Accessing Bridged Bicyclic Compounds or Meta Carbon-Functionalized Anilines from Dearomatization of Anilines

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Supporting Information

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General experimental methods:

All reactions were performed in test tubes under air. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63 µm, standard grade). Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr (house vacuum) at 25–35 °C. Commercial reagents and solvents were used as received. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale.

EXPERIMENTAL SECTION

Typical procedure for the oxidative dearomatization and domino Michael addition. PhI(OAc)₂ (354 mg, 1.1 mmol) was added into the solution of N-Ts p-toluidine (261 mg, 1 mmol) in MeOH (5 mL) at 25 °C. After 15 min, the reaction mixture was quenched with saturated NaHCO₃ (50 mL), and extracted by ethyl acetate (50 mL x 3). The organic layer was dried over anhydrated Na₂SO₄, and concentrated in vacuo. The crude product was dissolved in CH₃OH (5 mL) and treated with acetylacetone (300 mg, 3 mmol) and CH₃ONa (27 mg, 0.5 mmol) at room temperature. The mixture was stirred over 4 hours. Upon completion determined by TLC, the reaction mixture was concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2:1) to afford the pure product 4ea (355 mg, 91% yield).
Table 1. Condition Evaluation for the Reaction between Pentane-2,4-dione and N-Ts-4-methoxy-4-methylcyclohexa-2,5-dienimine

![Chemical Structure Image]

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<tr>
<th>entry</th>
<th>base (equiv)</th>
<th>solvent</th>
<th>yield (%)&lt;sup&gt;a,b&lt;/sup&gt;</th>
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<td>16&lt;sup&gt;d&lt;/sup&gt;</td>
<td>CH$_3$ONa (0.5)</td>
<td>CH$_3$OH</td>
<td>87</td>
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</table>

<sup>a</sup>Reaction conditions: compound 2e (0.2 mmol), pentane-2,4-dione (0.6 mmol), solvent (3 mL), unless noted. <sup>b</sup>Isolated yield based on compound 2e. <sup>c</sup>2 equivalents of pentane-2,4-dione was used. <sup>d</sup>The reaction was conducted in a 5 mmol scale.
N-(4-acetyl-9-methoxy-3,9-dimethyl-2-oxabicyclo[3.3.1]nona-3,7-dien-7-yl)-4-methylbenzenesulfonamide 4ea: colorless solid; m.p. 141-142 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.83 (s, 1 H), 7.72 (d, \(J = 7.8\) Hz, 2 H), 7.29 (d, \(J = 7.3\) Hz, 2 H), 5.53 (d, \(J = 6.4\) Hz, 1 H), 4.36 (d, \(J = 6.8\) Hz, 1 H), 3.12 (s, 3 H), 2.90 (s, 1 H), 2.42 (s, 3 H), 2.19-2.32 (m, 4 H), 2.05-2.14 (m, 4 H), 1.00 (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 197.6, 164.0, 143.8, 138.5, 136.1, 129.4, 127.4, 114.5, 104.8, 72.6, 69.5, 48.9, 35.2, 33.9, 30.5, 21.4, 21.3, 16.1; IR (KBr) 3220, 3054, 2968, 2304, 1651, 1598, 1422 cm\(^{-1}\); HRMS m/z calcd for C\(_{20}\)H\(_{26}\)NO\(_5\)S ([M+H]\(^+\)): 392.1526, found 392.1518.

\[
\begin{align*}
\text{N-(4-acetyl-9-methoxy-3,9-dimethyl-2-oxabicyclo[3.3.1]nona-3,7-dien-7-yl)methanesulfonamide 4da:} & \text{ yellow oil; } ^1\text{H NMR (400 MHz, CDCl}_3\text{)} \quad \delta \quad 7.40 (s, 1 H), 5.56 (d, } J = 6.0 \text{ Hz, 1 H), 4.52 (d, } J = 6.0 \text{ Hz, 1 H), 3.20 (s, 3 H), 2.98-3.11 (m, 4 H), 2.53 (d, } J = 17.4 \text{ Hz, 1 H), 2.34 (s, 3 H), 2.25 (s, 3 H), 2.16 (d, } J = 17.4 \text{ Hz, 1 H), 1.32 (s, 3 H); } ^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \quad \delta \quad 198.0, 164.5, 139.1, 114.9, 102.4, 73.0, 69.7, 49.3, 39.4, 35.6, 34.0, 31.0, 21.7, 16.8; \text{ IR (KBr) 3355, 3054, 2968, 2927, 2854, 2305, 1664, 1590, 1426, 1381 cm}^{-1}; \text{ HRMS m/z calcd for } C_{14}H_{22}NO_5S ([M+H]^+) \text{: 316.1213, found 316.1214.}
\end{align*}
\]

