Synthesis of Substituted Chromenes through DABCO-Catalyzed Reaction of But-3-yn-2-one and Methyl Propiolate with Salicyl N-Tosylimines

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Additional results on the PPh₂Me catalyzed reaction of salicyl N-tosylimine 1 (1.0 equiv) with ethyl 2,3-butadienoate 2c (1.2 equiv).

Table S1. Reaction of salicyl N-tosylimine 1a (1.0 equiv) with ethyl 2,3-butadienoate 2c (1.2 equiv) in the presence of 25 mol% PPh₂Me.

<table>
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<th>yield of s1 (%)^a</th>
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<tr>
<td>1</td>
<td>THF</td>
<td>1</td>
<td>82</td>
</tr>
<tr>
<td>2^b</td>
<td>THF</td>
<td>1</td>
<td>87</td>
</tr>
<tr>
<td>3^b</td>
<td>CH₂Cl₂</td>
<td>1</td>
<td>59</td>
</tr>
<tr>
<td>4^b</td>
<td>CH₃CN</td>
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<td>27</td>
</tr>
<tr>
<td>5^b</td>
<td>PhMe</td>
<td>3</td>
<td>66</td>
</tr>
<tr>
<td>6^b</td>
<td>DMF</td>
<td>1</td>
<td>13</td>
</tr>
</tbody>
</table>

^a) Isolated yields. b) Molecular sieves 4A was added.

Table S2. Reaction of other salicyl N-tosylimine 1 (1.0 equiv) with ethyl 2,3-butadienoate 2c (1.2 equiv) in the presence of 25 mol% PPh₂Me.

<table>
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<th>R²</th>
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<td>H</td>
<td>1</td>
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<td>H</td>
<td>Br</td>
<td>10</td>
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<tr>
<td>4</td>
<td>Cl</td>
<td>Cl</td>
<td>24</td>
<td>s5: 33</td>
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</table>

^a) Isolated yields.
Figures of $^1$H NMR spectroscopic trace of the reaction solution of 1a and methyl propiolate 2b in the presence of DABCO.

Figure S1. $^1$H NMR spectroscopy of 1a in CDCl$_3$.

Figure S2. D$_2$O was added to the solution of 1a in CDCl$_3$. 
Figure S3. $^1$H NMR spectroscopy of DABCO in CDCl$_3$.

Figure S4. $^1$H NMR spectroscopy of a mixture of 1a and 2b in CDCl$_3$. 

DABCO
Figure S5. 15 minutes after DABCO was added to the solution of 1a and 2b in CDCl₃.

Figure S6. Partial enlargement of Figure S5.
Figure S7. The assignment of Figure S6 ($^3J$ value of the olefinic protons is 12.0 Hz).

Figure S8. The assignment of Figure S6 ($^3J$ value of the olefinic protons is 14.7 Hz).
Experimental Details.

General. Unless otherwise stated, all reactions were carried out under argon atmosphere. All solvents were purified by distillation. Other commercially available reagents were used without further purification. Salicyl N-tosylimines,\(^1\) but-3-yn-2-one,\(^2\) and ethyl 2,3-butadienoate\(^3\) were prepared according to the literature. All reactions were monitored by TLC. Flash column chromatography was carried out at increased pressure. Infrared spectra were measured on a PERKIN-ELMER 983 spectrometer. \(^1\)H NMR and \(^{13}\)C NMR spectra were recorded on a Varian Mercury vx 300 NMR spectrometer in CDCl\(_3\) or CD\(_3\)SOCD\(_3\) using tetramethylsilane as the internal standard. Mass spectra were recorded with an HP-5989 instrument and HRMS was measured by an Ion Spec 4.7 Tesla FTMS mass spectrometer. Satisfactory CHN microanalyses were obtained with a Carlo-Erba 1106 analyzer. Melting points were obtained by means of a micro melting point apparatus and are uncorrected.

Typical Reaction Procedure for DABCO Catalyzed Reaction of But-3-yn-2-one with Salicyl N-tosylimine 1a.

To a flame-dried Schlenk tube at room temperature was in turn added molecular sieves 4A (100 mg), DABCO (5.6 mg, 0.05 mmol), salicyl N-tosylimine 1a (138 mg, 0.50 mmol), CH\(_2\)Cl\(_2\) (2.0 mL) and but-3-yn-2-one 2a (47 µL, 0.60 mmol) and the reaction mixture was further stirred at room temperature for 24 hours. Then the solvent was removed under reduced pressure and the residue was purified by flash chromatography (Eluent: EtOAc:Petroleum ether = 1:4-2:1) to yield 3a (122 mg, 71 %) as a colorless solid.

