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# **Supporting Information**

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#### **General methods**

Proton (<sup>1</sup>H NMR) and carbon (<sup>13</sup>C NMR) nuclear magnetic resonance spectra were recorded at 300 or 500 MHz and 75 or 126 MHz, respectively. The chemical shifts are given in parts per million (ppm) on the delta ( $\delta$ ) scale. The solvent peak was used as a reference value, for <sup>1</sup>H NMR: CDCl<sub>3</sub> = 7.27 ppm, C<sub>6</sub>D<sub>6</sub> = 7.16 ppm; for <sup>13</sup>C NMR: CDCl<sub>3</sub> = 77.23 ppm, C<sub>6</sub>D<sub>6</sub> = 128.06 ppm. Analytical TLC was performed on precoated silica gel GF254 plates. Column chromatography was carried out on silica gel (200–300 mesh). HRMS were carried out on an Orbitrap analyzer. Optical rotations were measured using a 2.5 mL cell with a 10 cm path length on Hanon P850 Automatic Polarimeter and concentrations (c) were reported in g×(100 mL)<sup>-1</sup>. Enantiomeric excesses were determined by HPLC using a Daicel Chiralpak AD-H, OD-H column with hexane/*i*-PrOH as the eluent.

#### **General procedures**

#### Procedure A for the synthesis of ketal substrates



A solution of lactone **A** (1 mmol, 1.0 equiv) and THF (2 mL) was cooled to -78 °C. Then RMgBr (1.2 mmol, 1.2 equiv) was added dropwise, and the reaction was stirred at -78 °C for 5-12 h. H<sub>2</sub>O was then added, and the mixture was warmed to room temperature. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the combined organic layers were washed with sat. brine, dried, filtered and concentrated. The residue was purified by silica gel chromatography (EtOAc/petroleum ether) to give hemiketal **B** as an oil, which was used as such. To a solution of **B** in MeOH was added *p*-TsOH (0.05 mmol, 0.05 equiv). The mixture was then stirred at room temperature for 12 h. K<sub>2</sub>CO<sub>3</sub> (0.5 mmol, 0.5 equiv) was added, and the mixture was concentrated. CH<sub>2</sub>Cl<sub>2</sub> was added to the resulting solid, and the mixture was filtered through a short pad of Celite. The filtrate was then concentrated. The crude material was then purified by silica gel chromatography (EtOAc/hexanes with 2% Et<sub>3</sub>N) to give ketal substrate **3** or **8**.<sup>1</sup>

# Procedure B for the asymmetric transfer hydrogenation of 6*H*-benzo[c]chromene-based ketals

To a solution of ketals **3** or **8** (0.1 mmol, 1.0 eq) in CH<sub>2</sub>Cl<sub>2</sub> (0.4 mL) and MTBE (2.6 mL) was added 5 Å molecular sieves (30 mg), Hantzsch ester **6** (0.14 mmol, 1.4 eq), and chiral imidodiphosphoric acid **7i** (5 mol%). The solution was stirred at room temperature for 48 h before it was quenched by saturated aqueous NaHCO<sub>3</sub>, extracted with EtOAc (10 mL  $\times$  3). The combined organic layer was dried over MgSO<sub>4</sub>, filtered

and evaporated under vacuum. The residue was purified by flash column chromatography to give the desired product.

# Procedure C for the asymmetric transfer hydrogenation of 1*H*-isochromene-based ketals

To a solution of **10** (0.1 mmol, 1.0 eq) was added in CH<sub>2</sub>Cl<sub>2</sub> (0.4 mL) and MTBE (4.0 mL) was added 5 Å molecular sieves (30 mg), Hantzsch ester **6** (0.14 mmol, 1.4 eq), and chiral imidodiphosphoric acid **7g** (5 mol%). The solution was stirred at room temperature for 48 h before it was quenched by saturated aqueous NaHCO<sub>3</sub>, extracted with EtOAc (10 mL  $\times$  3). The combined organic layer was dried over MgSO<sub>4</sub>, filtered and evaporated under vacuum. The residue was purified by flash column chromatography to give the desired product.

#### Analytical data for products



### 6-Methoxy-6-(4-methoxyphenyl)-6*H*-benzo[*c*]chromene (3a)

It was prepared following the general procedure A and purified by flash chromatography on silica gel by saturated Et<sub>3</sub>N using ethyl acetate/petroleum ether (5:95) as eluent to afford **3a** (280.2 mg, 88%). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.68 (dd, J = 7.8, 1.5 Hz, 1H), 7.65–7.56 (m, 3H), 7.21–7.16 (m, 1H), 7.15–7.07 (m, 3H), 7.02–6.90 (m, 2H), 6.82–6.75 (m, 2H), 3.27 (s, 3H), 3.23 (s, 3H); <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  160.3, 152.1, 134.9, 132.4, 130.2, 129.8, 129.5, 129.1, 127.8, 127.5, 123.4, 122.6, 122.5, 122.2, 118.30, 113.9, 103.4, 54.8, 51.6; HRMS (EI) m/z [M + H]<sup>+</sup> calculated for C<sub>21</sub>H<sub>19</sub>O<sub>3</sub>:319.1329, found 319.1317.



