 H), 1.32 (s, 3 H), 1.13 (s, 9 H), 0.68 (s, 9 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 185.3, \ldots\)
168.7, 148.3, 146.4, 144.5, 143.8, 140.6, 137.4, 137.2, 136.4, 135.2, 133.6, 133.3, 131.4, 131.2, 129.8, 129.0, 128.8, 128.6, 127.3, 125.5, 105.4, 50.3, 46.0, 45.4, 41.2, 35.0, 34.4, 34.1, 29.1, 28.6, 28.1 23.1, 21.5, 21.1; HRMS (ESI-TOF) m/z: [M+Na]+ calcld for C_{41}H_{46}O_{4}Cl_{2}NaS 727.2386, found 727.2385.

2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-7-(p-tolyl)-8-tosyl-11-(3,4,5-trimethoxyphenyl) spiro[5.5]undeca-1,4,8-trien-3-one(3q):

White solid, 107 mg, 57 % yield; mp = 192-194 °C; R_f = 0.3 (Pet. ether/Ethyl acetate- 90:10); ^1H NMR (400 MHz, CDCl_3) δ = 11.27 (s, 1 H), 7.59 - 7.53 (m, J = 8.2 Hz, 2 H), 7.20 - 7.16 (m, J = 8.2 Hz, 2 H), 7.07 - 7.01 (m, 3 H), 7.00 (d, J = 3.2 Hz, 1 H), 6.76 (d, J = 8.2 Hz, 1 H), 6.14 (d, J = 1.8 Hz, 1 H), 5.94 (d, J = 1.8 Hz, 1 H), 5.32 (d, J = 2.7 Hz, 1 H), 3.73 (s, 3 H), 3.70 (s, 3 H), 3.55 (s, 3 H), 3.42 (s, 1 H), 3.17 (s, 1 H), 2.38 (s, 3 H), 2.34 (s, 3 H), 1.43 (s, 3 H), 1.27 (s, 3 H), 1.12 (s, 9 H), 0.74 (s, 9 H); ^13C NMR (100 MHz, CDCl_3) δ = 186.0, 169.6, 152.5, 152.0, 147.6, 145.7, 145.5, 144.5, 142.5, 137.8, 137.3, 137.0, 135.4, 132.7, 131.5, 129.8, 128.7, 128.6, 128.5, 127.4, 110.0, 106.5, 105.3, 60.8, 56.6, 56.5, 53.4, 51.3, 44.5, 40.7, 35.0, 34.5, 29.3, 28.7, 28.4, 22.3, 21.5, 21.1; HRMS (ESI-TOF) m/z: [M+H]^+ calcld for C_{44}H_{55}O_{7}S 727.3663, found 727.3657.

9-Hydroxy-2,4-diisopropyl-10,10-dimethyl-11-phenyl-7-(p-tolyl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3r):

White solid, 153 mg, 67 % yield; mp = 166-168 °C; R_f = 0.4 (Pet. ether/Ethyl acetate- 95:05); ^1H NMR (400 MHz, CDCl_3) δ = 11.28 (s, 1 H), 7.60 - 7.55 (m, J = 8.2 Hz, 2 H), 7.21 - 7.16 (m, J = 8.2 Hz, 2 H), 7.12 - 6.99 (m, 5 H), 6.99 - 6.86 (m, 3 H), 6.75 (d, J = 7.3 Hz, 2 H), 5.28 (d, J = 2.3 Hz, 1 H), 3.43 (s, 1 H), 3.28 (s, 1 H), 3.01 (spt, J = 6.8 Hz, 1 H), 2.63 (spt, J = 6.8 Hz, 1 H), 2.39 (s, 3 H), 2.34 (s, 3 H), 1.40 (s, 3 H), 1.27 (s, 3 H), 1.08 (d, J = 6.9 Hz, 3 H), 0.85 (d, J = 6.9 Hz, 3 H), 0.63 (d, J = 6.9 Hz, 3 H), 0.09 (d, J = 6.9 Hz, 3 H); ^13C NMR (100 MHz, CDCl_3) δ = 184.5, 169.5, 145.8, 145.7, 144.5, 144.0, 141.9, 137.3, 137.0, 136.8, 135.5, 131.9, 131.6, 129.8, 128.6, 128.4, 127.6, 127.4, 127.2, 105.1, 53.3, 50.4, 44.6, 40.6, 28.1, 26.6, 25.4, 22.6, 21.6, 21.5, 21.3, 21.0, 20.7; HRMS (ESI-TOF) m/z: [M+H]^+ calcld for C_{39}H_{45}O_{6}S 609.3033, found 609.3024.
9-Hydroxy-2,4,10,10-tetramethyl-11-phenyl-7-(p-tolyl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3s):

White solid, 162 mg, 62 % yield; mp = 164-166 °C; Rf = 0.3 (Pet. ether/Ethyl acetate- 95:05); 1H NMR (400 MHz, CDCl3) δ = 11.21 (s, 1 H), 7.76 (dd, J = 1.4, 8.2 Hz, 1 H), 7.54 - 7.50 (m, 3 H), 7.18 (d, J = 8.2 Hz, 2 H), 7.13 - 7.05 (m, 2 H), 7.05 - 6.98 (m, 4 H), 6.93 (m, 1 H), 6.76 (m, 1 H), 5.43 (dd, J = 1.4, 3.2 Hz, 1 H), 3.45 (s, 1 H), 3.23 (s, 1 H), 2.40 (s, 3 H), 2.32 (s, 3 H), 2.29 (s, 3 H), 1.81 (s, 3 H), 1.40 (s, 3 H), 1.20 (s, 3 H); 13C NMR (100 MHz, CDCl3) δ = 186.5, 169.3, 156.5, 149.5, 146.1, 144.4, 138.4, 137.2, 137.0, 136.7, 131.9, 131.7, 131.5, 129.7, 129.5, 128.7, 128.1, 127.5, 127.2, 122.8, 105.2, 52.9, 51.0, 45.5, 40.6, 28.0, 22.7, 21.5, 21.0, 16.7, 15.9, 15.4; HRMS (ESI-TOF) m/z: [M+H]+ calcd for C35H37O4S 553.2412, found 553.2412.