N-(4-acetyl-9-ethyl-9-methoxy-3-methyl-2-oxabicyclo[3.3.1]nona-3,7-dien-7-yl)-4-methylbenzenesulfonamide 4fa: yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.72 (d, \(J = 7.8\) Hz, 2 H), 7.48 (s, 1 H), 7.29 (d, \(J = 8.2\) Hz, 2 H), 5.53 (d, \(J = 6.4\) Hz, 1 H), 4.40 (d, \(J = 6.8\) Hz, 1 H), 4.36 (d, \(J = 6.8\) Hz, 1 H), 3.12 (s, 3 H), 2.90 (s, 1 H), 2.42 (s, 3 H), 2.19-2.32 (m, 4 H), 2.05-2.14 (m, 4 H), 1.00 (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 198.0, 164.5, 139.1, 114.9, 102.4, 73.0, 69.7, 49.3, 39.4, 35.6, 34.0, 31.0, 21.7, 16.8; IR (KBr) 3355, 3054, 2968, 2927, 2854, 2305, 1664, 1590, 1426, 1381 cm\(^{-1}\); HRMS m/z calcd for C\(_{14}\)H\(_{22}\)NO\(_5\)S ([M+H]\(^+\)): 316.1213, found 316.1214.
Hz, 1 H), 3.07 (s, 3 H), 2.90 (s, 1 H), 2.43 (s, 3 H), 2.25 (s, 3 H), 2.15-2.20 (m, 1 H), 2.11 (s, 3 H), 2.05-2.25 (m, 1 H), 1.25 (q, J = 7.3 Hz, 2 H), 0.75 (t, J = 7.3 Hz, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 197.6, 164.0, 143.9, 138.8, 136.1, 129.4, 127.6, 114.7, 105.0, 71.2, 71.1, 48.5, 35.2, 32.7, 30.9, 27.2, 24.7, 22.9, 21.6, 21.5, 14.0; IR (KBr) 3259, 3055, 2984, 2825, 2299, 1717, 1666, 1599, 1421 cm\(^{-1}\); HRMS m/z calcd for C\(_{21}\)H\(_{27}\)NNaO\(_5\)S ([M+Na]+): 428.1508, found 428.1501.

![Structural diagram](image)

**N-(4-acetyl-9-buty)-9-methoxy-3-methyl-2-oxabicyclo[3.3.1]nona-3,7-dien-7-yli)-4-methylbenzenesulfonylamine (4ha):** colorless solid; m.p. 156-157 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.72 (d, J = 7.3 Hz, 2 H), 7.42 (s, 1 H), 7.29 (d, J = 8.2 Hz, 2 H), 5.54 (d, J = 6.0 Hz, 1 H), 4.40 (d, J = 5.5 Hz, 1 H), 3.08 (s, 3 H), 2.91 (s, 1 H), 2.42 (s, 3 H), 2.26 (s, 3 H), 2.00-2.18 (m, 5 H), 1.15-1.25 (m, 6 H), 0.75 (t, J = 7.3 Hz, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 197.6, 164.3, 144.0, 138.9, 136.1, 129.6, 127.7, 114.9, 104.7, 71.2, 71.1, 48.8, 35.2, 32.7, 30.9, 27.2, 24.7, 22.9, 21.6, 21.5, 14.0; IR (KBr) 3399, 2916, 1656, 1571, 1472, 1438 cm\(^{-1}\); HRMS m/z calcd for C\(_{21}\)H\(_{27}\)NNaO\(_5\)S ([M+Na]+): 456.1821, found 456.1819.