#### **3,6-Dimethoxy-6-(4-methoxyphenyl)-6***H***-benzo**[*c*]**chromene (3b)**

It was prepared following the general procedure A and purified by flash chromatography on silica gel by saturated Et<sub>3</sub>N using ethyl acetate/petroleum ether (5:95) as eluent to afford **3b** (313.1 mg, 90%). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.68–7.55 (m, 4H), 7.20–7.16 (m, 1H), 7.16–7.09 (m, 1H), 7.03–6.95 (m, 1H), 6.83–6.76 (m, 3H), 6.65 (dd, *J* = 8.7, 2.6 Hz, 1H), 3.31 (s, 3H), 3.28 (s, 6H); <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  161.8, 160.2, 153.5, 133.5, 133.0, 130.5, 129.4, 129.1, 127.6, 126.9, 124.4,

121.44, 115.3, 113.9, 109.5, 103.9, 103.1, 55.0, 54.8, 51.5; HRMS (EI) *m*/*z* [M + H]<sup>+</sup> calculated for C<sub>22</sub>H<sub>21</sub>O<sub>4</sub>:349.1434, found 349.1445.



#### 6-Methoxy-6-(4-methoxyphenyl)-3-methyl-6*H*-benzo[*c*]chromene (3c)

It was prepared following the general procedure A and purified by flash chromatography on silica gel by saturated Et<sub>3</sub>N using ethyl acetate/petroleum ether (5:95) as eluent to afford **3c** (282.4 mg, 85%). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.68–7.58 (m, 4H), 7.22–7.17 (m, 1H), 7.15–7.09 (m, 1H), 7.04–6.96 (m, 2H), 6.83–6.75 (m, 3H), 3.27 (s, 6H), 2.13 (s, 3H); <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  160.2, 152.1, 140.0, 134.4, 132.8, 130.4, 129.5, 129.1, 127.6, 127.4, 123.4, 123.22, 121.9, 119.8, 118.7, 113.9, 103.5, 54.8, 51.6, 21.4; HRMS (EI) *m/z* [M + H]<sup>+</sup> calculated for C<sub>22H21O3</sub>:333.1485, found 333.1476.



#### 6-Methoxy-6-(4-methoxyphenyl)-2-methyl-6*H*-benzo[*c*]chromene (3d)

It was prepared following the general procedure A and purified by flash chromatography on silica gel by saturated Et<sub>3</sub>N using ethyl acetate/petroleum ether (5:95) as eluent to afford **3d** (272.3 mg, 82%). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.74–7.63 (m, 3H), 7.59 (d, *J* = 1.4 Hz, 1H), 7.26–7.16 (m, 3H), 7.10–6.96 (m, 2H), 6.89–6.82 (m, 2H), 3.34 (s, 3H), 3.31 (s, 3H), 2.23 (s, 3H); <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  160.3,

149.9, 135.1, 132.4, 131.5, 130.5, 130.3, 129.6, 129.0, 127.5, 123.8, 122.4, 122.2, 118.1, 113.9, 103.3, 54.8, 51.6, 21.0; HRMS (EI) m/z [M + H]<sup>+</sup> calculated for C<sub>22</sub>H<sub>21</sub>O<sub>3</sub>:333.1485, found 333.1499.



#### 6,9-Dimethoxy-6-(4-methoxyphenyl)-6*H*-benzo[*c*]chromene (3e)

It was prepared following the general procedure A and purified by flash chromatography on silica gel by saturated Et<sub>3</sub>N using ethyl acetate/petroleum ether (5:95) as eluent to afford **3e** (302.2 mg, 87%). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.70–7.61 (m, 3H), 7.33 (d, *J* = 2.5 Hz, 1H), 7.22–7.17 (m, 1H), 7.15–7.10 (m, 1H), 7.10–7.05 (m, 1H), 6.96–6.88 (m, 1H), 6.86–6.78 (m, 2H), 6.63 (dd, *J* = 8.6, 2.5 Hz, 1H), 3.30 (d, *J* = 6.6 Hz, 6H), 3.25 (s, 3H); <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  160.7, 160.2, 152.4, 132.9, 131.6, 129.9, 129.5, 129.2, 127.7, 123.4, 122.5, 122.4, 118.3, 113.9, 113.8, 107.2, 103.5, 54.9, 54.8, 51.6; HRMS (EI) *m/z* [M + H]<sup>+</sup> calculated for C<sub>22</sub>H<sub>21</sub>O<sub>4</sub>:349.1434, found 349.1420.



