Supporting Information

Synergistic silver/scandium catalysis for divergent synthesis of skeletally diverse chromene derivatives

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General Information

$^1$H NMR ($^{13}$C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in DMSO-$d_6$ (CDCl$_3$, or Acetone-$d_6$) with chemical shift ($\delta$) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, t = triplet, br = broad singlet, m = multiplet), coupling constant (Hz)]. HRMS (ESI) was determined by using microTOF-QII HRMS/MS instrument (BRUKER). X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer.

Table 1. Optimization of Reaction Conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>Co-Catalyst (mol %)</th>
<th>Solvent</th>
<th>$T$ ($^\circ$C)</th>
<th>Yield$^b$ (%)</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3a</td>
</tr>
<tr>
<td>1$^a$</td>
<td>AgTFA (10)</td>
<td>Toluene</td>
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<td>trace</td>
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<td>2$^a$</td>
<td>AgTFA (10)/BiNPO$4$H (10)</td>
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<td>3$^a$</td>
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<td>Toluene</td>
<td>50</td>
<td>ND$^c$</td>
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<td>4$^a$</td>
<td>AgOTf (10)/BiNPO$4$H (10)</td>
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<td>5$^a$</td>
<td>AgNO$_3$ (10)/BiNPO$4$H (10)</td>
<td>Toluene</td>
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<td>6$^a$</td>
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<td>7$^a$</td>
<td>AgTFA (10)/Sc(OTf)$_3$ (10)</td>
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<td>8$^a$</td>
<td>AgTFA (10)/Sn(OTf)$_2$ (10)</td>
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<td>trace</td>
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<td>9$^a$</td>
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<td>10$^a$</td>
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<td>11$^a$</td>
<td>Cu(OTf)$_2$ (10)/Sc(OTf)$_3$ (10)</td>
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<td>12$^a$</td>
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<td>13$^a$</td>
<td>AgTFA (10)/Sc(OTf)$_3$ (10)</td>
<td>CH$_2$CN</td>
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<td>14$^a$</td>
<td>AgTFA (10)/Sc(OTf)$_3$ (10)</td>
<td>1,4-Dioxane</td>
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<td>15$^a$</td>
<td>AgTFA (10)/Sc(OTf)$_3$ (10)</td>
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<td>16$^a$</td>
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<td>17$^a$</td>
<td>AgTFA (10)/Sc(OTf)$_3$ (10)</td>
<td>Toluene</td>
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<td>ND</td>
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<td>ND</td>
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<td>25$^d$</td>
<td>AgTFA (10)/Sc(OTf)$_3$ (10)</td>
<td>Toluene</td>
<td>80</td>
<td>trace</td>
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</table>

$^a$Reaction conditions: 1a (0.3 mmol), 2a (0.2 mmol), Ag-catalyst (x mol%), Lewis acid/ catalyst (y mol%), solvent (3.0 mL), under air conditions.

$^b$Isolated yield based on substrate 2a.

$^c$Not detected (ND).

$^d$Using 1a (0.2 mmol) and 2a (0.6 mmol); isolated yield based on substrate 1a.

Our initial investigation was started with the treatment of $\beta$-alkynyl ketone 1a and o-hydroxybenzyl alcohol 2a in a 1.5:1 mole ratio under air conditions in toluene at 50 °C using silver trifluoroacetate.
(AgTFA, 10 mol %) as a catalyst, but the transformation did not proceed (Table S1, entry S1). Merging AgTFA with 1,1’-Binaphthyl-2,2’-diyl hydrogen phosphate (BiNPO₄H, 10 mol %) as co-catalytic system delivered the desired spiro[chromane-2,1’-isochromene] 3a, albeit with a low 35% yield (entry S2). Screening followed by several others silver salts often used in the catalytic transformations such as AgOAc, silver trifluormethanesulfonate (AgOTf) and silver nitrate (AgNO₃) showed that all these attempted silver catalysts showed a lower catalytic capability and gave unsatisfactory results as compared with AgTFA (entries S3-S5). Exchanging BiNPO₄H for trifluoroacetic acid (TFA, 10 mol %) as a Brønsted acid catalyst led to a poor yield of 23% (entry S6), indicating that Brønsted acid catalyst may disfavor this transformation. Next, we considered using Lewis acid catalyst to explore this bicyclization cascade. To our delight, the combination of AgTFA and Sc(OTf)₃ as a dual catalyst system makes these transformations work well, furnishing the desired 6,6-dibenzannulated spiroketal 3a in 68% yield (entry S7). The use of AgTFA/Sn(OTf)₂ or AgTFA/Zn(OTf)₂ as a co-catalytic system resulted in a very inferior outcome (entries S8-S9). When PdCl₂/Sc(OTf)₃ or Cu(OTf)₂/Sc(OTf)₃ was used as a bimetallic catalyst, the reaction did not work (entries S10-S11), indicating that silver catalyst is critical for this transformation. Employment of a lower loading of AgTFA resulted in a relatively lower yield of 3a (entry S12). The investigation of the solvent effect revealed that the use of solvents including acetonitrile (CH₃CN), 1,4-dioxane, tetrahydrofuran (THF), and 1,2-dichloroethane (DCE) has no positive effect on the yield of 3a (entries S13-S16). Lower conversion of 3a was observed with the reaction temperature being at room temperature (entry S17). Surprisingly, elevating the reaction temperature to 70 °C provided product 3a in 33% yield, along with two unexpected products, benzo[c]xanthenes 4a and spiro[chromane-2,5’-isochromeno[3,4-b]chromene] 5a (entry S18). Next, our endeavor aimed at improving the generation of products 4a and 5a was made by adjusting reaction conditions. It is found that the selectivity of reaction shows an important dependency on temperature (entries S19-S22). For instance, elevating the reaction temperature from 70 °C to 100 °C facilitated the formation of 4a (68%) and simultaneously suppressed the formation of 5a without observation of 3a. After careful optimizations, we found that the reaction in the presence of 10 mol % of AgTFA and 20 mol % of Sc(OTf)₃ worked more efficiently and offered a 78% yield of 4a (entry S23), whereas adjusting substrate ratio to 1:3 gave product 5a in 72% yield with use of 10 mol % of AgTFA and 10 mol % of Sc(OTf)₃ at 80 °C in the current catalytic tricyclization (entry S25).
Figure 1. The ORTEP Drawing of 3a

Figure 2. The ORTEP Drawing of 4b

Figure 3. The ORTEP Drawing of 5a
General procedure for the synthesis of compounds 3

Example for the synthesis of 3a:

![Chemical structure of 1a, 2a, and 3a]

A mixture of 1-(2-((phenylethynyl)phenyl)ethanone (1a, 0.3 mmol, 66.0 mg), 2-(hydroxy(phenyl)methyl)phenol (2a, 0.2 mmol, 40.0 mg), Sc(OTf)₃ (10 mol%, 9.8 mg) and AgTFA (10 mol%, 4.4 mg) were added in a 25-mL reaction vial, which was sealed and heated at 50 °C until TLC (petroleum ether: ethyl acetate= 12:1) revealed that conversion of the starting material 2a was completed. Then the reaction mixture was concentrated by vacuum distillation and was purified by flash column chromatography (silica gel, mixtures of petroleum ether / acetic ester, 50:1, v/v) to afford the desired pure products (3a, 54.7 mg, 68% yield) as white solid.