2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-7,11-diphenyl-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3ab):

White solid, 160 mg, 76 % yield; mp = 217-218 °C; Rf = 0.8 (Pet. ether/Ethyl acetate- 90:10); 1H NMR (400 MHz, CDCl3) δ = 11.27 (s, 1 H), 7.65 - 7.57 (m, 2 H), 7.29 - 7.20 (m, 6 H), 7.12 - 7.04 (m, 2 H), 7.02 - 6.92 (m, 2 H), 6.91 (d, J = 3.2 Hz, 1 H), 6.90 - 6.86 (m, 1 H), 6.77 - 6.68 (m, 1 H), 5.19 (d, J = 3.2 Hz, 1 H), 3.44 (s, 1 H), 3.22 (s, 1 H), 2.39 (s, 3 H), 1.42 (s, 3 H), 1.29 (s, 3 H), 1.14 (s, 9 H), 0.64 (s, 9 H); 13C NMR (100 MHz, CDCl3) δ = 185.7, 169.6, 147.6, 145.4, 144.6, 141.3, 138.8, 137.2, 136.7, 131.9, 131.7, 129.9, 128.5, 128.4, 128.0, 127.8, 127.6, 127.4, 127.2, 127.0, 104.9, 53.5, 50.9, 44.4, 40.5, 35.0, 34.3, 29.0, 28.6, 28.3, 22.7, 21.5; HRMS (ESI-TOF) m/z: [M+H]+ calcd for C40H47O4S 623.3190, found 623.3186.

2,4-Di-tert-butyl-9-hydroxy-7-(4-isopropylphenyl)-10,10-dimethyl-11-phenyl-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3ac):

White solid, 159 mg, 71 % yield; mp = 207-209 °C; Rf = 0.6 (Pet. ether/Ethyl acetate- 90:10); 1H NMR (400 MHz, CDCl3) δ = 11.24 (s, 1 H), 7.58 - 7.53 (m, 2 H), 7.19 - 7.14 (m, 2 H), 7.13 - 7.07 (m, 2 H), 7.05 (s, 3 H), 6.98 (d, J = 3.2 Hz, 3 H), 6.78 (d, J = 8.1 Hz, 2 H), 5.19 (d, J = 2.9 Hz, 1 H), 3.49 (s, 1 H), 3.23 (s, 1 H), 2.87 (spt, J = 6.9 Hz, 1 H), 2.37 (s, 3 H), 1.41 (s, 3 H), 1.29 (s, 3 H), 1.25 (d, J = 2.7 Hz, 3 H), 1.23 (d, J = 2.4 Hz, 3 H), 1.18 (s, 9 H), 0.64 (s, 9
H; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 185.7, 169.4, 147.9, 147.6, 145.6, 145.3, 144.2, 141.5, 137.6, 136.9, 135.9, 131.9, 131.6, 129.7, 128.6, 128.1, 127.3, 127.1, 127.0, 125.9, 125.8, 105.2, 53.5, 50.6, 44.5, 40.5, 35.0, 34.3, 33.6, 29.1, 28.5, 28.3, 24.1, 23.8, 22.8, 21.5; HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for C$_{43}$H$_{53}$O$_4$S 665.3659, found 665.3660.

2,4-Di-tert-butyl-9-hydroxy-7-(4-methoxyphenyl)-10,10-dimethyl-11-phenyl-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3ad):

![Diagram of 3ad]

White solid, 164 mg, 74% yield; mp = 170-172 °C; $R_f$ = 0.6 (Pet. ether/Ethyl acetate- 90:10); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 11.24 (s, 1 H), 7.66 - 7.57 (d, $J$ = 8.4 Hz, 2 H), 7.26 - 7.19 (d, $J$ = 8.4 Hz, 2 H), 7.13 (d, $J$ = 7.6 Hz, 1 H), 7.11 - 7.04 (m, 2 H), 7.01 - 6.88 (m, 3 H), 6.83 - 6.71 (m, 4 H), 5.26 (d, $J$ = 3.1 Hz, 1 H), 3.81 (s, 3 H), 3.40 (s, 1 H), 3.20 (s, 1 H), 2.40 (s, 3 H), 1.40 (s, 3 H), 1.28 (s, 3 H), 1.13 (s, 9 H), 0.66 (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 185.7, 169.4, 158.8, 147.6, 145.6, 144.5, 141.4, 137.4, 136.8, 132.5, 131.9, 130.7, 129.9, 129.5, 128.5, 127.6, 127.3, 127.1, 127.0, 113.5, 113.0, 105.2, 55.2, 53.5, 50.2, 44.6, 40.5, 35.0, 34.3, 29.0, 28.6, 28.3, 22.6, 21.5; HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for C$_{41}$H$_{48}$O$_5$NaS 675.3115, found 675.3109.

7-([1,1'-biphenyl]-4-yl)-2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-11-phenyl-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3ae):

![Diagram of 3ae]

White solid, 168 mg, 71% yield; mp = 227-228 °C; $R_f$ = 0.5 (Pet. ether/Ethyl acetate- 90:10); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 11.30 (s, 1 H), 7.64 - 7.58 (m, 4 H), 7.50 - 7.45 (m, 4 H), 7.40 - 7.35 (m, 1 H), 7.26 (m, 1 H), 7.21 (d, $J$ = 7.8 Hz, 2 H), 7.13 - 7.05 (m, 2 H), 7.04 - 6.91 (m, 4 H), 6.77 (s, 1 H), 5.29 (d, $J$ = 2.7 Hz, 1 H), 3.53 (s, 1 H), 3.26 (s, 1 H), 2.34 (s, 3 H), 1.45 (s, 3 H), 1.31 (s, 3 H), 1.17 (s, 9 H), 0.67 (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 185.7, 169.7, 147.7, 145.6, 145.3, 144.6, 141.3, 140.4, 140.1, 137.8, 137.4, 136.7, 132.1, 131.9, 130.3, 129.9, 129.0, 128.9, 128.8, 128.5, 127.7, 127.4, 127.2, 127.0, 126.6, 126.4, 105.0, 53.7, 50.7, 44.5, 40.6, 35.0, 34.4, 29.1, 28.6, 28.3, 22.7, 21.5; HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for C$_{46}$H$_{53}$O$_4$S 699.3503, found 699.3502.