#### 6,8-Dimethoxy-6-(4-methoxyphenyl)-6H-benzo[c]chromene (3f)

It was prepared following the general procedure A and purified by flash chromatography on silica gel by saturated Et<sub>3</sub>N using ethyl acetate/petroleum ether (5:95) as eluent to afford **3f** (308.7 mg, 89%). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.70–7.61 (m, 3H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.21–7.17 (m, 1H), 7.14–7.06 (m, 1H), 7.01–6.93

(m, 1H), 6.85 (d, J = 2.6 Hz, 1H), 6.83–6.73 (m, 3H), 3.26 (d, J = 4.0 Hz, 6H), 3.19 (s, 3H); <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  160.2, 160.0, 151.5, 136.3, 132.6, 129.4, 128.8, 123.8, 123.3, 122.8, 122.6, 122.52, 118.2, 115.3, 113.9, 112.8, 103.5, 54.8, 54.7, 51.6; HRMS (EI) m/z [M + H]<sup>+</sup> calculated for C<sub>22</sub>H<sub>21</sub>O<sub>4</sub> : 349.1434, found 349.1427.



#### 6-(4-Ethoxyphenyl)-6,9-dimethoxy-6*H*-benzo[c]chromene (8a)

It was prepared following the general procedure A and purified by flash chromatography on silica gel by saturated Et<sub>3</sub>N using ethyl acetate/petroleum ether (5:95) as eluent to afford **8a** (325.8 mg, 90%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.71–7.63 (m, 3H), 7.33 (d, *J* = 1.9 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.14–7.07 (m, 2H), 6.96–6.89 (m, 1H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.62 (dd, *J* = 8.6, 1.9 Hz, 1H), 3.61–3.53 (m, 2H), 3.30 (s, 3H), 3.26 (s, 3H), 1.10 (t, *J* = 6.9 Hz, 3H); <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  160.7, 159.6, 152.4, 132.8, 131.6, 129.9, 129.5, 129.2, 127.7, 123.4, 122.5, 122.4, 118.3, 114.3, 113.7, 107.2, 103.6, 63.3, 54.9, 51.6, 14.8; HRMS (EI) *m*/*z* [M + H]<sup>+</sup> calculated for C<sub>23</sub>H<sub>23</sub>O<sub>4</sub>:363.1591, found 363.1596.



# Tert-butyl(4-(6,9-dimethoxy-6*H*-benzo[*c*]chromen-6-yl)phenoxy)dimethylsilane (8b)

It was prepared following the general procedure A and purified by flash chromatography on silica gel by saturated Et<sub>3</sub>N using ethyl acetate/petroleum ether

(5:95) as eluent to afford **8b** (362.9 mg, 81%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.68–7.62 (m, 3H), 7.32 (d, *J* = 2.5 Hz, 1H), 7.19–7.16 (m, 1H), 7.14–7.09 (m, 1H), 7.06 (d, *J* = 8.6 Hz, 1H), 6.95–6.87 (m, 3H), 6.59 (dd, *J* = 8.6, 2.5 Hz, 1H), 3.31 (s, 3H), 3.24 (s, 3H), 0.99 (s, 9H), 0.10 (d, *J* = 1.7 Hz, 6H); <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  160.7, 156.2, 152.4, 133.8, 131.5, 129.9, 129.6, 129.2, 127.5, 123.4, 122.4, 119.9, 118.3, 113.7, 107.2, 103.5, 54.9, 51.7, 25.9, 18.4, -4.4; HRMS (EI) *m/z* [M + H]<sup>+</sup> calculated for C<sub>27</sub>H<sub>33</sub>O<sub>4</sub>Si :449.2143, found 449.2152.



Tert-butyl(4-(6-methoxy-6*H*-benzo[*c*]chromen-6-yl)phenoxy)dimethylsilane (8c) It was prepared following the general procedure A and purified by flash chromatography on silica gel by saturated Et<sub>3</sub>N using ethyl acetate/petroleum ether (5:95) as eluent to afford 8c (376.2 mg, 90%). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.67 (dd, J = 7.8, 1.4 Hz, 1H), 7.64–7.57 (m, 3H), 7.18 (d, J = 1.3 Hz, 1H), 7.15–7.08 (m, 3H), 7.01–6.90 (m, 2H), 6.90–6.84 (m, 2H), 3.21 (s, 3H), 0.98 (s, 9H), 0.09 (d, J = 0.6 Hz, 6H); <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) δ 156.3, 152.1, 134.8, 133.4, 130.1, 129.8, 129.6, 129.1, 127.9, 127.6, 123.4, 122.5, 122.1, 119.9, 118.3, 103.4, 51.7, 25.8, 18.4, -4.4; HRMS (EI) m/z [M + H]<sup>+</sup> calculated for C<sub>26</sub>H<sub>31</sub>O<sub>3</sub>Si:419.2037, found 419.2022.