**N-(4-acetyl-9-methoxy-3-methyl-2-oxabicyclo[3.3.1]nona-3,7-dien-7-yli)-4-methylbenzenesulfonylamine (4ha):** colorless solid; m.p. 188-190 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.62 (d, J = 7.8 Hz, 2 H), 7.23-7.27 (m, 4 H), 7.12-7.14 (m, 3 H), 5.72 (d, J = 6.4 Hz, 1 H), 5.04 (d, J = 6.0 Hz, 1 H), 3.18 (s, 1 H), 3.08 (s, 3 H), 2.84 (s, 3 H), 2.47 (s, 3 H), 2.27 (s, 3 H), 2.19 (s, 3 H), 1.91 (d, J = 17.0 Hz, 1 H), 1.68 (d, J = 17.0 Hz, 1 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 197.3, 164.2, 143.7, 139.1, 137.1, 136.2, 129.5, 127.9, 127.8, 127.5, 126.9, 115.0, 103.3, 73.8, 68.5, 49.9, 37.2, 34.7, 30.8, 21.6, 21.4; IR (KBr) 3259, 3055, 2984, 2825, 2299.
1717, 1666, 1599, 1422 cm\(^{-1}\); HRMS m/z calcd for C\(_{25}\)H\(_{28}\)NO\(_5\)S ([M+H]\(^+\)): 454.1683, found 454.1693.

\[\text{N-(4-acetyl-9,9-dimethoxy-3-methyl-2-oxabicyclo[3.3.1]nona-3,7-dien-7-yl)-4-methylbenzenesulfonamide 4ia: colorless solid; m.p. 143-144 °C; } ^1\text{H NMR (400 MHz, CDCl}_3\text{)} \]
\[\delta\] \, 7.71 (d, \(J = 7.8\) Hz, 2 H), 7.28 (d, \(J = 7.8\) Hz, 2 H), 7.17 (s, 1 H), 5.49 (d, \(J = 6.4\) Hz, 1 H), 4.47 (d, \(J = 6.8\) Hz, 1 H), 3.18 (s, 3 H), 3.09 (s, 3 H), 2.38-2.45 (m, 4 H), 2.18-2.26 (m, 4 H), 2.08 (s, 3 H), 1.93 (d, \(J = 12.0\) Hz, 1 H); \(^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \] \[\delta\] \, 196.8, 163.4, 143.7, 139.6, 136.1, 129.4, 127.4, 114.8, 103.9, 95.2, 68.9, 48.9, 48.1, 34.6, 32.4, 30.4, 21.4, 21.1; IR (KBr) 3360, 3256, 2925, 1664, 1597, 1435 cm\(^{-1}\); HRMS m/z calcd for C\(_{20}\)H\(_{26}\)NO\(_5\)S ([M+H]\(^+\)): 408.1481, found 408.1460.

\[\text{Methyl-9-ethoxy-3,9-dimethyl-7-(4-methylphenylsulfonamido)-2-oxabicyclo[3.3.1]nona-3,7-diene-4-carboxylate 4ja: colorless oil; } ^1\text{H NMR (400 MHz, CDCl}_3\text{)} \]
\[\delta\] \, 7.69 (d, \(J = 7.3\) Hz, 2 H), 7.28 (d, \(J = 7.3\) Hz, 2 H), 6.49 (s, 1 H), 5.43 (d, \(J = 6.4\) Hz, 1 H), 4.32 (d, \(J = 6.4\) Hz, 1 H), 3.65 (s, 3 H), 3.35 (q, \(J = 6.8\) Hz, 1 H), 3.29 (q, \(J = 6.8\) Hz, 1 H), 2.81 (s, 1 H), 2.43 (s, 3 H), 2.30 (d, \(J = 17.0\) Hz, 1 H), 2.20 (d, \(J = 17.0\) Hz, 1 H), 1.04-1.08 (m, 6 H); \(^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \] \[\delta\] \, 168.2, 163.7, 144.2, 138.4, 129.7, 127.5, 106.5, 102.7, 72.7, 69.4, 56.5, 51.0, 35.3, 34.6, 21.6, 19.8, 17.1, 16.0; IR (KBr) 3220, 3054, 2968, 2304, 1651, 1598 cm\(^{-1}\); HRMS m/z calcd for C\(_{21}\)H\(_{27}\)NNaO\(_6\)S ([M+Na]\(^+\)): 444.1457, found 444.1445.
N-(4-acetyl-9-methoxy-1,3,9-trimethyl-2-oxabicyclo[3.3.1]nona-3,7-dien-7-yl)