General procedure for the synthesis of compounds 4

Example for the synthesis of 4a

![Chemical structure of 1a, 2a, and 4a]

A mixture of 1-(2-((phenylethynyl)phenyl)ethanone (1a, 0.3 mmol, 66.0 mg), 2-(hydroxy(phenyl)methyl)phenol (2a, 0.2 mmol, 40.0 mg), Sc(OTf)₃ (20 mol%, 19.6 mg) and AgTFA (10 mol%, 4.4 mg) were added in a 25-mL reaction vial, which was sealed and heated at 100 °C until TLC (petroleum ether: ethyl acetate= 12:1) revealed that conversion of the starting material 2a was completed. Then the reaction mixture was concentrated by vacuum distillation and was purified by flash column chromatography (silica gel, petroleum ether) to afford the desired pure products (4a, 59.9 mg, 78% yield) as white solid.

General procedure for the synthesis of compounds 5

Example for the synthesis of 5a

![Chemical structure of 1a, 2a, and 5a]

A mixture of 1-(2-((phenylethynyl)phenyl)ethanone (1a, 0.2 mmol, 66.0 mg), 2-(hydroxy(phenyl)methyl)phenol (2a, 0.6 mmol, 40.0 mg), Sc(OTf)₃ (10 mol%, 9.8 mg) and AgTFA (10 mol%, 4.4 mg) were added in a 25-mL reaction vial. The solution was stirred at 80 °C for 30 min, the reaction mixture was concentrated by vacuum distillation and was purified by flash column chromatography (silica gel, petroleum ether / ethylacetate = 50/1, v/v) to afford the desired pure products (5a, 84.1 mg, 72% yield) as white solid.
**3',4-diphenylspiro[chroman-2,1'-isochromene] (3a)**

54.7 mg, 68%; white solid, mp 181-182 °C; 1H NMR (400 MHz, CDCl₃; δ, ppm) 7.54-7.48 (m, 3H), 7.46-7.39 (m, 5H), 7.37-7.31 (m, 6H), 7.16-7.11 (m, 1H), 6.97-6.90 (m, 2H), 6.85 (d, J = 8.0 Hz, 1H), 6.68 (s, 1H), 4.90-4.84 (m, 1H), 2.97-2.89 (m, 1H), 2.88-2.82 (m, 1H) 13C NMR (100 MHz, CDCl₃; δ, ppm) 152.3, 149.5, 144.2, 134.4, 130.8, 129.6, 129.3(8), 129.3(5), 129.1, 128.8(3), 128.8(0), 128.5, 128.0, 127.1, 127.0, 125.5, 125.2, 125.1, 123.7, 121.5, 117.6, 101.3, 98.6, 39.1, 39.0. IR (film, ν, cm⁻¹). 3022, 1787, 1499, 1254, 1045, 1003, 883, 749. HR-MS (APCI) m/z calcd for C₂₉H₂₃O₂ [M+H]+ 403.1698, found 403.1703.

**4-phenyl-3'- (p-tolyl) spiro[chroman-2,1'-isochromene] (3b)**

51.6 mg, 62%; white solid, mp 188-189 °C; 1H NMR (400 MHz, CDCl₃; δ, ppm) 7.49 (d, J = 7.6 Hz, 1H), 7.44-7.38 (m, 5H), 7.38-7.28 (m, 5H), 7.11 (d, J = 8.0 Hz, 3H), 6.97-6.88 (m, 2H), 6.82 (d, J = 8.0 Hz, 1H), 6.61 (s, 1H), 4.89-4.80 (m, 1H), 2.94-2.86 (m, 1H), 2.86-2.77 (m, 1H), 2.33 (s, 3H). 13C NMR (100 MHz, CDCl₃; δ, ppm) 152.3, 149.7, 144.3, 138.9, 131.7, 131.0, 129.5, 129.3, 129.2, 129.1, 128.8, 128.0, 126.9(4), 126.9(0), 125.5, 125.1, 123.7, 121.4, 117.6, 100.6, 98.5, 39.1, 39.0, 21.3. IR (film, ν, cm⁻¹). 3027, 1484, 1454, 1228, 1050, 1008, 879, 762. HR-MS (APCI) m/z calcd for C₃₀H₂₅O₂ [M+H]+ 417.1855, found 417.1854.

**4-phenyl-3'- (p-tolyl) spiro[chroman-2,1'-isochromene] (3c)**

50.8 mg, 61%; white solid, mp 160-161 °C; 1H NMR (400 MHz, CDCl₃; δ, ppm) 7.50 (d, J = 7.2 Hz, 1H), 7.44-7.39 (m, 5H), 7.35-7.29 (m, 4H), 7.19 (d, J = 7.2 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 6.97-6.92 (m, 2H), 6.83 (d, J = 8.0 Hz, 1H), 6.64 (s, 1H), 4.90-4.83 (m, 1H), 2.96-2.89 (m, 1H), 2.86-2.80 (m, 1H), 2.27 (s, 3H). 13C NMR (100 MHz, CDCl₃; δ, ppm) 152.4, 149.8, 144.4, 138.0, 134.5, 130.9, 129.7, 129.6, 129.3, 129.1, 128.8, 128.4, 128.0, 127.1, 127.0, 126.1, 125.7, 125.1, 123.7, 122.4, 121.6, 117.7, 101.4, 98.5, 39.1, 21.5. IR (film, ν, cm⁻¹) 3023, 1484, 1450, 1257, 1051, 1006, 872, 741. HR-MS (APCI) m/z calcd for C₃₀H₂₅O₂ [M+H]+ 417.1855, found 417.1861.

**3’-(4-ethylphenyl)-4-phenylspiro[chroman-2,1’-isochromene] (3d)**
54.2 mg, 63%; white solid, mp 184-185 °C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) 7.48 (d, J = 7.6 Hz, 1H), 7.44-7.37 (m, 7H), 7.34-7.28 (m, 3H), 7.14-7.08 (m, 3H), 6.93-6.87 (m, 2H), 6.82 (d, J = 8.4 Hz, 1H), 6.60 (s, 1H), 4.86-4.81 (m, 1H), 2.93-2.86 (m, 1H), 2.84-2.79 (m, 1H), 2.63 (m, 2H), 1.24-1.19 (t, J = 7.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) 152.3, 149.7, 145.3, 144.3, 131.9, 131.0, 129.5, 129.3, 129.1(4), 129.1(7), 128.8, 128.0, 126.9(4), 126.9(9), 125.5, 125.3, 125.0, 123.7, 121.4, 117.6, 100.6, 98.5, 39.1, 39.0, 28.7, 15.4. IR (film, ν, cm⁻¹) 3024, 1512, 1452, 1226, 1052, 913, 762. HR-MS (APCI) m/z calcd for C₃₁H₂₇O₂ [M+H]⁺ 431.2011, found 431.2009.