2,4-Di-tert-butyl-7-(4-fluorophenyl)-9-hydroxy-10,10-dimethyl-11-phenyl-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3af):
White solid, 176 mg, 81 % yield; mp = 209-211 °C; \( R_f = 0.6 \) (Pet. ether/Ethyl acetate- 90:10); \textsuperscript{1}H NMR \( (400 \text{ MHz, CDCl}_3) \) \( \delta = 11.27 \) (s, 1 H), 7.61 (d, \( J = 8.1 \text{ Hz, 2 H) , 7.24} \) (dd, \( J = 0.7, 8.6 \text{ Hz, 2 H) , 7.19} \) (br. s., 1 H), 7.13 - 7.06 (m, 2 H), 7.04 - 6.91 (m, 4 H), 6.90 (d, \( J = 3.2 \text{ Hz, 1 H) , 6.89} - 6.81 \text{ (m, 1 H) , 6.73} \) (m, 1 H), 5.19 (d, \( J = 3.2 \text{ Hz, 1 H) , 3.43} \) (s, 1 H), 3.15 (s, 1 H), 2.41 (s, 3 H), 1.41 (s, 3 H), 1.29 (s, 3 H), 1.14 (s, 9 H), 0.65 (s, 9 H); \textsuperscript{13}C NMR \( (100 \text{ MHz, CDCl}_3) \) \( \delta = 185.6, 169.8, 163.2, 160.8, 147.8, 145.8, 144.8, 141.1, 137.2, 136.6, 134.7, 133.1, 133.0, 131.9, 130.0, 128.4, 127.7, 127.3, 127.0, 114.9, 114.7, 105.0, 53.6, 50.3, 44.4, 44.3, 40.5, 35.0, 34.4, 29.0, 28.6, 28.4, 22.7, 21.5; \textsuperscript{19}F NMR \( (376 \text{ MHz, CDCl}_3) \) \( \delta = -114.9 \); HRMS (ESI-TOF) m/z: \[M+Na^+] \text{ calcd for } C_{40}H_{45}O_4FNaS 663.2915, \text{ found } 663.2899.

\textbf{2,4-Di-tert-butyl-7-(4-chlorophenyl)-9-hydroxy-10,10-dimethyl-11-phenyl-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3ag):}

White solid, 190 mg, 81 % yield; mp = 258-260 °C; \( R_f = 0.8 \) (Pet. ether/Ethyl acetate- 90:10); \textsuperscript{1}H NMR \( (400 \text{ MHz, CDCl}_3) \) \( \delta = 11.32 \) (s, 1 H), 7.54 (d, \( J = 8.3 \text{ Hz, 2 H) , 7.47} \) (d, \( J = 6.8 \text{ Hz, 2 H) , 7.31} - 7.23 \text{ (m, 1 H) , 7.21} - 7.16 \text{ (m, 2 H) , 7.11} \) (d, \( J = 6.6 \text{ Hz, 2 H) , 7.06} - 6.90 \text{ (m, 4 H) , 6.81} - 6.66 \text{ (m, 1 H) , 5.12} \) (d, \( J = 3.2 \text{ Hz, 1 H) , 3.57} \) (s, 1 H), 3.12 (s, 1 H), 2.38 (s, 3 H), 1.42 (s, 3 H), 1.31 (s, 3 H), 1.18 (s, 9 H), 0.64 (s, 9 H); \textsuperscript{13}C NMR \( (100 \text{ MHz, CDCl}_3) \) \( \delta = 185.5, 170.2, 148.0, 146.2, 144.9, 144.3, 143.1, 140.8, 137.1, 136.3, 132.1, 129.9, 129.4, 128.8, 128.4, 127.7, 127.3, 127.1, 104.8, 53.7, 50.4, 44.3, 40.6, 35.0, 34.4, 29.0, 28.6, 28.4, 22.7, 21.5; \textsuperscript{19}F NMR \( (376 \text{ MHz, CDCl}_3) \) \( \delta = -114.9 \); HRMS (ESI-TOF) m/z: \[M+Na^+] \text{ calcd for } C_{40}H_{45}O_4FNaS 679.2619, \text{ found } 679.2613.
127.8, 127.4, 127.3, 127.1, 125.3, 124.9, 124.5, 122.6, 104.6, 53.8, 50.8, 44.2, 40.7, 35.1, 34.4, 29.1, 28.6, 28.4, 22.8, 21.4; \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}) \(\delta = -62.4\); HRMS (ESI-TOF) m/z: [M+H]\(^+\) calcd for C\textsubscript{41}H\textsubscript{60}O\textsubscript{3}F\textsubscript{3}S 691.3063, found 691.3058.

\textbf{2,4-Di-tert-butyl-7-(2,4-dimethylphenyl)-9-hydroxy-10,10-dimethyl-11-phenyl-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3ai):}

White solid, 183 mg, 83 % yield; mp = 215-217 °C; \(R_f = 0.7\) (Pet. ether/Ethyl acetate- 90:10); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta = 11.17\) (s, 1 H), 7.59 - 7.51 (d, \(J = 8.4\) Hz, 2 H), 7.22 - 7.17 (d, \(J = 7.6\) Hz, 2 H), 7.08 (d, \(J = 3.8\) Hz, 2 H), 7.03 - 6.96 (m, 2 H), 6.96 - 6.91 (m, 1 H), 6.91 - 6.85 (m, 3 H), 6.79 - 6.70 (m, 1 H), 5.28 (d, \(J = 2.3\) Hz, 1 H), 3.82 (s, 1 H), 3.40 (s, 1 H), 2.40 (s, 3 H), 2.29 (s, 3 H), 2.05 (s, 3 H), 1.40 (s, 3 H), 1.30 (s, 3 H), 1.16 (s, 9 H), 0.57 (s, 9 H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta = 185.4, 169.2, 147.4, 145.9, 144.4, 144.2, 141.3, 137.7, 136.7, 136.5, 134.1, 132.1, 131.5, 129.7, 128.7, 128.5, 127.7, 127.1, 127.0, 126.5, 105.8, 53.3, 44.5, 44.2, 40.3, 35.0, 34.1, 29.1, 28.3, 28.1, 22.8, 21.5, 20.9, 20.6; HRMS (ESI-TOF) m/z: [M+H]\(^+\) calcd for C\textsubscript{42}H\textsubscript{51}O\textsubscript{4}F\textsubscript{3}S 691.2410, found 691.2402.

\textbf{2,4-Di-tert-butyl-7-(2,4-dimethylphenyl)-9-hydroxy-10,10-dimethyl-11-phenyl-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3aj):}

White solid, 183 mg, 78 % yield; mp = 239-241 °C; \(R_f = 0.8\) (Pet. ether/Ethyl acetate- 90:10); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta = 11.30\) (s, 1 H), 7.75 - 7.69 (m, 2 H), 7.38 (d, \(J = 1.8\) Hz, 1 H), 7.34 - 7.27 (m, 4 H), 7.15 - 7.08 (m, 2 H), 7.03 - 6.95 (m, 1 H), 6.91 (d, \(J = 8.2\) Hz, 1 H), 6.76 (br. s., 1 H), 6.70 (d, \(J = 3.2\) Hz, 1 H), 5.18 (d, \(J = 3.2\) Hz, 1 H), 4.05 (s, 1 H), 3.19 (s, 1 H), 2.43 (s, 3 H), 1.41 (s, 3 H), 1.29 (s, 3 H), 1.08 (s, 9 H), 0.61 (s, 9 H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta = 185.1, 170.1, 148.0, 146.6, 145.1, 142.4, 139.7, 136.6, 136.2, 136.0, 135.6, 133.8, 132.0, 131.1, 130.1, 129.6, 128.4, 127.8, 127.6, 127.4, 127.1, 127.0, 104.5, 53.7, 44.6, 44.0, 40.4, 34.9, 34.2, 28.9, 28.4, 28.2, 22.7, 21.5; HRMS (ESI-TOF) m/z: [M+H]\(^+\) calcd for C\textsubscript{40}H\textsubscript{45}O\textsubscript{4}Cl\textsubscript{2}S 691.2410, found 691.2402.