-4-methylbenzenesulfonamide 4ka: colorless solid; m.p. 148-149 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 7.69 (d, \(J = 7.8\) Hz, 2 H), 7.43 (s, 1 H), 7.26 (d, \(J = 8.2\) Hz, 2 H), 5.25 (s, 1 H), 3.05 (s, 1 H), 3.01 (s, 3 H), 2.39 (s, 3 H), 2.14-2.22 (m, 4 H), 1.99-2.07 (m, 4 H), 1.27 (s, 3 H), 0.91 (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta \) 197.3, 165.2, 143.9, 136.3, 136.0, 129.4, 127.6, 114.5, 111.6, 78.8, 71.0, 48.8, 34.8, 33.5, 30.8, 21.7, 21.5, 19.7, 16.2; IR (KBr) 3358, 2924, 1666, 1582 cm\(^{-1}\); HRMS m/z calcd for C\(_{21}\)H\(_{28}\)NO\(_5\)S ([M+H]\(^+\)): 406.1677, found 406.1662.

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N-(4-acetyl-9-methoxy-3,9-dimethyl-8-phenyl-2-oxabicyclo[3.3.1]nona-3,7-die\]
\[n-7-yl)-4-methylbenzenesulfonamide 4la: colorless solid; m.p. 170-171 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 7.50 (d, \(J = 6.9\) Hz, 2 H), 7.27-7.33 (m, 5 H), 6.81 (s, 2 H), 6.25 (s, 1 H), 4.34 (s, 1 H), 3.17 (s, 3 H), 3.03 (s, 1 H), 2.74 (s, 2 H), 2.46 (s, 3 H), 2.26 (s, 3 H), 2.16 (m, 3 H), 1.28 (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta \) 197.1, 162.2, 144.1, 136.5, 136.2, 134.1, 129.4, 128.3, 127.1, 114.0, 77.2, 69.2, 49.0, 34.8, 34.1, 29.9, 21.5, 20.8, 16.3; IR (KBr) 3328, 2947, 1702, 1613, 1492, 1434 cm\(^{-1}\); HRMS m/z calcd for C\(_{26}\)H\(_{30}\)NO\(_5\)S ([M+H]\(^+\)): 468.1834, found 468.1810.

Methyl-9-methoxy-3,9-dimethyl-7-(4-methylphenylsulfonamido)-2-oxabicyclo[3.3.1]nona-3,7-diene-4-carboxylate 4eb: colorless solid; m.p. 132-133 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 7.70 (d, \(J = 7.8\) Hz, 2 H), 7.28 (d, \(J = 7.3\) Hz, 2 H), 7.09 (s, 1 H), 5.44 (s, 1 H), 4.32 (s, 1 H), 3.65 (s, 3 H), 3.14 (s, 3 H), 2.82 (s, 1 H), 2.42 (s, 3 H), 2.20-2.31 (m, 2 H), 2.08 (s,
3 H), 1.01 (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.9, 163.4, 143.9, 138.5, 135.7, 129.5, 129.3, 127.3, 106.0, 102.6, 77.2, 72.2, 69.5, 50.9, 48.9, 35.0, 34.0, 21.4, 19.8, 16.2; IR (KBr) 3220, 3054, 2968, 2304, 1651, 1598 cm\(^{-1}\); HRMS m/z calcd for C\(_{20}\)H\(_{25}\)NNaO\(_6\)S ([M+Na]\(^+\)): 430.1300, found 430.1304.