\(N\)-(3-acetyl-4H-chromen-4-yl)-4-methylbenzenesulfonamide (3a): a colorless solid: mp. 184-186 °C; \(^1\)H NMR (CDCl\(_3\), TMS, 300 MHz) \(\delta = 2.12\) (s, 3H; Me), 2.39 (s, 3H; Me), 5.38 (d, \(^3J\) (H,H) = 5.4 Hz, 1H; NH), 5.51 (d, \(^3J\) (H,H) = 5.4 Hz, 1H; CH), 6.98-7.03 (m, 1H; Ar), 7.08-7.11 (m, 1H; Ar), 7.16 (d, \(^3J\) (H,H) = 8.4 Hz, 2H; Ar), 7.24-7.34 (m, 2H; Ar), 7.45 (d, \(^3J\) (H,H) = 8.4 Hz, 2H; Ar).
N-(3-acetyl-8-methoxy-4H-chromen-4-yl)-4-methylbenzenesulfonamide (3b): a white solid: mp. 179-181 °C; \(^1\)H NMR (CDCl\(_3\), TMS, 300 MHz) \(\delta = 2.06\) (s, 3H; Me), 2.40 (s, 3H; Me), 3.93 (s, 3H; Me), 5.35 (d, \(^3\)J (H,H) = 6.0 Hz, 1H; NH), 5.52 (d, \(^3\)J (H,H) = 6.0 Hz, 1H; CH), 6.83-6.88 (m, 1H; Ar), 6.98-7.04 (m, 2H; Ar), 7.18 (d, \(^3\)J (H,H) = 8.1 Hz, 2H; Ar), 7.52 (d, \(^3\)J (H,H) = 8.1 Hz, 2H; Ar), 7.69 (s, 1H; CH); \(^1\)C NMR (CD\(_3\)SOCD\(_3\), TMS, 75.44 MHz) \(\delta = 21.0, 25.1, 43.1, 55.9, 111.1, 115.5, 120.9, 122.5, 124.6, 126.3, 128.9, 139.7, 139.9, 141.7, 147.3, 154.3, 194.5; IR (KBr) \(\nu = 3278, 1641, 1585, 1266, 1226, 1201, 1150\) cm\(^{-1}\); MS (70eV): \(m/z\) (%): 373 (0.93) [\(M^+\)], 203 (100) [\(M^+\)-170]; HRMS Calcd. for C\(_{19}\)H\(_{19}\)NO\(_5\)SNa\(^+\) requires 396.0876, Found 396.0881.
**N-(3-acetyl-7-methoxy-4H-chromen-4-yl)-4-methylbenzenesulfonamide (3c):** a white solid: mp. 130-132 °C; $^1$H NMR (CDCl$_3$, TMS, 300 MHz) $\delta$ = 2.13 (s, 3H; Me), 2.39 (s, 3H; Me), 3.80 (s, 3H; Me), 5.30 (d, $^3$J (H,H) = 5.1 Hz, 1H; NH), 5.44 (d, $^3$J (H,H) = 5.1 Hz, 1H; CH), 6.54 (dd, $^3$J (H,H) = 8.4 Hz, $^4$J (H,H) = 2.7 Hz, 1H; Ar), 6.60 (d, $^4$J (H,H) = 2.7 Hz, 1H; Ar), 7.14-7.19 (m, 3H; Ar), 7.45 (d, $^3$J (H,H) = 8.1 Hz, 2H; Ar), 7.65 (s, 1H; CH); $^{13}$C NMR (CD$_3$SOCD$_3$, TMS, 75.44 MHz) $\delta$ = 20.9, 25.2, 42.8, 55.5, 100.8, 111.8, 113.7, 116.1, 126.2, 128.9, 130.7, 140.0, 141.7, 150.8, 154.5, 159.5, 194.5; IR (KBr) ν 3418, 1642, 1334, 1216, 1156, 1095 cm$^{-1}$; MS (70eV): m/z (%): 373 (3.68) [M$^+$], 203 (100) [M$^+$-170]; HRMS Calcd. for C$_{19}$H$_{19}$NO$_5$SNa$^+$ requires 396.0876, Found 396.0880.