#### 6,9-Dimethoxy-6-(4-(methylthio)phenyl)-6*H*-benzo[*c*]chromene (8d)

It was prepared following the general procedure A and purified by flash chromatography on silica gel by saturated Et<sub>3</sub>N using ethyl acetate/petroleum ether (5:95) as eluent to afford **8d** (327.6 mg, 90%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.67 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 2.3 Hz, 1H), 7.21–7.16 (m, 2H), 7.16–7.11 (m, 2H), 7.04 (d, *J* = 8.6 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.63 (dd, *J* = 8.6, 2.3 Hz, 1H), 3.32 (s, 3H), 3.23 (s, 3H), 1.98 (s, 3H); <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  160.7, 152.2, 139.7, 137.4, 131.5, 130.0, 129.1, 128.7, 127.2, 126.2, 123.4, 122.5, 122.4, 118.3, 113.8, 107.2, 103.3, 54.9, 51.7, 15.0; HRMS (EI) *m*/*z* [M + H]<sup>+</sup> calculated for C<sub>22</sub>H<sub>21</sub>O<sub>3</sub>S :365.1206, found 365.1211.



#### 6,9-Dimethoxy-6-(p-tolyl)-6*H*-benzo[*c*]chromene (8e)

It was prepared following the general procedure A and purified by flash chromatography on silica gel by saturated Et<sub>3</sub>N using ethyl acetate/petroleum ether (5:95) as eluent to afford **8e** (295.5 mg, 89%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.71–7.62 (m, 3H), 7.32 (d, *J* = 2.5 Hz, 1H), 7.21–7.17 (m, 1H), 7.14–7.09 (m, 1H), 7.05 (t, *J* = 8.5 Hz, 3H), 6.95–6.89 (m, 1H), 6.59 (dd, *J* = 8.6, 2.5 Hz, 1H), 3.30 (s, 3H), 3.24 (s, 3H), 2.11 (s, 3H); <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  160.7, 152.4, 138.1, 137.9, 131.5, 129.9, 129.2, 129.2, 128.2, 127.5, 123.4, 122.5, 122.4, 118.3, 113.7, 107.2, 103.5, 54.8, 51.7, 21.1; HRMS (EI) *m*/*z* [M + H]<sup>+</sup> calculated for C<sub>22</sub>H<sub>21</sub>O<sub>3</sub>S:333.1485, found 333.1490.



#### 6-Methoxy-6-(p-tolyl)-6*H*-benzo[*c*]chromene (8f)

It was prepared following the general procedure A and purified by flash chromatography on silica gel by saturated Et<sub>3</sub>N using ethyl acetate/petroleum ether (5:95) as eluent to afford **8f** (247.6 mg, 82%). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.68 (dd, J = 7.8, 1.5 Hz, 1H), 7.66–7.58 (m, 3H), 7.20–7.16 (m, 1H), 7.15–7.07 (m, 3H), 7.02 (d, J = 7.9 Hz, 2H), 6.99–6.90 (m, 2H), 3.22 (s, 3H), 2.09 (s, 3H); <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  152.0, 138.2, 137.5, 134.7, 130.1, 129.8, 129.2, 129.1, 128.3, 127.6, 123.4, 122.6, 122.5, 122.2, 118.3, 103.5, 51.7, 21.1; HRMS (EI) m/z [M + H]<sup>+</sup> calculated for C<sub>21</sub>H<sub>19</sub>O<sub>3</sub>:319.1329, found 319.1320.



#### 6-([1,1'-Biphenyl]-4-yl)-6,9-dimethoxy-6*H*-benzo[*c*]chromene (8g)

It was prepared following the general procedure A and purified by flash chromatography on silica gel by saturated Et<sub>3</sub>N using ethyl acetate/petroleum ether (5:95) as eluent to afford **8g** (358.5 mg, 91%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.81 (d, *J* = 8.2 Hz, 2H), 7.69–7.63 (m, 1H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.50–7.44 (m, 2H), 7.34 (d, *J* = 2.5 Hz, 1H), 7.26–7.18 (m, 3H), 7.15–7.10 (m, 2H), 7.08 (d, *J* = 8.6 Hz, 1H), 6.96–6.90 (m, 1H), 6.60 (dd, *J* = 8.6, 2.5 Hz, 1H), 3.29 (s, 3H), 3.26 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  160.7, 152.3, 141.7, 141.1, 139.8, 131.5, 130.0, 129.2, 129.1, 128.7, 127.7, 127.5, 127.3, 127.2, 123.5, 122.5, 122.4, 118.3, 113.8, 107.3,

54.8, 51.7; HRMS (EI) m/z [M + H]<sup>+</sup> calculated for C<sub>27</sub>H<sub>23</sub>O<sub>3</sub>: 395.1642, found 395.1649.