**Methyl-9-methoxy-3-methyl-7-(4-methylphenylsulfonamido)-9-phenyl-2-oxabicyclo[3.3.1]nona-3,7-diene-4-carboxylate 4hb:** colorless solid; m.p. 188-189 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.59 (d, \(J = 7.8\) Hz, 2 H), 7.23-7.27 (m, 3 H), 7.16 (m, 4 H), 6.44 (s, 1 H), 5.65 (d, \(J = 6.4\) Hz, 1 H), 5.03 (d, \(J = 6.4\) Hz, 1 H), 3.66 (s, 3 H), 3.13 (s, 1 H), 2.86 (s, 3 H), 2.47 (s, 3 H), 2.43 (s, 1 H), 2.06 (d, \(J = 17.0\) Hz, 1 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.9, 163.8, 143.9, 138.9, 137.1, 135.8, 129.7, 128.0, 127.9, 127.3, 126.8, 126.3, 104.6, 102.9, 73.8, 68.1, 51.0, 50.1, 37.4, 34.8, 21.6, 19.9; IR (KBr) 3247, 2937, 2891, 1681, 1450, 1332 cm\(^{-1}\); HRMS m/z calcd for C\(_{25}\)H\(_{27}\)NNaO\(_6\)S ([M+Na]\(^+\)): 492.1457, found 492.1461.

**Methyl-9-ethoxy-3,9-dimethyl-7-(4-methylphenylsulfonamido)-2-oxabicyclo[3.3.1]nona-3,7-diene-4-carboxylate 4jb:** colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.69 (d, \(J = 7.3\) Hz, 2 H), 7.28 (d, \(J = 7.3\) Hz, 2 H), 6.49 (s, 1 H), 5.43 (d, \(J = 6.4\) Hz, 1 H), 4.32 (d, \(J = 6.4\) Hz, 1 H), 3.65 (s, 3 H), 3.35 (q, \(J = 6.8\) Hz, 1 H), 3.29 (q, \(J = 6.8\) Hz, 1 H), 2.81 (s, 1 H), 2.43 (s, 3 H), 2.30 (d, \(J = 17.0\) Hz, 1 H), 2.20 (d, \(J = 17.0\) Hz, 1 H), 1.04-1.08 (m, 6 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.2, 163.7, 144.2, 138.4, 129.7, 127.5, 106.5, 102.7, 72.7, 69.4, 56.5, 51.0, 35.3, 34.6, 21.6, 19.8, 17.1, 16.0; IR (KBr) 3352, 3054, 2986, 2319, 1612, 1422 cm\(^{-1}\); HRMS m/z calcd for C\(_{21}\)H\(_{27}\)NNaO\(_6\)S ([M+Na]\(^+\)): 444.1457, found 444.1445.
Methyl-9-methoxy-1,3,9-trimethyl-7-(4-methylphenylsulfonamido)-2-oxabicyclo[3.3.1]nona-3,7-diene-4-carboxylate 4kb: colorless solid; m.p. 161-163 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.69 (d, $J = 7.3$ Hz, 2 H), 7.28 (d, $J = 7.3$ Hz, 2 H), 6.60 (s, 1 H), 5.18 (s, 1 H), 3.66 (s, 3 H), 3.06 (s, 3 H), 2.98 (s, 1 H), 2.43 (s, 3 H), 2.19 (s, 2 H), 2.07 (s, 3 H), 1.28 (s, 3 H), 0.97 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.1, 164.7, 144.1, 136.2, 135.7, 129.6, 129.6, 127.4, 113.0, 102.1, 78.2, 70.9, 50.9, 48.8, 34.8, 32.7, 21.5, 20.1, 19.7, 16.3; IR (KBr) 3249, 2924, 2845, 1651, 1607, 1434 cm$^{-1}$; HRMS m/z calcd for C$_{21}$H$_{28}$NO$_6$S ([M+H]$^+$): 422.1632, found 422.1629.