N-(3-acetyl-6-methoxy-4H-chromen-4-yl)-4-methylbenzenesulfonamide (3d): a white solid: mp. 182-183 °C; $^1$H NMR (CD$_3$H, TMS, 300 MHz) $\delta$ = 2.16 (s, 3H; Me), 2.38 (s, 3H; Me), 3.60 (s, 3H; Me), 5.42 (d, $^3$J (H,H) = 5.4 Hz, 1H; NH), 5.46 (d, $^3$J (H,H) = 5.4 Hz, 1H; CH), 6.66 (d, $^4$J (H,H) = 3.0 Hz, 1H; Ar), 6.80 (dd, $^3$J (H,H) = 9.0 Hz, $^4$J (H,H) = 3.0 Hz, 1H; Ar), 7.03 (d, $^3$J (H,H) = 9.0 Hz, 1H; Ar), 7.15 (d, $^3$J (H,H) = 8.4 Hz, 2H; Ar), 7.41 (d, $^3$J (H,H) = 8.4 Hz, 2H; Ar), 7.70 (s, 1H; CH); $^{13}$C NMR (CD$_3$SOCD$_3$, TMS, 75.44 MHz) $\delta$ = 20.9, 25.2, 43.6, 55.2, 113.3, 115.0, 115.3, 117.3, 121.8, 126.1, 128.9, 140.0, 141.7, 144.2, 154.7, 155.8, 194.5; IR (KBr) ν 3279, 1640, 1496, 1325, 1219, 1155 cm$^{-1}$; MS (70eV): m/z (%): 373 ($M^+$, 4.24), 203 ($M^+$-170, 100); Anal. Calcd. for C$_{19}$H$_{19}$NO$_5$S requires C, 61.11; H, 5.13; N, 3.75%. Found: C, 61.35; H, 5.26; N, 3.46%.
N-(3-acetyl-6-methyl-4H-chromen-4-yl)-4-methylbenzenesulfonamide (3e): a white solid: 
mp. 154-156 °C; $^1$H NMR (CDCl$_3$, TMS, 300 MHz) $\delta = 2.10$ (s, 3H; Me), 2.16 (s, 3H; Me), 2.38 (s, 3H; Me), 5.41 (d, $^3$J (H,H) = 5.4 Hz, 1H; NH), 5.44 (d, $^3$J (H,H) = 5.4 Hz, 1H; CH), 6.94-7.04 (m, 3H; Ar), 7.13 (d, $^3$J (H,H) = 8.4 Hz, 2H; Ar), 7.40 (d, $^3$J (H,H) = 8.4 Hz, 2H; Ar), 7.70 (s, 1H; CH); $^{13}$C NMR (CD$_3$SOCD$_3$, TMS, 75.44 MHz) $\delta = 20.2, 20.9, 25.3, 43.3, 115.8, 116.1, 120.5, 126.1, 128.9, 129.4, 130.0, 133.7, 140.1, 141.6, 148.1, 154.5, 194.6; IR (KBr) $\nu$ 3274, 1640, 1496, 1326, 1250, 1216, 1156 cm$^{-1}$; MS (70eV): $m/z$ (%): 202 (57.3) [M$^+$-155], 187 (100) [M$^+$-170]; HRMS Calcd. for C$_{19}$H$_{19}$NO$_4$SNa$^+$ requires 380.0927, Found 380.0929.
N-(3-acetyl-6-bromo-4H-chromen-4-yl)-4-methylbenzenesulfonamide (3f): a white solid; mp. 186-187 °C; $^1$H NMR (CDCl$_3$, TMS, 300 MHz) $\delta = 2.20$ (s, 3H; Me), 2.40 (s, 3H; Me), 5.39 (d, $^3$J (H,H) = 5.4 Hz, 1H; CH), 5.53 (d, $^3$J (H,H) = 5.4 Hz, 1H; NH), 6.97 (d, $^3$J (H,H) = 9.0 Hz, 1H; Ar), 7.15 (d, $^3$J (H,H) = 8.4 Hz, 2H; Ar), 7.18 (d, $^4$J (H,H) = 2.4 Hz, 1H; Ar), 7.30 (dd, $^3$J (H,H) = 9.0 Hz, $^4$J (H,H) = 2.4 Hz, 1H; Ar), 7.37 (d, $^3$J (H,H) = 8.4 Hz, 2H; Ar), 7.72 (s, 1H; CH); $^{13}$C NMR (CD$_3$SOCD$_3$, TMS, 75.44 MHz) $\delta = 21.0, 25.3, 42.9, 115.7, 116.2, 118.6, 123.2, 126.0, 129.1, 131.6, 132.4, 139.6, 142.0, 149.3, 154.2, 194.4; IR (KBr) ν 3431, 1644, 1575, 1476, 1323, 1236, 1152 cm$^{-1}$; MS (70eV): $m/z$ (%): 266 (64.6) [M$^+$-155], 251 (100) [M$^+$-170]; HRMS Calcd. for C$_{18}$H$_{16}$NO$_4$SBrNa$^+$ requires 443.9876, Found 443.9881.