#### 6,9-Dimethoxy-6-phenyl-6*H*-benzo[*c*]chromene (8h)

It was prepared following the general procedure A and purified by flash chromatography on silica gel by saturated Et<sub>3</sub>N using ethyl acetate/petroleum ether (5:95) as eluent to afford **8h** (286.2 mg, 90%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.77–7.72 (m, 2H), 7.63 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.32 (d, *J* = 2.5 Hz, 1H), 7.23–7.16 (m, 3H), 7.15–7.08 (m, 2H), 6.99 (d, *J* = 8.6 Hz, 1H), 6.94–6.88 (m, 1H), 6.55 (dd, *J* = 8.6, 2.5 Hz, 1H), 3.28 (s, 3H), 3.21 (s, 3H); <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  160.7, 152.3, 140.8, 131.4, 129.9, 129.2, 128.54, 128.4, 128.2, 127.3, 123.4, 122.5, 122.3, 118.3, 113.7, 107.2, 103.4, 54.8, 51.7; HRMS (EI) *m*/*z* [M + H]<sup>+</sup> calculated for C<sub>21</sub>H<sub>19</sub>O<sub>3</sub>: 319.1329, found 319.1340.



#### 6-(4-Chlorophenyl)-6,9-dimethoxy-6*H*-benzo[*c*]chromene (8j)

It was prepared following the general procedure A and purified by flash chromatography on silica gel by saturated Et<sub>3</sub>N using ethyl acetate/petroleum ether (5:95) as eluent to afford **8j** (302.7 mg, 86%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.62 (d, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 2.2 Hz, 1H), 7.16–7.08 (m, 4H), 6.94–6.89 (m, 1H), 6.86 (d, *J* = 8.6 Hz, 1H), 6.59 (dd, *J* = 8.6, 2.3 Hz, 1H), 3.30 (s,

3H), 3.12 (s, 3H); <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  160.8, 152.1, 139.5, 134.7, 131.5, 130.0, 129.6, 129.0, 128.6, 126.6, 123.4, 122.6, 122.1, 118.2, 113.9, 107.2, 103.0, 54.9, 51.6; HRMS (EI) *m*/*z* [M + H]<sup>+</sup> calculated for C<sub>21</sub>H<sub>18</sub>ClO<sub>3</sub>:353.0939, found 353.0930.



#### 6,9-Dimethoxy-6-(3-methoxyphenyl)-6*H*-benzo[*c*]chromene (8k)

It was prepared following the general procedure A and purified by flash chromatography on silica gel by saturated Et<sub>3</sub>N using ethyl acetate/petroleum ether (5:95) as eluent to afford **8k** (361.6 mg, 91%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.64 (d, *J* = 7.8 Hz, 1H), 7.51 (s, 1H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 2.1 Hz, 1H), 7.21–7.16 (m, 2H), 7.13–7.06 (m, 2H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.82 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.57 (dd, *J* = 8.6, 2.2 Hz, 1H), 3.28 (s, 6H), 3.25 (s, 3H); <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  160.3, 160.0, 151.8, 141.9, 131.0, 129.6, 129.1, 128.8, 127.0, 123.1, 122.2, 122.1, 120.3, 118.0, 114.2, 113.4, 113.4, 106.9, 103.1, 54.5, 54.4, 51.4; HRMS (EI) m/z [M + H]<sup>+</sup> calculated for C<sub>22</sub>H<sub>21</sub>O<sub>4</sub>:349.1434, found 349.1446.



#### 6,9-Dimethoxy-6-(m-tolyl)-6H-benzo[c]chromene (8i)

It was prepared following the general procedure A and purified by flash chromatography on silica gel by saturated Et<sub>3</sub>N using ethyl acetate/petroleum ether (5:95) as eluent to afford **8i** (308.7 mg, 93%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.70–7.63 (m, 2H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 1.7 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 2H),

7.12 (t, J = 7.6 Hz, 1H), 7.05 (d, J = 8.6 Hz, 1H), 7.00 (d, J = 7.5 Hz, 1H), 6.92 (t, J = 7.5 Hz, 1H), 6.57 (dd, J = 8.6, 1.7 Hz, 1H), 3.29 (s, 3H), 3.24 (s, 3H), 2.11 (s, 3H); <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  160.7, 152.3, 140.7, 138.0, 131.4, 129.9, 129.3, 129.3, 129.0, 128.3, 127.4, 125.4, 123.4, 122.5, 122.4, 118.3, 113.7, 107.2, 103.5, 54.9, 51.7, 21.5; HRMS (EI) m/z [M + H]<sup>+</sup> calculated for C<sub>22</sub>H<sub>21</sub>O<sub>3</sub>: 333.1485, found 333.1477.