3'-(4-(tert-butyl)phenyl)-4-phenylspiro[chroman-2,1'-isochromene] (3e)

48.5 mg, 53%; white solid, mp 201-202 °C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) 7.48 (d, J = 7.6 Hz, 2H), 7.44-7.38 (m, 4H), 7.35-7.30 (m, 5H), 7.14-7.09 (m, 1H), 6.95-6.89 (m, 2H), 6.82 (d, J = 8.0 Hz, 1H), 6.61 (s, 1H), 4.89-4.83 (m, 1H), 2.95-2.88 (m, 1H), 2.84-2.78 (m, 1H), 1.30 (s, 9H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) 152.3, 152.1, 149.7, 144.3, 131.7, 131.0, 129.5, 129.3, 129.1, 128.8, 128.0, 127.0, 126.9, 125.5, 125.4, 125.1, 125.0, 123.7, 121.5, 117.0, 100.6, 98.4, 39.1, 39.0, 34.7, 31.2. IR (film, ν, cm⁻¹) 3028, 1485, 1451, 1231, 1107, 1005, 879, 749. HR-MS (APCI) m/z calcd for C₃₃H₃₀O₂ [M+H]⁺ 459.2324, found 459.2328.

3'-(4-fluorophenyl)-4-phenylspiro[chroman-2,1'-isochromene] (3f)

48.7 mg, 58%; white solid, mp 181-182 °C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) 7.49 (d, J = 7.2 Hz, 1H), 7.45-7.40 (m, 4H), 7.39-7.36 (m, 3H), 7.34-7.30 (m, 3H), 7.13-7.09 (m, 1H), 7.00-6.95 (m, 2H), 6.93-6.88 (m, 2H), 6.83-6.80 (m, 1H), 6.58 (s, 1H), 4.84-4.78 (m, 1H), 2.94-2.87 (m, 1H), 2.84-2.79 (m, 1H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) 163.1(¹JC₅ = 243.7 Hz), 152.2, 148.7, 144.1, 130.7, 130.6(¹JC₅ = 3.2 Hz), 129.5(¹JC₅ = 8.6 Hz), 129.1, 129.0, 128.8, 128.1, 127.2, 127.1, 127.0(1), 127.0(0), 125.5, 125.1, 123.7, 121.6, 117.6, 115.5(¹JC₅ = 21.7 Hz), 101.1, 98.6, 39.0. IR (film, ν, cm⁻¹) 3022, 1507, 1482, 1227, 1044, 1008, 881, 763. HR-MS (APCI) m/z calcd for C₂₉H₂₂FO₂ [M+H]⁺ 421.1604, found 421.1602.

3'-(4-chlorophenyl)-4-phenylspiro[chroman-2,1'-isochromene] (3g)
37.5 mg, 43%; white solid, mp 230-231 °C; $^1$H NMR (400 MHz, CDCl$_3$; $\delta$, ppm) 7.48 (d, $J = 7.2$ Hz, 1H), 7.45-7.39 (m, 2H), 7.38-7.35 (m, 5H), 7.34-7.29 (m, 3H), 7.26-7.23 (m, 2H), 7.12-7.08 (m, 1H), 6.93-6.87 (m, 2H), 6.81-6.78 (m, 1H), 6.63 (s, 1H), 4.81-4.76 (m, 1H), 2.93-2.86 (m, 1H), 2.84-2.78 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$; $\delta$, ppm) 152.1, 148.5, 144.1, 134.6, 132.9, 130.5, 129.6, 129.3, 129.0, 128.8, 128.7, 128.1, 127.4, 127.0, 126.4, 125.4, 125.2, 123.7, 121.6, 117.5, 101.8, 98.6, 99.0. IR (film, $\nu$, cm$^{-1}$) 3025, 1491, 1453, 1227, 1048, 1009, 881, 766. HR-MS (APCI) m/z calcd for C$_{29}$H$_{22}$ClO$_2$ [M+H]$^+$ 437.1308, found 437.1306.

3’-(4-bromophenyl)-4-phenylspiro[chroman-2,1’-isochromene] (3h)

43.2 mg, 45%; white solid, mp 233-234 °C; $^1$H NMR (400 MHz, CDCl$_3$; $\delta$, ppm) 7.48 (d, $J = 7.6$ Hz, 1H), 7.44-7.41 (m, 2H), 7.40-7.37 (m, 4H), 7.35 (d, $J = 5.2$ Hz, 1H), 7.33-7.28 (m, 5H), 7.12-7.08 (m, 1H), 6.92-6.87 (m, 2H), 6.79 (d, $J = 8.0$ Hz, 1H), 6.64 (s, 1H), 4.80-4.75 (m, 1H), 2.93-2.86 (m, 1H), 2.83-2.78 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$; $\delta$, ppm) IR (film, $\nu$, cm$^{-1}$) 152.1, 148.5, 144.1, 133.3, 131.6, 130.5, 129.6, 129.3, 129.0, 128.8, 128.1, 127.4, 127.0, 126.6, 125.4, 125.2, 123.8, 122.9, 121.6, 117.5, 101.8, 98.6, 99.0. IR (film, $\nu$, cm$^{-1}$) 3022, 1489, 1452, 1277, 1071, 1006, 880, 765. HR-MS (APCI) m/z calcd for C$_{29}$H$_{22}$BrO$_2$ [M+H]$^+$ 481.0803, found 481.0799.

6’-fluoro-4-phenyl-3’-(p-tolyl)spiro[chroman-2,1’-isochromene] (3j)

50.3 mg, 58%; white solid, mp 244-245 °C; $^1$H NMR (400 MHz, CDCl$_3$; $\delta$, ppm) 7.47-7.43 (m, 1H), 7.42-7.37 (m, 3H), 7.37-7.30 (m, 4H), 7.13-7.09 (m, 3H), 7.00-6.95 (m, 2H), 6.94-6.88 (m, 2H), 6.83-6.79 (m, 1H), 6.55 (s, 1H), 4.85-4.79 (m, 1H), 2.89-2.83 (m, 1H), 2.83-2.78 (m, 1H), 2.34 (s, 3H), $^{13}$C NMR (100 MHz, CDCl$_3$; $\delta$, ppm) 163.4($^2J_{CF} = 245.5$ Hz), 152.2, 150.9, 144.1, 139.4, 133.5 ($^3J_{CF} = 9.2$ Hz), 131.2, 129.3, 129.2, 129.0, 128.8, 128.1, 127.0, 125.8($^5J_{CF} = 9.0$ Hz), 125.4, 125.3, 125.2($^6J_{CF} = 2.6$ Hz), 121.6, 117.5, 113.6($^7J_{CF} = 22.3$ Hz), 111.1($^8J_{CF} = 22.3$ Hz), 99.9, 98.4, 39.2, 39.0, 21.3. IR (film, $\nu$, cm$^{-1}$) 3026, 1611, 1511, 1205, 1050, 1009, 878, 762. HR-MS (APCI) m/z calcd for C$_{30}$H$_{25}$FO$_2$ [M+H]$^+$ 435.1760, found 435.1762.