N-(3-acetyl-6,8-dichloro-4H-chromen-4-yl)-4-methylbenzenesulfonamide (3g): a white solid: mp. 168-170 °C; ¹H NMR (CDCl₃, TMS, 300 MHz) δ = 2.18 (s, 3H; Me), 3.40 (s, 3H; Me), 5.41 (d, ³J (H,H) = 6.6 Hz, 1H; CH), 5.53 (d, ³J (H,H) = 6.6 Hz, 1H; NH), 7.06 (d, ⁴J (H,H) = 2.4 Hz, 1H; Ar), 7.18 (d, ³J (H,H) = 7.8 Hz, 2H; Ar), 7.27 (d, ⁴J (H,H) = 2.4 Hz, 1H; Ar), 7.43 (d, ³J (H,H) = 7.8 Hz, 2H; Ar), 7.76 (s, 1H; CH); ¹³C NMR (CDCl₃, TMS, 75.44 MHz) δ = 21.5, 24.9, 44.8, 106.3, 121.8, 122.7, 126.8, 128.6, 129.2, 129.6, 129.8, 138.4, 143.3, 145.3, 152.9, 195.2; IR (KBr) v 3300, 1649, 1458, 1324, 1246, 1194, 1159 cm⁻¹; MS (70eV): m/z(%): 256 (43.7) [M⁺-155], 241 (100) [M⁺-170]; HRMS Calcd. for C₁₈H₁₅NO₄SClNa⁺ requires 433.9991, Found 434.0005.
N-(3-acetyl-6-nitro-4H-chromen-4-yl)-4-methylbenzenesulfonamide (3h): a white solid: 
mp. 202-203 °C; ¹H NMR (CDCl₃, TMS, 300 MHz) δ = 2.25 (s, 3H; Me), 2.33 (s, 3H; Me), 5.47 (d, ³J (H,H) = 4.8 Hz, 1H; CH), 5.73 (d, ³J (H,H) = 4.8 Hz, 1H; NH), 7.09 (d, ³J (H,H) = 7.8 Hz, 2H; Ar), 7.22 (d, ³J (H,H) = 8.7 Hz, 1H; Ar), 7.33 (d, ³J (H,H) = 7.8 Hz, 2H; Ar), 7.75 (s, 1H; CH), 7.94 (s, 1H; Ar), 8.05-8.09 (m, 1H; Ar); ¹³C NMR (CD₃SOCD₃, TMS, 75.44 MHz) δ = 20.8, 25.5, 42.9, 116.1, 117.8, 121.5, 124.4, 125.9, 126.3, 129.1, 139.8, 142.0, 143.4, 153.8, 154.4, 194.4; IR (KBr) ν 3307, 1645, 1520, 1331, 1228; MS (70eV): m/z(%) 233 (55.4) [M⁺-155], 218 (100) [M⁺-170]; HRMS Calcd. for C₁₈H₁₆N₂O₆SNa⁺ requires 411.0621, Found 411.0628.
**N-(2-acetyl-1H-benzo[f]chromen-1-yl)-4-methylbenzenesulfonamide (3i):** a colorless solid: mp. 189-190 °C; \(^1^H\) NMR (CDCl\(_3\), TMS, 300 MHz) \(\delta = 2.14\) (s, 3H; Me), 2.31 (s, 3H; Me), 5.71 (d, \(^3^J\) (H,H) = 4.2 Hz, 1H; NH), 6.03 (d, \(^3^J\) (H,H) = 4.2 Hz, 1H; CH), 6.64 (d, \(^3^J\) (H,H) = 8.4 Hz, 2H; Ar), 6.98 (d, \(^3^J\) (H,H) = 8.4 Hz, 2H; Ar), 7.25 (d, \(^3^J\) (H,H) = 9.0 Hz, 1H; Ar), 7.29-7.40 (m, 2H; Ar), 7.59-7.62 (m, 1H; Ar), 7.68 (d, \(^3^J\) (H,H) = 9.0 Hz, 1H; Ar), 7.87 (s, 1H; CH), 7.91 (d, \(^3^J\) (H,H) = 8.4 Hz, 1H; Ar); \(^1^3^C\) NMR (CD\(_3\)SOCD\(_3\), TMS, 75.44 MHz) \(\delta = 20.8, 24.9, 40.3, 112.8, 116.1, 116.7, 122.8, 124.9, 125.5, 127.1, 128.3, 128.4, 130.0, 130.7, 130.8, 139.4, 141.1, 148.9, 154.3, 194.7; IR (KBr) v 3228, 1650, 1595. 1342, 1320, 1226, 1156 cm\(^{-1}\); MS (70eV): \(m/z\) (%): 393 (3.38) [\(M^+\)], 223 (100) [\(M^+\)-170]; HRMS Calcd. for C\(_{22}\)H\(_{19}\)NO\(_4\)SNa\(^+\) requires 416.0927, Found 416.0932.
Typical Reaction Procedure for DABCO Catalyzed Reaction of Methyl propiolate with Salicyl N-tosylimine 1a.