#### 6,9-Dimethoxy-6-(o-tolyl)-6*H*-benzo[*c*]chromene (8m)

It was prepared following the general procedure A and purified by flash chromatography on silica gel by saturated Et<sub>3</sub>N using ethyl acetate/petroleum ether (5:95) as eluent to afford **8m** (285.5 mg, 86%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.95 (dd, J = 7.6, 1.2 Hz, 1H), 7.65 (d, J = 7.5 Hz, 1H), 7.33 (d, J = 2.5 Hz, 1H), 7.21–7.17 (m, 1H), 7.16–7.14 (m, 1H), 7.14–7.09 (m, 2H), 7.09–7.05 (m, 1H), 6.95–6.83 (m, 2H), 6.50 (dd, J = 8.6, 2.5 Hz, 1H), 3.28 (s, 3H), 3.22 (s, 3H), 2.22 (s, 3H); <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  160.7, 152.4, 139.2, 138.5, 132.7, 131.7, 130.1, 129.0, 128.9, 128.2, 126.1, 125.5, 123.4, 122.3, 121.7, 117.9, 113.9, 106.8, 103.4, 54.8, 51.7, 21.6; HRMS (EI) m/z [M + H]<sup>+</sup> calculated for C<sub>22</sub>H<sub>21</sub>O<sub>3</sub>: 333.1485, found 333.1489.



#### 6,9-Dimethoxy-6-(thiophen-2-yl)-6*H*-benzo[*c*]chromene (8n)

It was prepared following the general procedure A and purified by flash chromatography on silica gel by saturated Et<sub>3</sub>N using ethyl acetate/petroleum ether (5:95) as eluent to afford **8n** (265.7 mg, 82%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.55 (d, J

= 7.7 Hz, 1H), 7.30 (d, J = 8.6 Hz, 1H), 7.26 (d, J = 2.4 Hz, 1H), 7.12 (d, J = 8.1 Hz, 1H), 7.06–7.00 (m, 2H), 6.88 (d, J = 5.0 Hz, 1H), 6.85 (t, J = 7.5 Hz, 1H), 6.68–6.65 (m, 1H), 6.63 (dd, J = 8.6, 2.3 Hz, 1H), 3.30 (d, J = 3.6 Hz, 6H); <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  160.9, 152.0, 145.3, 131.6, 130.0, 128.6, 127.1, 126.8, 126.5, 126.4, 123.3, 122.6, 121.9, 118.4, 114.0, 107.2, 102.7, 54.9, 51.8; HRMS (EI) m/z [M + H]<sup>+</sup> calculated for C<sub>19</sub>H<sub>17</sub>O<sub>3</sub>S:325.0893, found 325.0881.



#### 6-(2,2-Diphenylvinyl)-6,9-dimethoxy-6*H*-benzo[*c*]chromene (80)

It was prepared following the general procedure A and purified by flash chromatography on silica gel by saturated Et<sub>3</sub>N using ethyl acetate/petroleum ether (5:95) as eluent to afford **80** (247.8 mg, 59%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.47 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 8.6 Hz, 1H), 7.35–7.29 (m, 2H), 7.18–7.16 (m, 1H), 7.07–7.00 (m, 5H), 7.00–6.95 (m, 1H), 6.92 (s, 1H), 6.88–6.76 (m, 5H), 6.71 (dd, *J* = 8.6, 2.4 Hz, 1H), 3.34 (s, 3H), 3.14 (s, 3H); <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  160.5, 152.5, 146.7, 143.3, 139.9, 131.3, 129.9, 129.7, 129.0, 128.5, 128.1, 127.4, 126.8, 126.5, 122.8, 121.6, 120.1, 117.4, 114.3, 54.9, 50.2; HRMS (EI) *m/z* [M + H]<sup>+</sup> calculated for C<sub>29</sub>H<sub>25</sub>O<sub>3</sub>:421.1798, found 421.1791.



6,9-Dimethoxy-6-(phenylethynyl)-6*H*-benzo[*c*]chromene (8p)

It was prepared following the general procedure A and purified by flash chromatography on silica gel by saturated Et<sub>3</sub>N using ethyl acetate/petroleum ether (5:95) as eluent to afford **8p** (256.5 mg, 75%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  8.00 (d, *J* = 8.5 Hz, 1H), 7.58 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.43–7.38 (m, 2H), 7.26 (d, *J* = 2.4 Hz, 1H), 7.20 (dd, *J* = 8.0, 0.7 Hz, 1H), 7.11–7.06 (m, 1H), 6.96–6.91 (m, 3H), 6.91–6.87 (m, 1H), 6.77 (dd, *J* = 8.5, 2.5 Hz, 1H), 3.62 (s, 3H), 3.30 (s, 3H); <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  161.3, 151.0, 132.3, 129.9, 129.2, 128.6, 128.5, 128.4, 126.1, 123.5, 122.9, 122.5, 122.2, 118.4, 114.0, 107.5, 98.1, 87.8, 85.8, 54.9, 52.2; HRMS (EI) *m/z* [M + H]<sup>+</sup> calculated for C<sub>23</sub>H<sub>18</sub>O<sub>3</sub>:342.1256, found 342.1249.