\textbf{2,4-Di-tert-butyl-7-(3,4-dimethoxyphenyl)-9-hydroxy-10,10-dimethyl-11-phenyl-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3ak):}
White solid, 153 mg, 66% yield; dr = 57:43; mp = 199-201 °C; Rf = 0.4 (Pet. ether/Ethyl acetate- 90:10); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 11.24\) (s, 0.72 H), 11.20 (s, 1 H), 7.59 (d, \(J = 7.8\) Hz, 2 H), 7.54 (d, \(J = 7.8\) Hz, 1.46 H), 7.22 (d, \(J = 7.8\) Hz, 2 H), 7.18 (d, \(J = 7.8\) Hz, 1.60 H), 7.14 - 7.05 (m, 3.53 H), 7.03 - 6.89 (m, 5.32 H), 6.75 (d, \(J = 8.2\) Hz, 1.70 H), 6.72 (s, 2.81 H), 6.59 (s, 0.75 H), 6.48 (d, \(J = 7.3\) Hz, 0.75 H), 6.35 (s, 1 H), 5.31 (d, \(J = 2.7\) Hz, 1 H), 5.24 (d, \(J = 2.7\) Hz, 0.70 H), 3.89 (s, 5.37 H), 3.82 (d, \(J = 4.6\) Hz, 5.38 H), 3.53 (s, 0.75 H), 3.38 (s, 1 H), 3.27 (s, 1.76 H), 2.39 (s, 5.31 H), 1.40 (s, 5.37 H), 1.29 (d, \(J = 4.6\) Hz, 5.73 H), 1.18 (s, \(J = 7.3\) Hz, 16 H), 0.65 (s, 16 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 185.8, 185.7, 169.4, 148.3, 148.2, 148.1, 147.7, 145.5, 145.4, 144.4, 141.6, 141.3, 137.6, 136.8, 136.7, 131.9, 131.1, 129.8, 129.7, 128.5, 127.7, 127.3, 127.2, 127.0, 123.9, 121.2, 114.0, 111.7, 110.5, 110.2, 105.7, 105.5, 55.7, 55.7, 55.6, 53.8, 53.7, 50.5, 44.7, 40.5, 40.5, 35.0, 34.3, 29.1, 28.7, 28.7, 28.3, 22.7, 22.6, 21.5; HRMS (ESI-TOF) m/z: [M+H]^+ calcd for C\(_{42}\)H\(_{51}\)O\(_6\)S 683.3401, found 683.3408.

2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-7-(naphthalen-1-yl)-11-phenyl-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3al):

White solid, 155 mg, 68% yield; mp = 258-260 °C; Rf = 0.7 (Pet. ether/Ethyl acetate- 90:10); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 11.32\) (s, 1 H), 7.84 - 7.80 (m, 1 H), 7.74 (d, \(J = 7.8\) Hz, 1 H), 7.52 - 7.36 (m, 7 H), 7.05 (dd, \(J = 2.3, 5.5\) Hz, 4 H), 7.03 - 6.91 (m, 3 H), 6.67 (d, \(J = 7.3\) Hz, 1 H), 4.85 (d, \(J = 3.2\) Hz, 1 H), 4.47 (s, 1 H), 3.42 (s, 1 H), 2.32 (s, 3 H), 1.47 (s, 3 H), 1.35 (s, 3 H), 1.24 (s, 9 H), 0.19 (s, 9 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 185.4, 169.6, 148.0, 145.1, 145.0, 144.5, 141.1, 136.7, 136.6, 134.8, 133.7, 132.1, 131.9, 129.6, 128.8, 128.4, 128.1, 127.6, 127.53, 127.5, 127.1, 127.0, 126.3, 125.6, 124.6, 123.9, 105.4, 53.6, 44.8, 43.6, 40.5, 35.1, 33.8, 29.2, 28.1, 27.6, 22.9, 21.4; HRMS (ESI-TOF) m/z: [M+H]^+ calcd for C\(_{44}\)H\(_{49}\)O\(_4\)S 673.3346, found 673.3328.

2,4-Di-tert-butyl-7-(furan-2-yl)-9-hydroxy-10,10-dimethyl-11-phenyl-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3am):

White solid, 162 mg, 78% yield; mp = 183-184 °C; Rf = 0.7 (Pet. ether/Ethyl acetate- 90:10); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 11.15\) (s, 1 H), 7.70 - 7.66 (m, 2 H), 7.29 (dd, \(J = 1.0, 1.7\) Hz, 2 H), 7.27 (d, \(J = 0.7\) Hz, 1 H), 7.12 (s, 2
H), 7.00 (s, 1 H), 6.93 (s, 1 H), 6.84 (s, 1 H), 6.79 (d, J = 3.2 Hz, 1 H), 6.32 - 6.28 (m, 1 H), 6.09 (dd, J = 0.6, 2.6 Hz, 1 H), 5.37 (d, J = 3.2 Hz, 1 H), 3.49 (s, 1 H), 3.39 (s, 1 H), 2.41 (s, 3 H), 1.37 (s, 3 H), 1.25 (s, 3 H), 1.11 (s, 9 H), 0.70 (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 185.6, 169.9, 152.8, 148.4, 146.2, 144.6, 144.4, 141.8, 139.7, 137.3, 136.9, 130.0, 127.2, 110.7, 109.9, 103.6, 54.9, 44.8, 44.2, 40.5, 35.0, 34.2, 29.0, 28.6, 28.4, 22.5, 21.5; HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for C$_{38}$H$_{45}$O$_5$S 613.2982, found 613.2976.