To a flame-dried Schlenk tube at room temperature was in turn added molecular sieves 4A (100 mg), DABCO (14 mg, 0.125 mmol), salicyl N-tosylimine 1a (138 mg, 0.50 mmol), DMF (2.0 mL) and methyl propiolate 2b (45 µL, 0.50 mmol) and the reaction mixture was further stirred at 80 °C for 12 hours. Then the reaction mixture was cooled to room temperature, CH₂Cl₂ (40 mL) was added and the solution was washed with water (20 mL x 3), dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (Eluent: EtOAc:Petroleum ether = 1:4-2:1) to yield 4a (142 mg, 79 %) as a colorless solid.

**methyl 4-(4-methylphenylsulfonamido)-4H-chromene-3-carboxylate (4a):** a colorless solid: mp. 189-190 °C; ¹H NMR (CDCl₃, TMS, 300 MHz) δ = 2.40 (s, 3H; Me), 3.52 (s, 3H; Me), 5.10 (d, ³J (H,H) = 6.9 Hz, 1H; NH), 5.54 (d, ³J (H,H) = 6.9 Hz, 1H; CH), 7.05-7.11 (m, 2H; Ar), 7.21 (d, ³J (H,H) = 8.1 Hz, 2H; Ar), 7.25-7.31 (m, 1H; Ar), 7.44-7.48 (m, 1H; Ar), 7.58 (d, ³J (H,H) = 8.1 Hz, 2H; Ar), 7.75 (s, 1H; CH); ¹³C NMR (CD₂SOCD₃, TMS, 75.44 MHz) δ = 20.9, 44.4, 51.1, 106.7, 116.4, 121.5, 125.1, 126.0, 129.0, 129.1, 130.0, 140.1,
141.8, 149.8, 152.3, 165.2. IR (KBr) v 3283, 1687, 1343, 1334, 1239, 1151 cm⁻¹; MS (70eV): m/z(%) 204 (24.3) [M⁺-155], 40 (100) [M⁺-319]; Anal. Calcd. for C₁₈H₁₇NO₅S requires C, 60.15; H, 4.77; N, 3.90%. Found: C, 60.18; H, 4.74; N, 3.78%.