Methyl-9-methoxy-3,9-dimethyl-7-(4-methylphenylsulfonamido)-8-phenyl-2-oxabicyclo[3.3.1]nona-3,7-diene-4-carboxylate 4lb: colorless solid; m.p. 161-162 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49 (d, $J = 7.3$ Hz, 2 H), 7.28-7.34 (m, 5 H), 6.79 (d, $J = 3.7$ Hz, 2 H), 6.25 (s, 1 H), 4.32 (s, 1 H), 3.72 (s, 3 H), 2.98 (s, 1 H), 2.90 (d, $J = 18.8$ Hz, 1 H), 2.66 (dd, $J = 18.8$ Hz, $J = 4.1$ Hz, 1 H), 2.47 (s, 3 H), 2.18 (s, 3 H), 1.25 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.7, 162.8, 144.1, 136.6, 136.0, 134.4, 129.7, 129.5, 128.4, 127.1, 120.3, 103.4, 69.3, 51.0, 49.1, 34.3, 33.9, 21.6, 19.6, 16.3; IR (KBr) 3220, 3054, 2968, 2304, 1651, 1598 cm$^{-1}$; HRMS m/z calcd for C$_{26}$H$_{30}$NO$_6$S ([M+H]$^+$): 484.1788, found 484.1791.

Ethyl 9-methoxy-3,9-dimethyl-7-(4-methylphenylsulfonamido)-2-oxabicyclo[3.3.1]nona-3,7-diene-4-carboxylate 4ec: colorless solid; m.p. 135-136 °C; $^1$H NMR
(400 MHz, CDCl₃)  δ  7.70 (d, J = 7.3 Hz, 2 H), 7.29 (d, J = 7.3 Hz, 2 H), 6.82 (s, 1 H), 5.44 (d, J = 6.0 Hz, 1 H), 4.33 (d, J = 6.0 Hz, 1 H), 4.12 (q, J = 6.8 Hz, 2 H), 3.15 (s, 3 H), 2.83 (s, 1 H), 2.42 (s, 3 H), 2.21-2.33 (m, 2 H), 2.09 (s, 3 H), 1.25 (t, J = 6.8 Hz, 3 H), 1.03 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 167.6, 163.1, 144.0, 138.4, 135.8, 129.6, 127.3, 106.1, 102.8, 77.2, 72.2, 69.6, 59.6, 49.0, 35.1, 34.1, 21.5, 19.8, 16.2, 14.3; IR (KBr) 3220, 3054, 2968, 2304, 1651, 1598 cm⁻¹; HRMS m/z calcd for C₂₁H₂₈NO₆S ([M+H]⁺): 422.1637, found 422.1630.

N-(9-methoxy-3,9-dimethyl-4-(methylsulfonyl)-2-oxabicyclo[3.3.1]nona-3,7-dien-7-yl)-4-methylbenzenesulfonamide 4ed: colorless solid; m.p. 181-182 °C; ¹H NMR (400 MHz, CDCl₃)  δ  7.77 (d, J = 7.8 Hz, 2 H), 7.40 (s, 1 H), 7.30 (d, J = 7.8 Hz, 2 H), 5.51 (d, J = 6.0 Hz, 1 H), 4.38 (d, J = 6.0 Hz, 1 H), 3.17 (s, 3 H), 2.91 (s, 3 H), 2.69 (s, 1 H), 2.57 (d, J = 17.8 Hz, 1 H), 2.42 (s, 3 H), 2.33 (d, J = 17.8 Hz, 1 H), 2.08 (s, 3 H), 1.01 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 161.7, 143.9, 138.4, 135.9, 129.6, 127.5, 110.9, 103.8, 72.6, 69.4, 49.1, 43.5, 36.1, 35.8, 21.5, 18.3, 15.9; IR (KBr) 3388, 2932, 1651, 1452 cm⁻¹; HRMS m/z calcd for C₁₉H₂₅NNaO₆S₂ ([M+Na]⁺): 450.1021, found 450.1015.

Methyl-9-methoxy-3,9-dimethyl-7-(4-methylphenylsulfonamido)-2-azabicyclo[3.3.1]nona-3,7-diene-4-carboxylate 4ee: colorless oil; ¹H NMR (400 MHz, CDCl₃)  δ  7.79 (d, J = 7.8 Hz, 2 H), 7.31 (d, J = 7.8 Hz, 2 H), 5.83 (s, 1 H), 5.67 (d, J = 10.0 Hz, 1 H), 5.55 (d, J = 10.0 Hz, 1 H), 4.77 (s, 1 H), 3.17 (s, 3 H), 3.13 (s, 1 H), 2.44 (s, 3 H), 2.04 (s, 3 H), 1.93 (d, J = 11.4 Hz, 1 H), 1.76 (d, J = 9.6 Hz, 1 H), 1.19 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 169.9,
146.9, 143.9, 139.1, 133.4, 129.7, 127.0, 125.9, 97.6, 79.6, 66.3, 51.1, 50.7, 39.2, 32.9, 22.4, 21.5, 20.4; IR (KBr) 3404, 2924, 2839, 1648, 1457 cm⁻¹; HRMS m/z calcd for C₂₀H₂₇N₂O₅S ([M+H]+): 407.1641, found 407.1632.