2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-11-phenyl-7-(thiophen-2-yl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3an):

White solid, 134 mg, 63 % yield; mp = 213-215 °C; $R_f$ = 0.8 (Pet. ether/Ethyl acetate- 90:10); $^1$H NMR (400 MHz, CDCl$_3$) δ = 11.17 (s, 1 H), 7.64 (d, J = 8.2 Hz, 2 H), 7.25 (d, J = 7.8 Hz, 2 H), 7.20 (dd, J = 0.9, 5.0 Hz, 1 H), 7.12 (d, 2 H), 7.01 (m, 1 H), 6.96 (m, 1 H), 6.91 (dd, J = 3.7, 5.0 Hz, 1 H), 6.87 (d, J = 3.2 Hz, 1 H), 6.84 (m, 1 H), 6.73 (d, J = 3.2 Hz, 1 H), 5.51 (d, J = 3.2 Hz, 1 H), 3.70 (s, 1 H), 3.52 (s, 1 H), 2.41 (s, 3 H), 1.41 (s, 3 H), 1.27 (s, 3 H), 1.13 (s, 9 H), 0.69 (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 185.6, 169.5, 148.2, 145.9, 145.0, 144.6, 143.6, 140.4, 137.4, 136.8, 131.9, 129.9, 128.4, 127.8, 127.7, 127.2, 127.1, 126.7, 125.3, 106.6, 54.1, 46.0, 44.5, 40.5, 35.0, 34.4, 29.0, 28.6, 28.3, 22.7, 21.5; HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for C$_{38}$H$_{45}$O$_5$S 629.2754, found 629.2749.

(E)-2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-11-phenyl-7-styryl-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3ao):

White solid, 146 mg, 66 % yield; mp = 247-249 °C; $R_f$ = 0.6 (Pet. ether/Ethyl acetate- 90:10); $^1$H NMR (500 MHz, CDCl$_3$) δ = 11.21 (s, 1 H), 7.77 (d, J = 8.4 Hz, 2 H), 7.33 (d, J = 7.2 Hz, 2 H), 7.30 - 7.21 (m, 5 H), 7.15 (m, 2 H), 7.03 (m, 1 H), 6.94 (m, 2 H), 6.90 (d, J = 3.1 Hz, 1 H), 6.32 (d, J = 15.6 Hz, 1 H), 6.09 - 5.98 (m, 2 H), 3.26 (s, 1 H), 3.03 (d, J = 7.6 Hz, 1 H), 2.30 (s, 3 H), 1.36 (s, 3 H), 1.25 (s, 3 H), 1.16 (s, 9 H), 0.79 (s, 9 H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ = 185.6, 169.5, 148.0, 146.4, 144.8, 140.8, 137.7, 137.0, 136.4, 135.0, 131.9, 131.4, 130.1, 129.1, 128.6, 128.5, 128.3, 127.8, 127.5, 127.3, 127.1, 126.4, 104.9, 55.2, 47.9, 45.1, 40.7, 35.0, 34.5, 29.0, 28.9, 28.7, 22.6, 21.4; HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for C$_{42}$H$_{48}$O$_4$SNa 671.3448, found 671.3448.
2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-11-phenyl-8-(phenylsulfonyl)-7-(p-tolyl)spiro[5.5]undeca-1,4,8-trien-3-one (3ap):

White solid, 150 mg, 71 % yield; mp = 192-194 °C; Rf = 0.7 (Pet. ether/Ethyl acetate- 90:10); 1H NMR (400 MHz, CDCl3) δ = 11.25 (s, 1 H), 7.75 - 7.68 (m, 2 H), 7.58 - 7.51 (m, 1 H), 7.45 - 7.38 (m, 2 H), 7.14 - 6.98 (m, 6 H), 6.96 (d, J = 3.2 Hz, 2 H), 6.82 - 6.68 (m, 2 H), 5.25 (d, J = 3.2 Hz, 1 H), 3.47 (s, 1 H), 3.23 (s, 1 H), 2.32 (s, 3 H), 1.41 (s, 3 H), 1.30 (s, 3 H), 1.15 (s, 9 H), 0.66 (s, 9 H); 13C NMR (100 MHz, CDCl3) δ = 185.7, 169.7, 157.3, 147.5, 145.6, 145.5, 141.6, 137.5, 136.9, 136.8, 135.7, 132.0, 131.9, 131.6, 128.6, 128.5, 128.3, 127.6, 127.2, 105.0, 53.5, 50.6, 44.5, 40.6, 35.0, 34.4, 29.2, 28.6, 28.3, 22.7, 21.1; HRMS (ESI-TOF) m/z: [M+Na]+ calcd for C40H46O4SNa 645.3439, found 645.3439.

2,4-Di-tert-butyl-8-((4-(tert-butyl)phenyl)sulfonyl)-9-hydroxy-10,10-dimethyl-11-phenyl-7-(p-tolyl)spiro[5.5]undeca-1,4,8-trien-3-one (3aq):

White solid, 180 mg, 78 % yield; mp = 192-194 °C; Rf = 0.7 (Pet. ether/Ethyl acetate- 90:10); 1H NMR (400 MHz, CDCl3) δ = 11.25 (s, 1 H), 7.64 - 7.60 (m, 2 H), 7.43 - 7.38 (m, 2 H), 7.12 - 7.06 (m, 2 H), 7.06 - 7.00 (m, 3 H), 7.00 - 6.92 (m, 3 H), 6.79 (d, J = 7.3 Hz, 1 H), 6.74 ( s, 1 H), 5.25 (d, J = 3.2 Hz, 1 H), 3.51 (s, 1 H), 3.22 (s, 3 H), 1.41 (s, 3 H), 1.32 (s, 3 H), 1.29 (s, 3 H), 1.15 (s, 9 H), 0.65 (s, 9 H); 13C NMR (100 MHz, CDCl3) δ = 185.7, 169.7, 157.3, 147.5, 145.6, 145.5, 141.6, 137.5, 136.9, 136.8, 135.7, 132.0, 131.9, 131.6, 128.6, 128.5, 128.3, 127.6, 127.2, 105.0, 53.5, 50.6, 44.5, 40.6, 35.2, 35.1, 34.4, 31.0, 29.3, 28.6, 28.3, 22.7, 21.1; HRMS (ESI-TOF) m/z: [M+Na]+ calcd for C44H54O4SNa 701.8619, found 701.8619.