**methyl 8-methoxy-4-(4-methylphenylsulfonamido)-4H-chromene-3-carboxylate (4b):** a colorless solid: mp. 189-191 °C; ¹H NMR (CDCl₃, TMS, 300 MHz) δ = 2.41 (s, 3H; Me), 3.49 (s, 3H; Me), 3.92 (s, 3H; Me), 5.08 (d, 3 J (H,H) = 7.2 Hz, 1H; NH), 5.55 (d, 3 J (H,H) = 7.2 Hz, 1H; CH), 6.86 (dd, 3 J (H,H) = 4.5 Hz, 4 J (H,H) = 1.8 Hz, 1H; Ar), 7.04-7.12 (m, 2H; Ar), 7.22 (d, 3 J (H,H) = 8.1 Hz, 2H; Ar), 7.62 (d, 3 J (H,H) = 8.1 Hz, 2H; Ar), 7.77 (s, 1H; CH); ¹³C NMR (CD₃SOCD₃, TMS, 75.44 MHz) δ = 20.9, 44.4, 51.2, 55.8, 106.6, 111.2, 120.8, 122.2, 124.9, 126.1, 129.1, 139.5, 140.2, 141.8, 147.3, 152.1, 165.3; IR (KBr) v 3279, 1714, 1645, 1586, 1487, 1318, 1204 cm⁻¹; MS (70eV): m/z(%) 234 (41.6) [M⁺-155], 219 (100) [M⁺-170]; HRMS Calcd. for C₁₉H₁₉NO₆SNa⁺ requires 412.0825, Found 412.0828.
methyl 6-methoxy-4-(4-methylphenylsulfonamido)-4H-chromene-3-carboxylate (4c): a white solid; mp. 164-166 °C; $^1$H NMR (CDCl$_3$, TMS, 300 MHz) $\delta$ = 2.40 (s, 3H; Me), 3.54 (s, 3H; Me), 3.66 (s, 3H; Me), 5.19 (d, $^3$J (H,H) = 6.6 Hz, 1H; NH), 5.49 (d, $^3$J (H,H) = 6.6 Hz, 1H; CH), 6.79-6.84 (m, 2H; Ar), 7.01 (d, $^3$J (H,H) = 8.4 Hz, 1H; Ar), 7.20 (d, $^3$J (H,H) = 8.4 Hz, 2H; Ar), 7.55 (d, $^3$J (H,H) = 8.4 Hz, 2H; Ar), 7.75 (s, 1H; CH); $^{13}$C NMR (CD$_3$SOCD$_3$, TMS, 75.44 MHz) $\delta$ = 20.9, 44.9, 51.2, 55.2, 105.8, 113.1, 115.5, 117.5, 121.7, 126.0, 129.0, 140.2, 141.8, 144.0, 152.5, 156.0, 165.4; IR (KBr) ν 3279, 1714, 1645, 1496, 1319, 1219, 1165, 1092 cm$^{-1}$; MS (70eV): m/z(%): 389 (1.79) [M$^+$], 219 (100) [M$^+$-170]; HRMS Calcd. for C$_{19}$H$_{19}$NO$_6$SNa$^+$ requires 412.0825, Found 412.0830.
methyl 6-methyl-4-(4-methylphenylsulfonylamido)-4H-chromene-3-carboxylate (4d): a white solid: mp. 178-179 °C; \(^1\)H NMR (CDCl\(_3\), TMS, 300 MHz) \(\delta = 2.16\) (s, 3H; Me), 2.40 (s, 3H; Me), 3.56 (s, 3H; Me), 5.15 (d, \(3^J\) (H,H) = 6.3 Hz, 1H; NH), 5.46 (d, \(3^J\) (H,H) = 6.3 Hz, 1H; CH), 6.94-6.97 (m, 1H; Ar), 7.02-7.05 (m, 2H; Ar), 7.19 (d, \(3^J\) (H,H) = 8.4 Hz, 2H; Ar), 7.53 (d, \(3^J\) (H,H) = 8.4 Hz, 2H; Ar), 7.75 (s, 1H; CH); \(^{13}\)C NMR (CD\(_3\)SOCD\(_3\), TMS, 75.44 MHz) \(\delta = 20.2, 20.8, 44.6, 51.2, 106.8, 116.2, 120.4, 126.0, 129.0, 129.6, 129.8, 134.0, 140.3, 141.8, 147.9, 152.4, 165.4\); IR (KBr) \(\nu\) 3447, 1692, 1649, 1323, 1216 , 1156, 1091 cm\(^{-1}\); MS (70eV): \(m/z\)%: 218 (52.4) \([M^+ - 155]\), 203 (100) \([M^+ - 170]\); HRMS Calcd. for C\(_{19}\)H\(_{19}\)NO\(_5\)SNa\(^+\) requires 396.0876, Found 396.0883.
methyl 6-bromo-4-(4-methylphenylsulfonamido)-4H-chromene-3-carboxylate (4e): a colorless solid: mp. 158-160 °C; $^1$H NMR (CDCl$_3$, TMS, 300 MHz) $\delta$ = 2.42 (s, 3H; Me), 3.62 (s, 3H; Me), 5.31 (d, $^3$J (H,H) = 6.3 Hz, 1H; NH), 5.41 (d, $^3$J (H,H) = 6.3 Hz, 1H; CH), 6.96 (d, $^3$J (H,H) = 8.4 Hz, 1H; Ar), 7.19 (d, $^3$J (H,H) = 7.8 Hz, 2H; Ar), 7.28 (d, $^4$J (H,H) = 2.1 Hz, 1H; Ar), 7.32 (dd, $^3$J (H,H) = 9.0 Hz, $^4$J (H,H) = 2.1 Hz, 1H; Ar), 7.49 (d, $^3$J (H,H) = 7.8 Hz, 2H; Ar), 7.76 (s, 1H; CH); $^{13}$C NMR (CDCl$_3$, TMS, 75.44 MHz) $\delta$ = 21.5, 45.6, 51.7, 106.8, 117.4, 118.5, 121.0, 126.6, 129.2, 132.2, 132.9, 138.8, 143.1, 149.5, 152.2, 165.8; IR (KBr) ν 3220, 1689, 1651, 1435, 1313, 1237, 1156, 1090 cm$^{-1}$; MS (70eV): $m/z$(%): 282 (57.7) [$M^+ - 155$], 267 (100) [$M^+ - 170$]; HRMS Calcd. for C$_{18}$H$_{16}$NO$_3$SBrNa requires 459.9825, Found 459.9824.