6-fluoro-3’,4-diphenylspiro[chroman-2,1’-isochromene] (3k)
48.7 mg, 58%; white solid, mp 185-186 °C; 1H NMR (400 MHz, CDCl3; δ, ppm) 7.50-7.38 (m, 6H), 7.38-7.32 (m, 4H), 7.32-7.27 (m, 4H), 6.84-6.74 (m, 2H), 6.66 (s, 1H), 6.65-6.61 (m, 1H), 4.84-4.77 (m, 1H), 2.93-2.86 (m, 1H), 2.84-2.78 (m, 1H). 13C NMR (100 MHz, CDCl3; δ, ppm) 157.5 (JCF = 237.4 Hz), 149.4, 148.2, 143.4, 134.3, 130.8, 129.7, 129.0 (6), 128.9, 128.5, 127.2 (JCF = 9.4 Hz), 126.9, 126.8, 125.1 (JCF = 2.4 Hz), 123.7, 118.6 (JCF = 8.1 Hz), 115.3 (JCF = 23.4 Hz), 114.9 (JCF = 23.1 Hz), 101.4, 98.5, 39.2, 38.6. IR (film, ν, cm⁻¹) 3023, 1484, 1453, 1256, 1046, 818, 759. HR-MS (APCI) m/z calcd for C29H22FO2 [M+H]+ 421.1604, found 421.1607.

6-bromo-3',4-diphenylspiro[chroman-2,1'-isochromene] (3l)

49.9 mg, 52%; white solid, mp 212-213 °C; 1H NMR (400 MHz, CDCl3; δ, ppm) 7.50-7.46 (m, 3H), 7.45-7.40 (m, 3H), 7.36 (d, J = 8.0 Hz, 3H), 7.35-7.30 (m, 5H), 7.23-7.19 (m, 1H), 7.05 (d, J = 1.2 Hz, 1H), 6.70 (d, J = 8.8 Hz, 1H), 6.66 (s, 1H), 4.87-4.78 (m, 1H), 2.93-2.85 (m, 1H), 2.84-2.78 (m, 1H). 13C NMR (100 MHz, CDCl3; δ, ppm) 151.4, 149.3, 143.2, 134.5, 130.8, 130.6, 129.5, 129.4, 129.1, 128.9, 128.7, 128.6, 127.7, 127.3, 127.2, 125.2, 125.1, 123.7, 119.5, 113.8, 101.3, 98.6, 39.0, 38.7. IR (film, ν, cm⁻¹) 3029, 1471, 1453, 1229, 1074, 885, 776. HR-MS (APCI) m/z calcd for C29H22BrO2 [M+H]+ 481.0803, found 481.0805.

6-methyl-3',4-diphenylspiro[chroman-2,1'-isochromene](3m)

59.9 mg, 72%; white solid, mp 188-189 °C; 1H NMR (400 MHz, CDCl3; δ, ppm) 7.50-7.46 (m, 3H), 7.43-7.37 (m, 5H), 7.34-7.28 (m, 6H), 6.92-6.88 (m, 1H), 6.71 (d, J = 8.0 Hz, 2H), 6.64 (s, 1H), 4.82-4.76 (m, 1H), 2.89-2.82 (m, 1H), 2.81-2.76 (m, 1H), 2.19 (s, 3H). 13C NMR (100 MHz, CDCl3; δ, ppm) 150.1, 149.6, 144.3, 134.5, 130.8, 129.5, 129.4, 129.1, 128.9, 128.7, 128.6, 127.1, 126.9, 125.2, 125.0 (3), 125.0 (9), 123.7, 117.3, 101.2, 98.5, 39.2, 39.0, 20.7. IR (film, ν, cm⁻¹) 3029, 1492, 1452, 1230, 1061, 1003, 872, 760. HR-MS (APCI) m/z calcd for C30H25O2 [M+H]+ 417.1855, found 417.1851.

6-chloro-3'-phenyl-4-(m-tolyl)spiro[chroman-2,1'-isochromene] (3n)
54.0 mg, 60%; white solid, mp 199-200 °C; 1H NMR (400 MHz, CDCl3; δ, ppm) 7.50-7.45 (m, 3H), 7.45-7.41 (m, 1H), 7.36-7.29 (m, 6H), 7.15 (d, J = 8.0 Hz, 3H), 7.07-7.03 (m, 1H), 6.92-6.89 (m, 1H), 6.74 (d, J = 8.8 Hz, 1H), 6.65 (s, 1H), 4.78-4.73 (m, 1H), 2.92-2.85 (m, 1H), 2.81-2.76 (m, 1H), 2.39 (s, 3H). 13C NMR (100 MHz, CDCl3; δ, ppm) 150.9, 149.4, 143.1, 138.7, 134.2, 130.7, 129.7, 128.9(4), 128.9(9), 128.9(8), 128.8, 128.5, 128.1, 127.3, 127.2, 126.3, 126.0, 125.1(4), 125.1(8), 123.7, 119.0, 101.3, 98.6, 38.9, 38.6, 21.5. IR (film, ν, cm\(^{-1}\)) 3024, 1489, 1454, 1228, 1047, 1007, 890, 752. HR-MS (APCI) m/z calcd for C\(_{30}\)H\(_{24}\)ClO\(_2\) [M+H]\(^+\) 451.1465, found 451.1466.

3'-phenyl-4-(p-tolyl)spiro[chroman-2,1'-isochromene] (3o)

45.8 mg, 55%; white solid, mp 186-187 °C; 1H NMR (400 MHz, CDCl3; δ, ppm) 7.51-7.45 (m, 3H), 7.45-7.40 (m, 1H), 7.32 (d, J = 7.6 Hz, 2H), 7.30-7.26 (m, 5H), 7.21 (d, J = 7.6 Hz, 2H), 7.12-7.07 (m, 1H), 6.94 (d, J = 7.6 Hz, 1H), 6.91-6.86 (m, 1H), 6.81 (d, J = 8.0 Hz, 1H), 6.65 (s, 1H), 4.85-4.78 (m, 1H), 2.93-2.85 (m, 1H), 2.83-2.77 (m, 1H), 2.39 (s, 3H). 13C NMR (100 MHz, CDCl3; δ, ppm) 152.2, 149.5, 141.2, 136.6, 134.4, 130.8, 129.5(4), 129.5(0), 129.3, 128.9, 128.8, 128.4, 127.9, 127.1, 125.7, 125.2, 125.1, 123.7, 121.5, 117.5, 101.3, 98.6, 39.1, 38.5, 21.1. IR (film, ν, cm\(^{-1}\)) 3029, 1483, 1453, 1253, 1045, 1008, 881, 752. HR-MS (APCI) m/z calcd for C\(_{30}\)H\(_{25}\)O\(_2\) [M+H]\(^+\) 417.1855, found 417.1856.

6,7-diphenyl-7H-benzo[c]xanthene (4a)

59.9 mg, 78%; white solid, mp 191-192 °C; 1H NMR (400 MHz, CDCl3; δ, ppm) 8.57 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.64-7.54 (m, 2H), 7.43 (s, 1H), 7.41-7.31 (m, 4H), 7.24 (d, J = 7.2 Hz, 1H), 7.16 (d, J = 7.6 Hz, 1H), 7.11-6.96 (m, 6H), 6.75-6.69 (m, 2H), 5.37 (s, 1H). 13C NMR (100 MHz, CDCl3; δ, ppm) 150.7, 147.0, 146.3, 140.5, 140.3, 133.0, 129.5, 129.1, 128.2, 127.9, 127.6, 127.5(0), 127.5(7), 127.1, 126.7, 126.1, 126.0, 125.7, 123. 8, 123.7, 121.9, 117.4, 116.7, 42.9. IR (film, ν, cm\(^{-1}\)) 3023, 1487, 1387, 1234, 1090, 887, 750. HR-MS (APCI) m/z calcd for C\(_{30}\)H\(_{21}\)O [M+H]\(^+\) 385.1592, found 385.1594.