**Methyl-9-methoxy-3-methyl-7-(4-methylphenylsulfonamido)-9-phenyl-2-aza bicyclo[3.3.1]nona-3,7-diene-4-carboxylate 4he:** colorless oil; ¹H NMR (400 MHz, CDCl₃)  δ 7.79 (d, J = 7.3 Hz, 2 H), 7.21-7.22 (m, 7 H), 6.02 (d, J = 10.0 Hz, 1 H), 5.97 (d, J = 10.0 Hz, 1 H), 5.60 (s, 1 H), 4.77 (s, 1 H), 3.75 (s, 3 H), 3.35 (s, 1 H), 2.89 (s, 3 H), 2.45 (s, 3 H), 2.10 (s, 3 H), 1.64 (d, J = 11.9 Hz, 1 H), 1.46 (d, J = 8.2 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃)  δ 170.3, 147.2, 143.9, 141.8, 139.3, 129.9, 128.4, 128.1, 127.8, 127.6, 127.1, 98.1, 84.3, 66.4, 50.9, 42.1, 31.6, 29.8, 21.7, 20.2; IR (KBr) 3376, 2926, 2849, 1659, 1596, 1478 cm⁻¹; HRMS m/z calcd for C₂₅H₂₉N₂O₅S ([M+H]⁺): 469.1797, found 469.1780.

**N-(3-(2-hydroxy-4-oxopent-2-en-3-yl)-2,4,6-trimethylphenyl)-4-methylbenz enesulfonamide 6na:** colorless solid; m.p. 185-187 °C; ¹H NMR (400 MHz, CDCl₃)  δ 7.58 (d, J = 7.8 Hz, 2 H), 7.22 (d, J = 7.8 Hz, 2 H), 6.99 (s, 1 H), 6.46 (s, 1 H), 2.42 (s, 3 H), 2.15 (s, 3 H), 2.08 (s, 3 H), 1.74 (s, 3 H), 1.69 (s, 6 H); ¹³C NMR (100 MHz, CDCl₃)  δ 190.5, 143.7, 137.7, 137.5, 137.4, 134.1, 130.8, 130.5, 129.6, 127.2, 111.7, 23.0, 21.5, 20.2, 18.8, 16.2; IR (KBr) 3253, 2978, 2840, 1598, 1421 cm⁻¹; HRMS m/z calcd for C₂₁H₂₆NO₄S ([M+H]+): 388.1577, found 388.1574.


**N-(3-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl)-4-methylphenyl)-4-methylenesulfonamide 6eh:** colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.63 (d, $J = 7.8$ Hz, 2 H), 7.33 (s, 1 H), 7.08 (d, $J = 7.8$ Hz, 1 H), 6.90 (d, $J = 7.8$ Hz, 1 H), 6.66 (s, 1 H), 6.00 (s, 1 H), 2.37 (s, 1 H), 2.35 (s, 4 H), 2.03 (s, 3 H), 1.15 (s, 3 H), 1.15 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.8, 136.3, 135.9, 135.0, 131.7, 131.7, 129.6, 127.4, 124.7, 122.3, 115.9, 32.0, 29.0, 27.9, 21.6, 19.3; IR (KBr) 3054, 2968, 1651, 1438 cm$^{-1}$; HRMS m/z calcd for C$_{22}$H$_{26}$NO$_4$S ([M+H]$^+$): 400.1583, found 400.1586.

\[ \text{NHTs} \quad \text{Me} \quad \text{O} \quad \text{OH} \quad \text{O} \]