methyl 6,8-dichloro-4-(4-methylphenylsulfonamido)-4H-chromene-3-carboxylate (4f): a colorless solid: mp. 174-176 °C; $^1$H NMR (CDCl$_3$, TMS, 300 MHz) δ = 2.41 (s, 3H; Me), 3.60 (s, 3H; Me), 5.41 (d, $^3$J (H,H) = 6.6 Hz, 1H; CH), 5.46 (d, $^3$J (H,H) = 6.6 Hz, 1H; NH), 7.15 (d, $^4$J (H,H) = 1.8 Hz, 1H; Ar), 7.21 (d, $^3$J (H,H) = 7.8 Hz, 2H; Ar), 7.27-7.29 (m, 1H; Ar), 7.53 (d, $^3$J (H,H) = 7.8 Hz, 2H; Ar), 7.78 (s, 1H; CH); $^{13}$C NMR (CDCl$_3$, TMS, 75.44 MHz) δ = 21.5, 45.8, 51.8, 107.2, 122.1, 122.9, 126.8, 128.4, 129.3, 129.77, 129.82, 138.5, 143.3, 145.2, 151.8, 165.4; IR (KBr) ν 3276, 1719, 1651, 1459, 1318, 1193, 1157, 1092 cm$^{-1}$; MS (70eV): m/z(%): 272 (43.7) [M$^+$-155], 49 (100) [M$^+$-378]; HRMS Calcd. for C$_{18}$H$_{15}$NO$_5$SClNa$^+$ requires 449.9940, Found 449.9940.
methyl 4-(4-methylphenylsulfonamido)-6-nitro-4H-chromene-3-carboxylate (4g): a white solid: mp. 178-179 °C; $^1$H NMR (CDCl$_3$, TMS, 300 MHz) $\delta = 2.35$ (s, 3H; Me), 3.70 (s, 3H; Me), 5.46 (d, $^3$J (H,H) = 5.4 Hz, 1H; CH), 5.58 (d, $^3$J (H,H) = 5.4 Hz, 1H; NH), 7.13 (d, $^3$J (H,H) = 8.4 Hz, 2H; Ar), 7.20 (d, $^3$J (H,H) = 9.0 Hz, 1H; Ar), 7.42 (d, $^3$J (H,H) = 8.4 Hz, 2H; Ar), 7.78 (s, 1H; CH), 8.02 (d, $^4$J (H,H) = 2.4 Hz, 1H; Ar), 8.10 (dd, $^3$J (H,H) = 9.0 Hz, $^4$J (H,H) = 2.4 Hz, 1H; Ar); $^{13}$C NMR (CD$_2$SOCD$_3$, TMS, 75.44 MHz) $\delta = 20.8, 44.1, 51.5, 107.5, 117.9, 121.3, 124.5, 125.8, 126.2, 129.1, 139.8, 142.0, 143.5, 151.8, 154.2, 164.8; IR (KBr) $\nu = 3308, 1709, 1524, 1341, 1309, 1239, 1158, 1090$ cm$^{-1}$; MS (70eV): $m/z$ (%): 249 (53.8) [M$^-$-155], 234 (100) [M$^-$-170]; HRMS Calcd. for C$_{18}$H$_{16}$N$_2$O$_7$SNa$^+$ requires 427.0570, Found 427.0580.
methyl 1-(4-methylphenylsulfonamido)-1H-benzo[f]chromene-2-carboxylate (4h): a white solid; mp. 188-190 °C; \(^1\)H NMR (CDCl\(_3\), TMS, 300 MHz) \(\delta = 2.17\) (s, 3H; Me), 3.77 (s, 3H; Me), 5.53 (d, \(^3\)J (H,H) = 5.4 Hz, 1H; NH), 6.02 (d, \(^3\)J (H,H) = 5.4 Hz, 1H; CH), 6.70 (d, \(^3\)J (H,H) = 8.4 Hz, 2H; Ar), 7.06 (d, \(^3\)J (H,H) = 8.4 Hz, 2H; Ar), 7.24 (d, \(^3\)J (H,H) = 9.0 Hz, 1H; Ar), 7.33-7.40 (m, 2H; Ar), 7.62-7.64 (m, 1H; Ar), 7.70 (d, \(^3\)J (H,H) = 9.0 Hz, 1H; Ar), 7.88 (s, 1H; CH), 7.94 (d, \(^3\)J (H,H) = 8.4 Hz, 1H; Ar); \(^13\)C NMR (CD\(_3\)SOCD\(_3\), TMS, 75.44 MHz) \(\delta = 20.8, 42.0, 51.3, 107.3, 112.3, 116.8, 122.8, 125.0, 125.3, 127.2, 128.3, 128.5, 130.2, 130.5, 130.8, 139.6, 141.2, 148.9, 152.0, 165.4; IR (KBr) \(\nu = 3437, 1692, 1662, 1319, 1228, 1156, 1092\) cm\(^{-1}\); MS (70eV): \(m/z(\%): 253\) (7.95) [M\(^-1\)-156], 238 (100) [M\(^-1\)-171]; HRMS Calcd. for C\(_{22}\)H\(_{19}\)NO\(_5\)SNa\(^+\) requires 432.0876, Found 432.0880.
Typical Reaction Procedure for PPh$_2$Me Catalyzed Reaction of Ethyl 2,3-butadienoate with Salicyl N-tosylimine 1a.