### 6,9-Dimethoxy-6-methyl-6*H*-benzo[*c*]chromene (8q)

It was prepared following the general procedure A and purified by flash chromatography on silica gel by saturated Et<sub>3</sub>N using ethyl acetate/petroleum ether (5:95) as eluent to afford **8q** (179.2 mg, 70%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.57 (d, *J* = 7.8 Hz, 1H), 7.26 (s, 1H), 7.20 (d, *J* = 8.5 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.10–7.04 (m, 1H), 6.89–6.83 (m, 1H), 6.74 (d, *J* = 8.5 Hz, 1H), 3.34 (s, 3H), 3.15 (s, 3H), 1.79 (s, 3H); <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  160.6, 153.1, 131.5, 129.9, 127.0, 126.9, 123.3, 121.9, 121.3, 118.0, 114.3, 106.8, 102.2, 54.9, 50.3, 26.1; HRMS (EI) *m/z* [M + H]<sup>+</sup> calculated for C<sub>16</sub>H<sub>17</sub>O<sub>3</sub>:257.1172, found 257.1183.



6-Isopropyl-6,9-dimethoxy-6*H*-benzo[*c*]chromene (8r)

It was prepared following the general procedure A and purified by flash chromatography on silica gel by saturated Et<sub>3</sub>N using ethyl acetate/petroleum ether (5:95) as eluent to afford **8r** (184.6 mg, 65%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.53 (dd, J = 7.8, 1.3 Hz, 1H), 7.27 (d, J = 2.5 Hz, 1H), 7.20 (d, J = 8.6 Hz, 1H), 7.09–7.02 (m, 2H), 6.84–6.79 (m, 1H), 6.74 (dd, J = 8.6, 2.5 Hz, 1H), 3.35 (s, 3H), 3.17 (s, 3H), 2.34–2.24 (m, 1H), 1.22 (d, J = 6.8 Hz, 3H), 0.99 (d, J = 6.9 Hz, 3H): <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  160.6, 154.5, 133.0, 130.2, 128.3, 124.2, 123.1, 121.4, 120.0, 117.5, 114.2, 106.9, 106.3, 54.8, 50.8, 39.4, 16.9, 16.3; HRMS (EI) m/z [M + H]<sup>+</sup> calculated for C<sub>18</sub>H<sub>21</sub>O<sub>3</sub>: 285.1485, found 285.1498.



#### 1-Methoxy-1,3-diphenyl-1*H*-isochromene (10a)

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.64–7.56 (m, 2H), 7.57–7.46 (m, 2H), 7.02–6.96 (m, 3H), 6.95–6.81 (m, 6H), 6.75–6.67 (m, 1H), 6.30 (s, 1H), 3.00 (s, 3H); <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  150.4, 141.9, 134.6, 131.8, 130.9, 129.0, 129.0, 128.8, 128.5, 128.4, 127.2, 127.0, 125.3, 124.6, 104.5, 100.6, 51.2; HRMS (EI) *m*/*z* [M + H]<sup>+</sup> calculated for C<sub>22</sub>H<sub>19</sub>O<sub>2</sub>: 315.1380, found 315.1367.



#### Methoxy-1-methyl-3-phenyl-1*H*-isochromene (10b)

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.82–7.75 (m, 2H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.21–7.17 (m, 2H), 7.14–7.10 (m, 2H), 7.07–7.02 (m, 1H), 6.99–6.95 (m, 1H), 6.26 (s, 1H), 3.13 (s, 3H), 1.82 (s, 3H); <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  151.4, 134.9, 132.2, 130.8, 129.0, 128.9, 128.7, 127.1, 125.3, 125.1, 124.6, 103.9, 99.2, 50.4, 27.2; HRMS (EI) *m*/*z* [M + H]<sup>+</sup> calculated for C<sub>17</sub>H1<sub>7</sub>O<sub>2</sub>: 253,1223, found 253,1237.



#### (R)-6-(4-Methoxyphenyl)-6H-benzo[c]chromene (5a)

It was prepared following the general procedure B and purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **5a** (27.5mg, 95%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.86–7.78 (m, 2H), 7.49–7.42 (m, 1H), 7.40–7.34 (m, 2H), 7.32–7.26 (m, 2H), 7.15–7.03 (m, 2H), 6.98–6.89 (m, 3H), 6.20 (s, 1H), 3.82 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  159.8, 153.8, 134.4, 131.9, 130.2, 129.7, 129.7, 128.5, 127.7, 126.4, 123.2, 122.9, 122.2, 122.2, 118.1, 114.0, 79.4, 55.3; these data are consistent with reported literature values.<sup>2</sup> HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 5/95, 1.0 mL/min, 215 nm), retention time: t<sub>minor</sub> = 7.660 min, t<sub>major</sub> = 9.117 min, ee = 94%; [ $\alpha$ ]p<sup>25</sup> = + 31.2 (c = 0.80, CHCl<sub>3</sub>).