2,4-Di-tert-butyl-10-ethyl-9-hydroxy-10-methyl-11-phenyl-7-(p-tolyl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3ar):

White solid, 152 mg, 69 % yield; dr = 67:34; mp = 185-186 °C; Rf = 0.7 (Pet. ether/Ethyl acetate- 90:10); 1H NMR (400 MHz, CDCl3) δ = 11.34 (s, 0.97 H), 11.28 (s, 0.51 H), 7.64 - 7.56 (m, 3.13 H), 7.26 - 7.20 (m, 3.36 H), 7.18 - 7.13 (m, 0.92 H), 7.09 - 7.05 (m, 3 H), 7.04 - 7.02 (m, 3.38 H), 7.00 - 6.94 (m, 1.64 H), 6.94 - 6.86 (m, 2.98 H), 6.76 (d, J = 6.1 Hz, 2.25 H), 5.25 (d, J
= 2.9 Hz, 1 H), 5.20 (d, \( J = 2.9 \) Hz, 0.51 H), 3.45 (s, 1 H), 3.38 (s, 1 H), 3.37 (s, 0.50 H), 3.24 (s, 0.51 H), 2.41 (s, 4.76 H), 2.36 - 2.31 (m, 4.71 H), 2.07 - 1.97 (m, 0.53 H), 1.93 - 1.83 (m, 1 H), 1.64 (qd, \( J = 7.4 \), 14.6 Hz, 0.68 H), 1.45 (s, 1.62 H), 1.39 - 1.34 (m, 1.17 H), 1.32 (s, 3.30 H), 1.25 - 1.19 (m, 3.30 H), 1.14 (s, 9.40 H), 1.12 (s, 4.72 H), 0.77 (t, \( J = 7.5 \) Hz, 1.93 H), 0.66 (s, 4.80 H), 0.63 (s, 9.50 H); \(^{13}\text{C} \) NMR (100 MHz, CDCl\(_3\)) \( \delta = 185.8, 170.4, 169.0, 147.0, 146.8, 146.1, 146.0, 145.3, 145.0, 144.5, 144.5, 142.3, 142.0, 137.7, 137.6, 137.3, 137.1, 137.0, 136.9, 136.0, 135.8, 129.9, 129.8, 128.5, 127.7, 127.3, 127.2, 127.1, 106.8, 105.4, 76.7, 54.3, 51.1, 50.2, 48.9, 44.5, 44.2, 44.2, 42.9, 35.0, 34.9, 34.4, 34.3, 32.7, 29.0, 29.0, 28.6, 28.6, 27.8, 24.5, 23.2, 21.5, 21.5, 21.1, 21.0, 10.8, 10.4; HRMS (ESI-TOF) \( m/z: [M+H]^+ \) calcd for C\(_{42}\)H\(_{51}\)O\(_4\)S 651.3499, found 651.3499.

4-Methyl-1-(p-tolyl)-2-tosylpent-1-en-3-one (2aa‘):

Brown liquid, 57 mg, 57 % yield; \( R_f = 0.3 \) (Pet. ether/Ethyl acetate-80:20); \(^1\text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta = 7.97 \) (s, 1 H), 7.79 (d, \( J = 8.7 \) Hz, 2 H), 7.33 (d, \( J = 8.2 \) Hz, 2 H), 7.18 (s, 4 H), 2.69 (spt, \( J = 6.9 \) Hz, 1 H), 2.43 (s, 3 H), 2.37 (s, 3 H), 1.06 (d, \( J = 6.9 \) Hz, 6 H); \(^{13}\text{C} \) NMR (100 MHz, CDCl\(_3\)) \( \delta = 206.0, 144.5, 141.9, 141.8, 141.0, 137.5, 129.8, 129.7, 129.5, 129.2, 128.5, 41.7, 21.6, 21.4, 18.0; HRMS (ESI-TOF) \( m/z: [M+H]^+ \) calcd for C\(_{20}\)H\(_{23}\)O\(_3\)S 343.1362, found 343.1359.

1-Cyclohexyl-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-4,4-dimethyl-5-phenyl-2-tosylpent-1-en-3-one (4):

Brown liquid, 0.162 mg, 76 % yield; \( R_f = 0.6 \) (Pet. ether/Ethyl acetate-80:20); \(^1\text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta = 7.53 \) (d, \( J = 8.2 \) Hz, 2 H), 7.41 (d, \( J = 7.8 \) Hz, 2 H), 7.27 (s, 1 H), 7.25 - 7.18 (m, 5 H), 7.17 - 7.11 (m, 1 H), 6.58 (d, \( J = 10.1 \) Hz, 1 H), 5.04 (s, 1 H), 4.55 (s, 1 H), 2.41 (s, 3 H), 1.52 (s, 3 H), 1.45 (d, \( J = 12.4 \) Hz, 3 H), 1.39 (s, 18 H), 1.25 (s, 3 H), 1.19 (d, \( J = 8.7 \) Hz, 1 H), 1.16 - 0.99 (m, 2 H), 0.97 - 0.70 (m, 5 H); \(^{13}\text{C} \) NMR (100 MHz, CDCl\(_3\)) \( \delta = 207.6, 152.4, 149.4, 144.3, 142.5, 140.5, 136.8, 135.1, 131.8, 130.7, 129.6, 128.3, 128.1, 127.0, 126.4, 57.4, 53.8, 37.2, 34.3, 31.0, 30.9, 30.4, 26.4, 25.2, 23.9, 23.7, 21.7; HRMS (ESI-TOF) \( m/z: [M+Na]^+ \) calcd for C\(_{40}\)H\(_{52}\)O\(_4\)NaS 651.3479, found 651.3474.
2,4-Di-tert-butyl-8,8-dimethyl-7-phenyl-11-(p-tolyl)-10-tosylspiro[5.5]undeca-1,4-diene-3,9-dione (5):

White solid, 71 mg, 71 % yield; mp = 107-109 °C; \( R_f = 0.5 \) (Pet. ether/Ethyl acetate- 90:10); \( ^1\text{H NMR (400 MHz, CDCl}_3\text{)} \, \delta = 7.59 \, (d, J = 8.2 \text{ Hz, } 2 \text{ H}), 7.29 - 7.24 \, (m, \, 1 \text{ H}), 7.21 \, (d, \, J = 8.2 \text{ Hz, } 2 \text{ H}), 7.19 - 7.14 \, (m, \, 2 \text{ H}), 7.03 \, (t, \, J = 7.3 \text{ Hz, } 1 \text{ H}), 6.90 \, (d, \, J = 7.8 \text{ Hz, } 1 \text{ H}), 6.85 - 6.78 \, (m, \, J = 7.8 \text{ Hz, } 2 \text{ H}), 6.71 - 6.63 \, (m, \, J = 8.2 \text{ Hz, } 2 \text{ H}), 6.55 \, (d, \, J = 3.2 \text{ Hz, } 1 \text{ H}), 6.12 \, (s, \, 1 \text{ H}), 4.62 \, (d, \, J = 9.2 \text{ Hz, } 1 \text{ H}), 4.24 \, (d, \, J = 8.7 \text{ Hz, } 1 \text{ H}), 3.84 \, (s, \, 1 \text{ H}), 2.38 \, (s, \, 3 \text{ H}), 2.18 \, (s, \, 3 \text{ H}), 1.48 \, (s, \, 3 \text{ H}), 1.17 \, (s, \, 9 \text{ H}), 1.17 \, (s, \, 3 \text{ H}), 0.67 \, (s, \, 9 \text{ H}); \( ^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \, \delta = 206.7, 185.1, 149.8, 147.3, 145.3, 144.8, 137.3, 137.0, 136.6, 134.6, 134.6, 131.3, 129.7, 129.6, 128.8, 128.5, 128.4, 128.1, 127.9, 127.8, 127.4, 127.3, 76.5, 60.3, 52.8, 48.3, 47.9, 35.4, 34.1, 28.8, 28.5, 28.4, 24.6, 21.6, 20.9; \( \text{HRMS (ESI-TOF) m/z: } [\text{M+H}]^+ \text{ calcd for C}_{41}\text{H}_{41}\text{O}_4\text{S 637.3346, found 637.3345.} \)