7-phenyl-6-(p-tolyl)-7H-benzo[c]xanthene (4b)
70.0 mg, 88%; white solid, mp 185-186 °C; $^1$H NMR (400 MHz, CDCl$_3$; $\delta$, ppm) 8.56 (d, $J$ = 8.4 Hz, 1H), 7.80 (d, $J$ = 8.0 Hz, 1H), 7.63-7.52 (m, 2H), 7.42 (s, 1H), 7.34-7.31 (m, 1H), 7.25-7.20 (m, 1H), 7.18-7.11 (m, 3H), 7.06-6.99 (m, 4H), 6.96 (d, $J$ = 6.8 Hz, 2H), 6.77-6.73 (m, 2H), 5.37 (s, 1H), 2.44 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$; $\delta$, ppm) 150.8, 147.0, 146.3, 140.3, 137.6, 136.8, 133.0, 129.4, 129.0, 128.6, 128.2, 127.6, 127.5(7), 127.5(5), 126.6, 126.1, 126.0, 125.9, 123.9, 123.7(1), 123.7(6), 121.8, 117.6, 116.7, 43.0, 21.3. IR (film, v, cm$^{-1}$) 3024, 1487, 1387, 1234, 1090, 814, 749. HR-MS (APCI) m/z calcd for C$_{30}$H$_{23}$O $[\text{M+H}]^+$ 399.1749, found 399.1750.

7-phenyl-6-(m-tolyl)-7H-benzo[c]xanthene (4c)

70.0 mg, 88%; white solid, mp 185-186 °C; $^1$H NMR (400 MHz, CDCl$_3$; $\delta$, ppm) 8.57 (d, $J$ = 8.4 Hz, 1H), 7.80 (d, $J$ = 8.0 Hz, 1H), 7.64-7.60 (m, 1H), 7.58-7.53 (m, 1H), 7.42 (s, 1H), 7.33 (d, $J$ = 8.0 Hz, 1H), 7.24-7.15 (m, 4H), 7.05-6.99 (m, 4H), 6.90 (s, 1H), 6.81-6.71 (m, 3H), 5.31 (s, 1H), 2.29 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$; $\delta$, ppm) 150.7, 146.9, 146.5, 140.5, 140.4, 137.4, 133.0, 130.4, 129.0, 128.2, 127.8, 127.7, 127.6, 127.5(2), 127.5(8), 126.7, 126.4, 126.1, 125.9, 125.8, 123.7, 123.6, 121.8, 117.5, 116.7, 43.1, 21.4. IR (film, v, cm$^{-1}$) 3021, 1487, 1387, 1234, 1090, 883, 750. HR-MS (APCI) m/z calcd for C$_{30}$H$_{23}$O $[\text{M+H}]^+$ 399.1749, found 399.1754.

6-(4-ethylphenyl)-7-phenyl-7H-benzo[c]xanthene (4d)

66.7 mg, 81%; white solid, mp 156-157 °C; $^1$H NMR (400 MHz, CDCl$_3$; $\delta$, ppm) 8.56 (d, $J$ = 8.0 Hz, 1H), 7.80 (d, $J$ = 8.0 Hz, 1H), 7.64-7.54 (m, 2H), 7.43 (s, 1H), 7.33 (d, $J$ = 8.4 Hz, 1H), 7.25-7.21 (m, 1H), 7.17 (d, $J$ = 7.6 Hz, 3H), 7.05-6.94 (m, 6H), 6.75-6.70 (m, 2H), 5.39 (s, 1H), 2.77-2.71 (m, 2H), 1.33 (t, $J$ = 7.6 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$; $\delta$, ppm) 150.7, 146.9, 146.4, 143.3, 140.3, 137.8, 133.0, 129.4, 129.1, 128.2, 127.6, 127.5, 127.4, 126.7, 126.0, 125.9, 123.8, 123.7, 123.6, 121.8, 117.6, 116.7, 42.9, 28.7, 15.9. IR (film, v, cm$^{-1}$) 3026, 1487, 1383, 1235, 1090, 852, 751. HR-MS (APCI) m/z calcd for C$_{31}$H$_{25}$O $[\text{M+H}]^+$ 413.1905, found 413.1909.
6-(4-(tert-butyl)phenyl)-7-phenyl-7H-benzo[c]xanthene (4e)

69.5 mg, 79%; white solid, mp 202-203 °C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) 8.57 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.64-7.60 (m, 1H), 7.57-7.53 (m, 1H), 7.45 (s, 1H), 7.38-7.32 (m, 3H), 7.25-7.21 (m, 1H), 7.17-7.15 (m, 1H), 7.03-6.97 (m, 6H), 6.71-6.67 (m, 2H), 5.42 (s, 1H), 1.42 (s, 9H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) 150.6, 150.1, 146.8, 146.4, 140.3, 137.6, 133.0, 129.2, 129.1, 128.1, 127.6(7), 127.6(5), 127.5, 126.6, 126.0, 125.8, 125.7, 124.8, 123.7(2), 123.7(9), 123.6, 121.8, 117.6, 116.6, 42.8, 34.6, 31.5. IR (film, ν, cm⁻¹) 3023, 1485, 1389, 1253, 1174, 1087, 830, 747. HR-MS (APCI) m/z calcd for C₃₃H₂₉O [M+H⁺] 441.2218, found 441.2220.

6-(4-methoxyphenyl)-7-phenyl-7H-benzo[c]xanthene (4f)

52.2 mg, 63%; white solid, mp 196-197 °C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) 8.57 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.65-7.53 (m, 2H), 7.42 (s, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.26-7.17 (m, 2H), 7.06-6.96 (m, 6H), 6.88 (d, J = 8.0 Hz, 2H), 6.77 (d, J = 6.8 Hz, 2H), 5.37 (s, 1H), 3.89 (s, 3H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) 158.9, 150.8, 147.0, 146.4, 140.0, 133.0(2), 133.0(8), 130.6, 129.0, 128.3, 127.6, 127.5, 126.7, 126.1, 125.9(8), 125.9(5), 124.0, 123.7(9), 123.7(6), 121.8, 117.8, 116.7, 113.3, 55.4, 43.0. IR (film, ν, cm⁻¹) 3026, 1487, 1388, 1254, 1091, 825. HR-MS (APCI) m/z calcd for C₃₀H₂₃O₂ [M+H⁺] 415.1698, found 415.1703.