To a flame-dried Schlenk tube at room temperature was in turn added molecular sieves 4A (50 mg), PPh$_2$Me (11.5 µL, 0.0625 mmol), salicyl N-tosylimine 1a (69 mg, 0.25 mmol), THF (1.0 mL) and ethyl 2,3-butadienoate 2c (35 µL, 0.30 mmol) and the reaction mixture was further stirred at room temperature for 1 hour. The reaction was monitored by TLC. When 1a disappeared, the solvent was removed under reduced pressure and the residue was purified by flash chromatography (Eluent: EtOAc:Petroleum ether = 1:4-2:1) to yield s1 (84 mg, 87 %) as a colorless solid.

2-(2-Hydroxy-phenyl)-1-(toluene-4-sulfonyl)-2,5-dihydro-1H-pyrrole-3-carboxylic acid ethyl ester (s1): a colorless solid: This is a known compound.[4] mp. 156-158 °C; $^1$H NMR (CDCl$_3$, TMS, 300 MHz) $\delta = 1.12 \ (t, \ 3J \ (H,H) = 7.2 \ Hz, \ 3H; \ CH_3), \ 2.38 \ (s, \ 3H; \ Me), \ 3.98-4.16 \ (m, \ 2H; \ CH_2), \ 4.35-4.53 \ (m, \ 2H; \ CH_2), \ 6.07 \ (t, \ 3J \ (H,H) = 2.7 \ Hz, \ 1H; \ CH), \ 6.77-6.91 \ (m, \ 4H; \ Ar), \ 7.00-7.03 \ (m, \ 1H; \ Ar), \ 7.12-7.22 \ (m, \ 3H; \ Ar), \ 7.56 \ (d, \ 3J \ (H,H) = 8.4 \ Hz, \ 2H; \ Ar).
ethyl 2(2-hydroxy-3-methoxyphenyl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (s2):
a colorless solid: mp.160-161 °C; $^1$H NMR (CDCl$_3$, TMS, 300 MHz) δ = 1.10 (t, $^3$J (H,H) = 7.2 Hz, 3H; CH$_3$), 2.37 (s, 3H; Me), 3.82 (s, 3H; Me), 3.93-4.11 (m, 2H; CH$_2$), 4.46-4.48 (m, 2H; CH$_2$), 5.66 (s, 1H; OH), 5.96-5.99 (m, 1H; CH), 6.70-6.82 (m, 4H; Ar), 7.13 (d, $^3$J (H,H) = 8.4 Hz, 2H; Ar), 7.48 (d, $^3$J (H,H) = 8.4 Hz, 2H; Ar); $^{13}$C NMR (CDCl$_3$, TMS, 75.44 MHz) δ = 13.8, 21.4, 55.2, 55.8, 60.6, 64.2, 109.9, 119.2, 121.8, 124.5, 127.1, 129.1, 134.1, 135.1, 136.0, 142.8, 143.8, 146.4, 161.9; IR (KBr) ν 3421, 1717, 1481, 1342, 1277, 1162, 1093 cm$^{-1}$; MS (70eV): $m/z$(%): 417 (33.6) [M$^+$], 233 (100) [M$^-$-184]; Anal. Calcd. for C$_{21}$H$_{23}$NO$_6$S requires C, 60.42; H, 5.55; N, 3.36%; Found: C, 60.22; H, 5.54; N, 3.14%.
ethyl 2-(2-hydroxy-5-methylphenyl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (s3): a colorless solid: mp. 155-156 °C; $^1$H NMR (CDCl$_3$, TMS, 300 MHz) $\delta$ = 1.14 (t, $^3$J (H,H) = 7.2 Hz, 3H; CH$_3$), 2.12 (s, 3H; Me), 2.38 (s, 3H; Me), 3.98-4.18 (m, 2H; CH$_2$), 4.38-4.56 (m, 2H; CH$_2$), 6.05-6.08 (m, 1H; CH), 6.65-6.78 (m, 1H; OH), 6.70 (d, $^4$J (H,H) = 2.1 Hz, 1H; Ar), 6.76-6.78 (m, 1H; Ar), 6.81 (d, $^3$J (H,H) = 8.1 Hz, 1H; Ar), 6.93 (dd, $^3$J (H,H) = 8.1 Hz, $^4$J (H,H) = 2.1 Hz, 1H; Ar), 7.19 (d, $^3$J (H,H) = 8.4 Hz, 2H; Ar), 7.54 (d, $^3$J (H,H) = 8.4 Hz, 2H; Ar); $^{13}$C NMR (CDCl$_3$, TMS, 75.44 MHz) $\delta$ = 13.7, 20.5, 21.4, 54.9, 61.3, 63.0, 118.2, 126.3, 127.1, 128.2, 129.5, 129.8, 130.1, 134.7, 135.2, 136.1, 143.5, 151.4, 162.8; IR (KBr) v 3431, 1719, 1344, 1268, 1163, 1106 cm$^{-1}$; MS (70eV): m/z(%): 401 (27.3) [M$^+$], 91 (100) [M$^+$-310]; Anal. Calcd. for C$_{21}$H$_{23}$NO$_5$S requires C, 62.82; H, 5.77; N, 3.49%; Found: C, 62.58; H, 5.80; N, 3.36%.
ethyl 2-(5-bromo-2-hydroxyphenyl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (s4): a colorless solid: mp. 170-171 °C; $^1$H NMR (CDCl$_3$, TMS, 300 MHz) δ = 1.18 (t, $^3$J (H,H) = 7.2 Hz, 3H; CH$_3$), 2.40 (s, 3H; Me), 4.02-4.21 (m, 2H; CH$_2$), 4.40-4.61 (m, 2H; CH$_2$), 6.02-6.05 (m, 1H; CH), 6.79-6.82 (m, 2H; Ar), 6.97 (d, $^4$J (H,H) = 2.4 Hz, 1H; Ar), 7.06 (s, 1H; OH), 7.19-7.23 (m, 3H; Ar), 7.55 (d, $^3$J (H,H) = 8.4 Hz, 2H; Ar); $^{13}$C NMR (CDCl$_3$, TMS, 75.44 MHz) δ = 14.1, 22.6, 55.0, 61.7, 62.5, 113.4, 120.6, 127.1, 129.2, 129.7, 130.5, 132.0, 134.6, 134.9, 136.8, 144.0, 152.9, 162.9; IR (KBr) ν 3416, 1719, 1334, 1278, 1162, 1093 cm$^{-1}$; MS (70eV): $m/z$ (%): 465 (22.8) [$M^+*$], 91 (100) [$M^+-374$]; Anal. Calcd. for C$_{20}$H$_{20}$BrNO$_5$S requires C, 51.51; H, 4.32; N, 3.00%; Found: C, 51.58; H, 4.28; N, 2.81%.
ethyl 2-(3,5-dichloro-2-hydroxyphenyl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (s5): a colorless solid: mp. 168-169 °C; $^1$H NMR (CDCl$_3$, TMS, 300 MHz) $\delta = 1.15$ (t, $^3J$ (H,H) = 7.2 Hz, 3H; CH$_3$), 2.40 (s, 3H; Me), 3.98-4.16 (m, 2H; CH$_2$), 4.43-4.57 (m, 2H; CH$_2$), 5.93-5.97 (m, 1H; CH), 6.11 (s, 1H; OH), 6.80-6.82 (m, 1H; Ar), 6.99 (d, $^4J$ (H,H) = 2.7 Hz, 1H; Ar), 7.18-7.21 (m, 3H; Ar), 7.52 (d, $^3J$ (H,H) = 8.1 Hz, 2H; Ar); $^{13}$C NMR (CDCl$_3$, TMS, 75.44 MHz) $\delta =$ 13.8, 21.5, 53.3, 61.2, 63.6, 121.9, 125.3, 127.1, 128.1, 128.2, 128.7, 129.5, 133.8, 134.6, 137.1, 143.8, 148.2, 162.0. IR (KBr) $\nu$ 3415, 1719, 1466, 1347, 1268, 1163, 1094 cm$^{-1}$; MS (70eV): $m/z$ (%): 455 (8.27) [$M^+$], 91 (100) [$M^+-364$]; Anal. Calcd. for C$_{20}$H$_{19}$Cl$_2$NO$_5$S requires C, 52.64; H, 4.20; N, 3.07%; Found: C, 52.67; H, 4.22; N, 2.91%. 

![Chemical structure of ethyl 2-(3,5-dichloro-2-hydroxyphenyl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (s5)](image-url)
References