2,4-Di-tert-butyl-9-hydroxy-8,8-dimethyl-7-phenyl-11-(p-tolyl)-10-tosylspiro[5.5]undeca-1,4-dien-3-one (6):

White solid, 99 mg, 99 % yield; mp = 173-175 °C; \( R_f = 0.3 \) (Pet. ether/Ethyl acetate- 90:10); \( ^1\text{H NMR (400 MHz, CDCl}_3\text{)} \, \delta = 7.17 - 7.06 \, (m, \, 5 \text{ H}), 7.00 \, (d, \, J = 9.2 \text{ Hz, } 5 \text{ H}), 6.76 - 6.69 \, (d, \, J = 7.3 \text{ Hz, } 2 \text{ H}), 6.36 - 6.20 \, (m, \, 3 \text{ H}), 5.30 \, (s, \, 1 \text{ H}), 4.73 - 4.60 \, (d, \, 1 \text{ H}), 4.28 \, (d, \, J = 12.2 \text{ Hz, } 1 \text{ H}), 3.87 \, (d, \, J = 12.2 \text{ Hz, } 1 \text{ H}), 3.50 \, (s, \, 1 \text{ H}), 3.30 \, (d, \, J = 4.3 \text{ Hz, } 1 \text{ H}), 2.38 \, (s, \, 3 \text{ H}), 2.13 \, (s, \, 3 \text{ H}), 1.44 \, (s, \, 3 \text{ H}), 1.12 \, (s, \, 9 \text{ H}), 0.92 \, (s, \, 3 \text{ H}), 0.70 \, (s, \, 9 \text{ H}); \( ^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \, \delta = 185.0, 148.4, 146.9, 146.7, 143.6, 138.1, 137.6, 137.4, 136.5, 132.6, 131.6, 131.4, 129.0, 128.8, 128.5, 127.9, 127.6, 127.1, 126.8, 126.6, 126.2, 74.6, 65.6, 55.5, 53.4, 50.7, 47.8, 40.1, 35.2, 34.0, 28.6, 28.5, 23.5, 21.5, 20.9; \( \text{HRMS (ESI-TOF) m/z: } [\text{M+H}]^+ \text{ calcd for C}_{41}\text{H}_{51}\text{O}_4\text{S 639.3506, found 639.3506.} \)
4. X-ray crystallography:

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CCDC No - **1950350**

An X-ray intensity data measurement of compound **3ai** was carried out on a Bruker D8 VENTURE Kappa Duo PHOTON II CPAD diffractometer equipped with Incoatech multilayer mirrors optics. The intensity measurements were carried out at 100(2) K temperature with Mo micro-focus sealed tube diffraction source (MoK$_\alpha$= 0.71073 Å). The X-ray generator was operated at 50 kV and 1.4. A preliminary set of cell constants and an orientation matrix were calculated from three sets of 36 frames. Data were collected with $\omega$ scan width of 0.5° at different settings of $\varphi$ and $2\theta$ with a frame time of 15 secs keeping the sample-to-detector distance fixed at 5.00 cm. The X-ray data collection was monitored by APEX3 program (Bruker, 2016). All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2016). Using APEX3 (Bruker) program suite, the structure was solved with the ShelXS-97 (Sheldrick, 2008) structure solution program, using direct methods. The model was refined with version of ShelXL-2013 (Sheldrick, 2015) using Least Squares minimisation. All the hydrogen atoms were placed in a geometrically idealized position and constrained to ride on its parent atoms. An ORTEP III view of compounds was drawn with 30% probability displacement ellipsoids and H atoms are omitted for clarity.
Crystal data of 3ai: C₄₂H₅₀O₄S, M = 650.88, colorless block, 0.48 x 0.23 x 0.14 mm³, monoclinic, space group P2₁/c, a = 17.0878(7) Å, b = 10.7963(4) Å, c = 21.0437(9) Å, β = 109.074(2)°, V = 3669.1(3) Å³, Z = 4, T = 100(2) K, 2θmax = 61.052°, Dcalc (g cm⁻³) = 1.178, F(000) = 1400, μ (mm⁻¹) = 0.128, 130989 reflections collected, 11176 unique reflections (Rint = 0.0458, Rsig = 0.0219), 9223 observed (I > 2σ(I)) reflections, multi-scan absorption correction, Tmin = 0.941, Tmax = 0.982, 436 refined parameters, Good of Fit = S = 1.069, R1 = 0.0391, wR2 = 0.0968 (all data R = 0.0530, wR2 = 0.1089), maximum and minimum residual electron densities; Δρmax = 0.392, Δρmin = -0.386 (e Å⁻³), CCDC No. 1950350.

5. References:


6. Spectral Data

\[ \text{CHLOROFORM-d} \]

\[ \begin{align*}
7.62 & \quad 7.27 \\
7.60 & \quad 7.23 \\
7.58 & \quad 7.21 \\
7.08 & \quad 6.91 \\
7.05 & \quad 6.90 \\
6.98 & \quad 6.77 \\
6.90 & \quad 6.76 \\
6.91 & \quad 6.76 \\
6.95 & \quad 6.76 \\
5.25 & \quad 5.25 \\
3.40 & \quad 3.40 \\
3.05 & \quad 3.05 \\
3.01 & \quad 3.01 \\
1.95 & \quad 1.95 \\
1.94 & \quad 1.94 \\
5.18 & \quad 5.18 \\
2.02 & \quad 2.02 \\
1.99 & \quad 1.99 \\
0.97 & \quad 0.97
\end{align*} \]

\[ ^1\text{H NMR (500 MHz), CDCl}_3 \]
CHLOROFORM-d

$^{13}$C NMR (125 MHz), CDCl$_3$
COSY: 3a
HMBC: 3a
HSQC: 3a
NOESY: 3a
\[ \text{CHLOROFORM-d} \]