6-(4-fluorophenyl)-7-phenyl-7H-benzo[c]xanthene (4g)

66.7 mg, 83%; white solid, mp 184-185 °C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) 8.57 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.65-7.54 (m, 2H), 7.39 (s, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.25-7.21 (m, 1H), 7.16 (d, J = 7.6 Hz, 1H), 7.01-6.94 (m, 8H), 6.76-6.72 (m, 2H), 5.29 (s, 1H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) 162.2(¹JCF = 244.4Hz), 150.5, 147.0, 146.3, 139.3, 136.5(¹JCF = 3.3Hz), 132.9, 131.1(¹JCF = 7.9Hz), 129.1, 128.3, 127.7, 127.5, 126.8, 126.2, 126.1, 125.4, 123.9, 123.8, 123.7, 121.9, 117.3, 116.7, 114.7(¹JCF = 21.2 Hz), 43.0. IR
(film, ν, cm\(^{-1}\)) 3030, 1487, 1386, 1232, 1092, 830, 748. HR-MS (APCI) m/z calcd for C\(_{29}H_{20}FO\) [M+H]\(^+\) 403.1498, found 403.1497.

**6-(4-chlorophenyl)-7-phenyl-7H-benzo[c]xanthene (4h)**

63.5 mg, 76%; white solid, mp 196-197 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\); \(\delta\), ppm) 8.56 (d, \(J = 8.4\) Hz, 1H), 7.80 (d, \(J = 8.0\) Hz, 1H), 7.65-7.54 (m, 2H), 7.38 (s, 1H), 7.34-7.27 (m, 3H), 7.25-7.20 (m, 1H), 7.18-7.14 (m, 1H), 7.07-6.92 (m, 6H), 6.78-6.73 (m, 2H), 5.28 (s, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\); \(\delta\), ppm) 150.5, 147.0, 146.2, 139.0, 133.2, 132.9, 129.0, 128.4, 128.0, 127.7, 127.5(8), 127.5(5), 126.9, 126.3, 126.2, 125.4, 123.9, 123.8(9), 123.8(6), 121.9, 117.1, 116.7, 43.0. IR (film, ν, cm\(^{-1}\)) 3028, 1487, 1386, 1233, 1087, 848, 747. HR-MS (APCI) m/z calcd for C\(_{29}H_{20}ClO\) [M+H]\(^+\) 419.1203, found 419.1208.

**6-(4-bromophenyl)-7-phenyl-7H-benzo[c]xanthene (4i)**

72.1 mg, 78%; white solid, mp 192-193 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\); \(\delta\), ppm) 8.54-8.50 (m, 1H), 7.81 (d, \(J = 8.0\) Hz, 1H), 7.65-7.60 (m, 1H), 7.58-7.53 (m, 1H), 7.43 (s, 1H), 7.40-7.32 (m, 3H), 7.31-7.27 (m, 2H), 7.21 (d, \(J = 8.4\) Hz, 1H), 7.08-6.97 (m, 5H), 6.70-6.66 (m, 2H), 5.31 (s, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\); \(\delta\), ppm) IR (film, ν, cm\(^{-1}\)) 149.8, 146.6, 145.6, 140.2, 140.1, 133.0, 131.7, 130.6, 129.4, 128.4, 128.0, 127.8, 127.6, 127.4, 127.3, 126.9, 126.4, 126.1, 124.1, 123.6, 121.7, 118.5, 116.8, 115.8, 42.8. IR (film, ν, cm\(^{-1}\)) 3041, 1487, 1385, 1234, 1092, 827, 755. HR-MS (APCI) m/z calcd for C\(_{29}H_{20}BrO\) [M+H]\(^+\) 463.0698, found 463.0691.

**6-butyl-7-phenyl-7H-benzo[c]xanthene (4j)**

35.7 mg, 49%; white solid, mp 140-141 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\); \(\delta\), ppm) 8.51-8.48 (m, 1H), 7.78-7.74 (m, 1H), 7.57-7.49 (m, 2H), 7.40-7.35 (m, 2H), 7.31-7.27 (m, 1H), 7.24-7.17 (m, 5H), 7.13-7.08 (m, 1H), 7.07-7.03 (m, 1H), 5.46 (s, 1H), 2.81-2.73 (m, 1H), 2.61-2.52 (m, 1H), 1.66-1.57 (m, 1H), 1.42-1.34 (m, 3H), 0.90 (t, \(J = 7.2\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\); \(\delta\), ppm) 150.6, 147.1, 146.2, 139.1, 133.4, 128.9, 128.8, 127.6, 127.4, 126.9, 126.5, 126.3, 125.7, 125.1, 123.5, 123.0, 122.2, 121.8, 117.8, 116.7, 42.8, 32.8, 32.2, 22.8,
14.0. IR (film, ν, cm⁻¹) 3021, 1487, 1394, 1258, 1098, 848, 750. HR-MS (APCI) m/z calcd for C₁₂H₁₀O [M+H]^+ 365.1905, found 365.1907.

9-fluoro-6,7-diphenyl-7H-benzo[c]xanthene (4l)

![9-fluoro-6,7-diphenyl-7H-benzo[c]xanthene (4l)]

57.9 mg, 72%; white solid, mp 164-165 °C; ¹H NMR (400 MHz, CDCl₃; δ, ppm). 8.56-8.52 (m, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.64-7.60 (m, 1H), 7.59-7.54 (m, 1H), 7.43 (s, 1H), 7.38-7.27 (m, 4H), 7.08-6.99 (m, 5H), 6.95-6.90 (m, 1H), 6.86-6.83 (m, 1H), 6.71-6.67 (m, 2H), 5.32 (s, 1H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) 158.7 (Jₐ = 239.9Hz), 146.8 (Jₐ = 2.1Hz), 145.7, 140.4, 140.1, 133.0, 129.4, 128.3, 127.9, 127.5, 127.4, 127.2, 127.0 (Jₐ = 7.5Hz), 126.8, 126.4, 126.1, 123.9, 123.6, 121.8, 117.8 (Jₐ = 8.3Hz), 116.4, 115.0 (Jₐ = 23.1Hz), 114.6 (Jₐ = 23.5Hz), 43.1. IR (film, ν, cm⁻¹) 3023, 1490, 1394, 1214, 1026, 852, 766. HR-MS (APCI) m/z calcd for C₁₉H₁₅F [M+H]^+ 403.1498, found 403.1497.

9-bromo-6,7-diphenyl-7H-benzo[c]xanthene (4m)

![9-bromo-6,7-diphenyl-7H-benzo[c]xanthene (4m)]

55.4 mg, 60%; white solid, mp 209-210 °C; ¹H NMR (400 MHz, CDCl₃; δ, ppm). 8.57 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.66-7.62 (m, 1H), 7.59-7.55 (m, 1H), 7.45 (d, J = 8.4 Hz, 2H), 7.39 (s, 1H), 7.35-7.31 (m, 1H), 7.25-7.21 (m, 1H), 7.18-7.15 (m, 1H), 7.06-7.01 (m, 4H), 6.92 (d, J = 5.6 Hz, 2H), 6.78-6.75 (m, 2H), 5.29 (s, 1H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) 150.5, 147.1, 146.2, 139.5, 139.0, 132.9, 131.2, 131.0, 129.0, 128.4, 127.7, 127.5(0), 127.5(6), 126.9, 126.3, 126.2, 125.4, 123.9, 123.8(8), 123.8(5), 121.9, 121.4, 117.0, 116.7, 43.0. IR (film, ν, cm⁻¹) 3056, 1492, 1394, 1254, 1091, 850, 757. HR-MS (APCI) m/z calcd for C₁₉H₁₅BrO [M+H]^+ 463.0698, found 463.0693.