**N-(3-(4-hydroxy-2-oxo-2H-chromen-3-yl)-4-methylphenyl)-4-methylbenzenesulfonamide 6ei:** colorless solid; m.p. 120-122 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87 (d, $J = 7.8$ Hz, 2 H), 7.56-7.65 (m, 4 H), 7.32 (d, $J = 7.8$ Hz, 2 H), 7.17 (d, $J = 7.8$ Hz, 2 H), 7.09 (d, $J = 8.2$ Hz, 1 H), 7.00 (d, $J = 7.8$ Hz, 1 H), 6.91 (s, 1 H), 2.31 (s, 3 H), 2.11 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.1, 160.4, 152.9, 143.8, 135.9, 135.1, 132.5, 131.8, 129.6, 129.3, 127.2, 124.2, 124.1, 123.7, 122.7, 116.5, 115.0, 104.9, 60.5, 21.4, 20.9, 18.9, 14.1; IR (KBr) 3250, 2911, 2845, 1680, 1610, 1568, 1496 cm$^{-1}$; HRMS m/z calcd for C$_{23}$H$_{20}$NO$_5$S ([M+H]$^+$): 422.1062, found 422.1065.

\[ \text{NHTs} \quad \text{Me} \quad \text{O} \quad \text{Me} \quad \text{COOEt} \]

**Methyl 2-(2-methyl-5-(4-methylphenylsulfonamido)phenyl)acetate 6ef:** colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.64 (d, $J = 7.3$ Hz, 2 H), 7.20 (d, $J = 7.3$ Hz, 2 H),
7.01 (d, J = 7.8 Hz, 1 H), 6.95 (d, J = 8.7 Hz, 2 H), 6.87 (d, J = 7.8 Hz, 1 H), 6.12 (q, J = 6.9 Hz, 2 H), 3.52 (s, 2 H), 2.36 (s, 3 H), 2.21 (s, 3 H), 1.22 (t, J = 6.9 Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 171.1, 143.6, 136.1, 134.4, 134.1, 133.8, 131.0, 129.5, 127.2, 123.8, 120.8, 60.9, 39.1, 21.4, 18.9, 18.9, 14.1; IR (KBr) 3259, 2982, 2876, 1731, 1615, 1504, 1467 cm$^{-1}$; HRMS m/z calcd for C$_{18}$H$_{22}$NO$_4$S ([M+H]$^+$): 348.1264, found 348.1271.

![N-(3-(2-hydroxy-4-oxopent-2-en-3-yl)-4-methylphenyl)-4-methylbenzenesulfonamide 6ea: colorless solid; m.p. 176-178 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.64 (d, J = 7.3 Hz, 2 H), 7.14-7.27 (m, 3 H), 7.07 (d, J = 7.8 Hz, 1 H), 6.75 (s, 1 H), 2.36 (s, 3 H), 2.08 (s, 3 H), 6.5 (s, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 190.6, 144.0, 137.0, 135.7, 135.4, 134.8, 131.4, 129.7, 127.5, 125.1, 122.5, 112.9, 23.6, 21.6, 19.3; IR (KBr) 3236, 2922, 2850, 1597, 1495, 1375, 1320 cm$^{-1}$; HRMS m/z calcd for C$_{19}$H$_{22}$NO$_4$S ([M+H]$^+$): 360.1270, found 360.1257.](attachment:6ea.png)

![5ma: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.32-7.35 (m, 5 H), 7.17 (d, J = 8.5 Hz, 2 H), 7.13 (d, J = 8.5 Hz, 2 H), 6.14 (s, 1 H), 4.78 (s, 1 H), 3.26 (s, 3 H), 3.19 (s, 2 H), 3.09 (d, J = 4.8 Hz, 1 H), 2.37 (s, 3 H), 2.30 (s, 3 H), 2.10 (s, 3 H), 1.5 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 197.6, 162.6, 144.7, 138.6, 133.7, 132.2, 130.5, 129.5, 128.2, 127.4, 126.4, 122.1, 115.4, 113.9, 71.7, 70.7, 49.3, 35.7, 31.9, 30.1, 21.6, 21.1, 16.3; IR (KBr) cm$^{-1}$; HRMS m/z calcd for C$_{19}$H$_{22}$NO$_4$S ([M+H]$^+$): 492.1839, found 492.1842.](attachment:5ma.png)
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[Chemical structure image]

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