\[ 11.24 \quad 7.62 \quad 7.60 \quad 7.27 \quad 7.10 \quad 7.07 \quad 7.05 \quad 6.99 \quad 6.87 \quad 6.80 \quad 6.62 \quad 5.25 \quad 5.24 \quad 3.21 \quad 3.01 \quad 3.05 \quad 3.06 \quad 1.03 \quad 1.02 \quad 3.21 \quad 2.15 \quad 3.15 \quad 2.03 \quad 2.00 \]

\[ \text{CHLOROFORM-d} \]

\[ 7.8 \quad 7.7 \quad 7.6 \quad 7.5 \quad 7.4 \quad 7.3 \quad 7.2 \quad 7.1 \quad 7.0 \quad 6.9 \quad 6.8 \quad 6.7 \quad 6.6 \quad 6.5 \quad 6.4 \quad 1.02 \quad 3.15 \quad 2.15 \quad 3.21 \]

\[ \text{CHLOROFORM-d} \]

\[ 3b \]

\[ \text{\textsuperscript{1}H NMR (400 MHz), CDCl\textsubscript{3}} \]

\[ 0.95 \quad 2.00 \quad 2.03 \quad 3.15 \quad 2.15 \quad 3.21 \quad 1.02 \quad 1.03 \quad 1.02 \quad 1.03 \quad 3.05 \quad 3.02 \quad 3.01 \quad 3.21 \quad 9.05 \quad 9.04 \]

\[ \text{S33} \]
$^{13}$C NMR (100 MHz), CDCl$_3$
$^1$H NMR (400 MHz), CDCl$_3$
$^{1}$H NMR (400 MHz), CDCl$_3$
$^{13}$C NMR (100 MHz), CDCl$_3$
$^{19}$F NMR (376 MHz), CDCl$_3$
$^1$H NMR (400 MHz), CDCl$_3$
13C NMR (100 MHz), CDCl₃

CHLOROFORM-d
$^1$H NMR (400 MHz), CDCl$_3$
$^1$H NMR (400 MHz), CDCl$_3$
$^{13}$C NMR (100 MHz), CDCl$_3$
$^{19}$F NMR (376 MHz), CDCl$_3$
\(^1^3\)C NMR (100 MHz), CDCl\(_3\)
\[ \text{CHLOROFORM-d} \]

\[ ^1H \text{ NMR (400 MHz), CDCl}_3 \]
\(^1\)H NMR (400 MHz), CDCl\(_3\)
13C NMR (100 MHz), CDCl₃

CHLOROFORM-d
$^1$H NMR (400 MHz), CDCl$_3$
$^1$H NMR (400 MHz), CDCl$_3$
$^{13}$C NMR (100 MHz), CDCl$_3$
$^{19}$F NMR (376 MHz), CDCl$_3$
\(^1H\) NMR (400 MHz), CDCl\(_3\)
\( ^{13}C \) NMR (100 MHz), CDCl\(_3\)
\[13^C\text{ NMR (100 MHz), CDCl}_3\]
$^{13}$C NMR (100 MHz), CDCl$_3$
CHLOROFORM-d

$^{1}$H NMR (400 MHz), CDCl$_3$
$^{13}$C NMR (100 MHz), CDCl$_3$
$^1$H NMR (400 MHz), CDCl$_3$
CHLOROFORM-d

S NMR (100 MHz), CDCl3

13C NMR (100 MHz), CDCl3
$^{13}$C NMR (100 MHz), CDCl$_3$
$^1$H NMR (400 MHz), CDCl$_3$
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\[ ^{13}\text{C NMR (100 MHz), CDCl}_3 \]
$^1$H NMR (400 MHz), CDCl$_3$
$^{13}$C NMR (100 MHz), CDCl$_3$

CHLOROFORM-d
$^{19}$F NMR (376 MHz), CDCl$_3$
\(^1\)H NMR (400 MHz), CDCl\(_3\)
\textbf{CHLOROFORM-d}

$^{13}\text{C NMR (100 MHz), CDCl}_3$
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CHLOROFORM-d

1H NMR (400 MHz), CDCl₃
$^{13}$C NMR (100 MHz), CDCl$_3$

CHLOROFORM-d
$^{19}$F NMR (376 MHz), CDCl$_3$
$^1$H NMR (400 MHz), CDCl$_3$
$^{13}$C NMR (100 MHz), CDCl$_3$


\[ \text{CHLOROFORM-d} \]

\[ ^1H \text{NMR (400 MHz), CDCl}_3 \]
$^{13}$C NMR (100 MHz), CDCl$_3$
\[13^C\text{ NMR (100 MHz), CDCl}_3\]
$^{13}$C NMR (100 MHz), CDCl$_3$
CHLOROFORM-d

$^1$H NMR (400 MHz), CDCl$_3$
$^1$H NMR (500 MHz), CDCl$_3$
$^{13}$C NMR (125 MHz), CDCl$_3$
\textsuperscript{1}H NMR (400 MHz), CDCl\textsubscript{3}

\begin{align*}
\text{CHLOROFORM-d} & \\
11.25 & 7.72 & 7.70 & 7.69 & 7.54 & 7.43 & 7.41 & 7.40 & 7.27 & 7.03 & 6.96 & 6.95 & 6.79 & 5.25 & 5.25 & 3.47 & 3.23 & 2.32 & 1.41 & 1.30 & 1.15 & 0.66 & 0.01
\end{align*}
$^{13}$C NMR (100 MHz), CDCl$_3$
\[ ^1\text{H NMR (400 MHz), CDCl}_3 \]
$^1$H NMR (400 MHz), CDCl$_3$
$^{13}$C NMR (100 MHz), CDCl$_3$
$^1$H NMR (400 MHz) CDCl$_3$
$^{13}$C NMR (100 MHz) CDCl$_3$

CHLOROFORM-d
GSG-G-821 #264  RT: 1.17  AV: 1  NL: 2.55E7
T: FTMS + p ESI Full ms [133.4000-2000.0000]

342.1517  R=59607

343.1359  R=60202
C_{20} H_{23} O_3 S = 343.1362
-1.1002 ppm

344.1387  R=55302

C_{20} H_{23} O_3 S = 343.1362
-1.1002 ppm
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Note: The image contains a chemical structure labeled as 4, a CHLOROFORM-d solvent reference, and an NMR spectrum indicating chemical shifts for various compounds. The spectrum includes peaks at 1.99, 2.11, 5.31, 0.98, 1.00, 0.99, 3.10, 3.11, 3.13, 18.13, 3.21, 1.29, 2.06, and 5.08 ppm.
$^{13}$C NMR (100 MHz), CDCl$_3$
$^1$H NMR (400 MHz), CDCl$_3$
$^1$H NMR (400 MHz), CDCl$_3$
$^{13}$C NMR (100 MHz), CDCl$_3$