3-chloro-6-(4-chlorophenyl)-7-phenyl-7H-benzo[c]xanthene (4n)

![3-chloro-6-(4-chlorophenyl)-7-phenyl-7H-benzo[c]xanthene (4n)]

55.1 mg, 61%; white solid, mp 196-197 °C; ¹H NMR (400 MHz, CDCl₃; δ, ppm). 8.55 (d, J = 2.0 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.54-7.50 (m, 1H), 7.38-7.30 (m, 4H), 7.28-7.24 (m, 1H), 7.19-7.16 (m, 1H), 7.09-7.03 (m, 4H), 6.98 (s, 2H), 6.78-6.73 (m, 2H), 5.29 (s, 1H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) 150.7, 146.9, 146.4, 143.3, 140.3, 137.8, 133.0, 129.4, 129.1, 128.2, 127.6, 127.5, 127.4, 126.7, 126.0, 125.9, 123.8, 123.7, 123.7, 123.6,
121.8, 117.6, 116.7, 42.9, 28.7, 15.9. IR (film, ν, cm⁻¹) 3014, 1493, 1382, 1250, 1098, 887, 748. HR-MS (APCI) m/z calcd for C₂₉H₁₉Cl₂O [M+H]⁺ 453.0813, found 453.0819.

6-phenyl-7-(p-tolyl)-7H-benzo[c]xanthene (4o)

![Image of 6-phenyl-7-(p-tolyl)-7H-benzo[c]xanthene (4o)]

60.5 mg, 76%; white solid, mp 160-161 °C; ¹H NMR (400 MHz, CDCl₃; δ, ppm). 8.56 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.63-7.59 (m, 1H), 7.56-7.53 (m, 1H), 7.43 (s, 1H), 7.38-7.30 (m, 4H), 7.23-7.19 (m, 1H), 7.16-7.14 (m, 1H), 7.09 (s, 2H), 7.02-6.98 (m, 1H), 6.81 (d, J = 8.0 Hz, 2H), 6.60 (d, J = 8.0 Hz, 2H), 5.31 (s, 1H), 2.17 (s, 3H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) 150.8, 147.0, 143.4, 140.6, 135.6, 132.9, 129.5, 128.9(4), 128.9(2), 127.9, 127.5, 127.2, 127.1, 126.6, 126.1, 125.9, 123.8, 123.7, 121.8, 117.6, 116.6, 42.9, 20.9. IR (film, ν, cm⁻¹) 3021, 1485, 1391, 1238, 1088, 820, 752. HR-MS (APCI) m/z calcd for C₃₀H₂₃O [M+H]⁺ 399.1749, found 399.1740.

4,6a',12'-triphenyl-12',12a'-dihydro-6a'H-spiro[chroman-2,5'-isochromeno[3,4-b]chromene] (5a)

4,12'-diphenyl-6a'-(p-tolyl)-12',12a'-dihydro-6a'H-spiro[chroman-2,5'-isochromeno[3,4-b]chromene] (5b)

63.4 mg, 53%; white solid, mp 227-228 °C; ¹H NMR (400 MHz, CDCl₃; δ, ppm). 7.34-7.26 (m, 9H), 7.24 (s, 2H), 7.20-7.14 (m, 3H), 7.04-6.92 (m, 5H), 6.96-6.92 (m, 1H), 6.89-6.84 (m, 2H), 6.80 (d, J = 7.6 Hz, 1H), 6.73 (d, J = 7.6 Hz, 1H), 6.53-6.49 (m, 1H), 6.29 (d, J = 7.2 Hz, 1H), 4.57-4.50 (m, 1H), 4.15 (d, J = 10.8 Hz, 1H), 3.88 (s, 3H), 2.50 (s, 2H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) 152.6, 151.9, 143.9, 141.9, 140.5, 135.7, 134.9, 130.2, 129.2(0), 129.2(5), 129.1, 128.6(3), 128.6(5), 128.5, 128.3, 128.0, 127.9, 127.8, 127.6, 127.5(9), 127.5(5), 127.2, 126.9, 126.8, 125.9, 124.3, 121.3, 120.9, 117.9, 117.1, 99.3, 99.1, 48.0, 45.3, 45.2, 38.8. IR (film, ν, cm⁻¹) 3022, 1487, 1455, 1227, 1003, 884, 750. HR-MS (APCI) m/z calcd for C₄₂H₃₃O₃ [M+H]⁺ 585.2430, found 585.2433.
3.92 (d, $J = 10.4$ Hz, 1H), 2.52-2.45 (m, 2H), 2.30 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$; $\delta$, ppm) 150.5, 149.8, 144.1, 142.1, 140.7, 135.7, 135.0, 130.4, 130.2, 130.0, 129.4, 129.3, 129.1, 128.6, 128.5, 128.4, 128.2, 128.2, 127.9, 127.7, 127.6, 127.4, 127.1, 126.9, 126.7, 125.5, 123.9, 117.7, 116.9, 99.2, 99.1, 48.1, 45.7, 45.4, 38.8, 20.7. IR (film, $\nu$, cm$^{-1}$) 3028, 1486, 1451, 1230, 1005, 823, 758. HR-MS (APCI) m/z calcd for C$_{44}$H$_{35}$O$_3$ [M+H]$^+$ 599.2586, found 599.2587.

4,12'-diphenyl-6a'-(m-tolyl)-12',12a'-dihydro-6a'H-spiro[chroman-2,5'-isochromeno[3,4-b]chromene] (5c)

IR (film, $\nu$, cm$^{-1}$) 3028, 1486, 1451, 1230, 1005, 823, 758. HR-MS (APCI) m/z calcd for C$_{44}$H$_{35}$O$_3$ [M+H]$^+$ 599.2586, found 599.2587.

6a'-(4-(tert-butyl)phenyl)-4,12'-diphenyl-12',12a'-dihydro-6a'H-spiro[chroman-2,5'-isochromeno[3,4-b]chromene] (5d)

HR-MS (APCI) m/z calcd for C$_{46}$H$_{41}$O$_3$ [M+H]$^+$ 641.3056, found 641.3060.

6a'-(4-fluorophenyl)-4,12'-diphenyl-12',12a'-dihydro-6a'H-spiro[chroman-2,5'-isochromeno[3,4-b]chromene] (5e)
69.8 mg, 58%; white solid, mp 285-286 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\); \(\delta\), ppm). 7.37-7.27 (m, 9H), 7.25-7.20 (m, 3H), 7.19-7.14 (m, 2H), 7.03-6.98 (m, 3H), 6.95-6.92 (m, 1H), 6.90-6.84 (m, 4H), 6.80 (d, \(J = 8.0\) Hz, 1H), 6.74 (d, \(J = 8.0\) Hz, 1H), 6.50-6.46 (m, 1H), 6.29 (d, \(J = 7.2\) Hz, 1H), 4.56-4.49 (m, 1H), 4.14 (d, \(J = 10.8\) Hz, 1H), 3.88 (d, \(J = 10.8\) Hz, 1H), 2.52-2.43 (m, 2H). \(^1\)C NMR (100 MHz, CDCl\(_3\); \(\delta\), ppm) 162.4 (\(J_{CF} = 239.9\) Hz), 152.5, 151.8, 143.8, 141.7, 136.5 (\(J_{CF} = 3.3\) Hz), 135.4, 134.8, 130.2, 129.6, 129.5 (\(J_{CF} = 8.3\) Hz), 129.3, 129.2, 129.1, 128.7, 128.5, 128.1, 128.0, 127.9, 127.6, 127.3, 127.0, 126.9, 125.9, 124.2, 121.4, 121.0, 117.7, 117.0, 114.3 (\(J_{CF} = 21.3\)), 99.3, 98.7, 47.9, 45.4, 45.2, 38.7. IR (film, \(\nu\), cm\(^{-1}\)) 3028, 1488, 1449, 1231, 1040, 918, 747. HR-MS (APCI) m/z calcd for C\(_{42}\)H\(_{32}\)FO\(_3\) [M+H]\(^+\) 603.2335, found 603.2343.

6a'-phenyl-4,12'-di-p-tolyl-12',12a'-dihydro-6a'H-spiro[chroman-2,5'-isochromeno[3,4-b]chromene] (5e)

77.1 mg, 63%; white solid, mp 234-235 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\); \(\delta\), ppm) 7.38 (d, \(J = 7.2\) Hz, 2H), 7.33-7.29 (m, 6H), 7.25-7.22 (m, 3H), 7.21-7.15 (m, 4H), 7.02-6.94 (m, 5H), 6.83 (d, \(J = 8.0\) Hz, 1H), 6.55 (d, \(J = 26.4\) Hz, 2H), 6.37 (d, \(J = 8.4\) Hz, 1H), 6.28 (d, \(J = 8.0\) Hz, 1H), 4.49-4.44 (m, 1H), 4.09 (d, \(J = 10.4\)Hz, 1H), 3.89 (d, \(J = 10.8\) Hz, 1H), 2.47-2.41 (m, 2H), 2.19 (s, 3H), 2.18 (s, 3H). \(^1\)C NMR (100 MHz, CDCl\(_3\); \(\delta\), ppm) 150.5, 149.8, 144.1, 142.1, 140.7, 135.7, 135.0, 130.4, 130.2, 130.0, 129.4, 129.3, 129.1, 128.6, 128.5, 128.4, 128.3, 128.2(3), 128.2(9), 127.9, 127.7, 127.6, 127.4, 127.3, 127.1, 126.9, 126.7, 125.5, 123.9, 117.7, 116.9, 99.2, 99.1, 48.1, 45.7, 45.4, 38.8, 20.7. IR (film, \(\nu\), cm\(^{-1}\)) 3025, 1485, 1450, 1232, 1004, 912, 754. HR-MS (APCI) m/z calcd for C\(_{44}\)H\(_{37}\)O\(_3\) [M+H]\(^+\) 613.2743, found 613.2749.
$^1$H NMR Spectrum of Compound 3a
$^{13}$C NMR Spectrum of Compound 3a
$^1$H NMR Spectrum of Compound 3b
$^{13}$C NMR Spectrum of Compound 3b
$^1$H NMR Spectrum of Compound 3c
$^{13}$C NMR Spectrum of Compound 3c
$^{13}$C NMR Spectrum of Compound 3d
$^1$H NMR Spectrum of Compound 3e
$^{13}$C NMR Spectrum of Compound 3e
$^1$H NMR Spectrum of Compound 3f
$^{13}$C NMR Spectrum of Compound 3f
$^{19}$F NMR Spectrum of Compound 3f
$^1$H NMR Spectrum of Compound 3g
$^{13}$C NMR Spectrum of Compound 3g
$^1$H NMR Spectrum of Compound 3h
$^{13}$C NMR Spectrum of Compound 3h
$^1$H NMR Spectrum of Compound 3j
$^{13}$C NMR Spectrum of Compound 3j
$^{19}$F NMR Spectrum of Compound 3j
$^1$H NMR Spectrum of Compound 3k
$^{13}$C NMR Spectrum of Compound 3k
$^1$H NMR Spectrum of Compound 3k

![NMR Spectrum of Compound 3k](image)
$^1$H NMR Spectrum of Compound 3l
$^{13}$C NMR Spectrum of Compound 31
$^1$H NMR Spectrum of Compound 3m
$^{13}$C NMR Spectrum of Compound 3m
$^1$H NMR Spectrum of Compound 3n
$^{13}$C NMR Spectrum of Compound 3n
$^1$H NMR Spectrum of Compound 3o
$^{13}$C NMR Spectrum of Compound 3o
$^1$H NMR Spectrum of Compound 4a
$^{13}$C NMR Spectrum of Compound 4a
$^1$H NMR Spectrum of Compound 4b
$^{13}$C NMR Spectrum of Compound 4b
$^1$H NMR Spectrum of Compound 4c
$^{13}$C NMR Spectrum of Compound 4c
\(^1\text{H NMR Spectrum of Compound 4d}\)
$^{13}$C NMR Spectrum of Compound 4d
$^1$H NMR Spectrum of Compound 4e
$^{13}$C NMR Spectrum of Compound 4e
$^1$H NMR Spectrum of Compound 4f
$^{13}$C NMR Spectrum of Compound 4f
$^1$H NMR Spectrum of Compound 4g
$^{13}$C NMR Spectrum of Compound 4g
$^{19}$F NMR Spectrum of Compound 4g
$^1$H NMR Spectrum of Compound 4h
$^{13}$C NMR Spectrum of Compound 4h
$^1$H NMR Spectrum of Compound 4i
$^{13}$C NMR Spectrum of Compound 4i
$^1$H NMR Spectrum of Compound 4j
$^{13}$C NMR Spectrum of Compound 4j
$^1$H NMR Spectrum of Compound 4l
$^{13}$C NMR Spectrum of Compound 4I
$^{19}$F NMR Spectrum of Compound 4l
$^1$H NMR Spectrum of Compound 4m
$^{13}$C NMR Spectrum of Compound 4m
$^1$H NMR Spectrum of Compound 4n
$^{13}$C NMR Spectrum of Compound 4n
$^1$H NMR Spectrum of Compound 4o
$^{13}$C NMR Spectrum of Compound 4o
$^1$H NMR Spectrum of Compound 5a
$^{13}$C NMR Spectrum of Compound 5a
\(^{13}\)C NMR Spectrum of Compound 5b
$^{1}$H NMR Spectrum of Compound 5c
$^{13}$C NMR Spectrum of Compound 5c
$^1$H NMR Spectrum of Compound 5d
$^{13}$C NMR Spectrum of Compound 5d
$^1$H NMR Spectrum of Compound 5e

587
$^{13}$C NMR Spectrum of Compound 5e
$^{19}$F NMR Spectrum of Compound 5e
$^1$H NMR Spectrum of Compound 5f
$^{13}$C NMR Spectrum of Compound 5f