#### (*R*)-3-Methoxy-6-(4-methoxyphenyl)-6*H*-benzo[*c*]chromene (5b)

It was prepared following the general procedure B and purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **5b** (29.9 mg, 94%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.71–7.64 (m, 2H), 7.41–7.34 (m, 1H), 7.30 (d, 2H), 7.21–7.15 (m, 1H), 6.91–6.86 (m, 2H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.62 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.55 (d, *J* = 2.5 Hz, 1H), 6.12 (s, 1H), 3.80 (d, *J* = 7.5 Hz, 6H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  161.3, 159.9, 155.1, 133.2, 132.0, 130.5, 129.7, 128.6, 126.8, 126.4, 124.2, 121.5, 116.0, 114.1, 109.1, 102.9, 79.9, 55.6, 55.5;

these data are consistent with reported literature values.<sup>2</sup> HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 215 nm), retention time:  $t_{minor} = 10.447 \text{ min}$ ,  $t_{major} = 11.237 \text{ min}$ , ee = 92%;  $[\alpha]_D^{25} = -27.2$  (c = 0.70, CHCl<sub>3</sub>).



#### (*R*)-6-(4-Methoxyphenyl)-3-methyl-6*H*-benzo[*c*]chromene (5c)

It was prepared following the general procedure B and purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **5c** (28.7mg, 95%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.74 (d, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.41–7.35 (m, 1H), 7.34–7.27 (m, 2H), 7.25–7.18 (m, 1H), 6.91–6.84 (m, 4H), 6.81 (s, 1H), 6.12 (s, 1H), 3.80 (s, 3H), 2.32 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  159.9, 153.7, 140.2, 134.0, 132.1, 130.4, 129.7, 128.52, 127.3, 126.4, 123.1, 123.0, 121.9, 120.2, 118.5, 114.0, 79.5, 55.5, 21.6; these data are consistent with reported literature values.<sup>2</sup> HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 5/95, 1.0 mL/min, 215 nm), retention time: t<sub>minor</sub> = 8.340 min, t<sub>major</sub> = 8.923 min, ee = 95%; [ $\alpha$ ] $p^{25}$  = – 7.7 (c = 0.40, CHCl<sub>3</sub>).



(R)-6-(4-Methoxyphenyl)-2-methyl-6H-benzo[c]chromene (5d)

It was prepared following the general procedure B and purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **5d** (28.4mg, 94%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.77 (d, *J* = 7.7 Hz, 1H), 7.57 (d, *J* = 1.5 Hz, 1H), 7.42–7.38 (m, 1H), 7.32–7.28 (m, 2H), 7.26–7.21 (m, 1H), 7.03 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.91–6.86 (m, 4H), 6.10 (s, 1H), 3.80 (s, 3H), 2.36 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  159.8, 151.6, 134.5, 132.0, 131.4, 130.4, 129.7, 128.5, 127.6, 126.4, 123.6, 122.6, 122.2, 117.8, 114.0, 79.4, 55.4, 21.2; these data are consistent with reported literature values.<sup>2</sup> HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 215 nm), retention time: t<sub>minor</sub> = 7.110 min, t<sub>major</sub> = 8.410 min, ee = 93%; [ $\alpha$ ]<sub>D</sub><sup>25</sup> = + 30.2 (c = 0.50, CHCl<sub>3</sub>).



#### (R)-9-Methoxy-6-(4-methoxyphenyl)-6H-benzo[c]chromene (5e)

It was prepared following the general procedure B and purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **5e** (30.2mg, 95%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.64 (dd, J = 7.7, 1.2 Hz, 1H), 7.24–7.19 (m, 3H), 7.16–7.11 (m, 1H), 6.98–6.93 (m, 1H), 6.89 (d, J = 8.1 Hz, 1H), 6.83–6.77 (m, 2H), 6.70 (s, 2H), 6.01 (s, 1H), 3.79 (s, 3H), 3.72 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  160.0, 159.8, 154.0, 132.2, 131.6, 129.9, 129.7, 127.6, 127.1, 123.3, 122.9, 122.1, 118.2, 114.0, 113.2, 107.7, 79.3, 55.6, 55.5; these data are consistent with reported literature values.<sup>2</sup> HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 215 nm), retention time: t<sub>minor</sub> = 11.247 min, t<sub>major</sub> = 12.250 min, ee = 99%; [ $\alpha$ ] $\rho$ <sup>25</sup> = + 36.0 (c = 0.50, CHCl<sub>3</sub>).



#### (*R*)-8-Methoxy-6-(4-methoxyphenyl)-6*H*-benzo[*c*]chromene (5f)

It was prepared following the general procedure B and purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **5f** (30.5mg, 96%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.74–7.66 (m, 2H), 7.33–7.27 (m, 2H), 7.20–7.13 (m, 1H), 7.05–6.99 (m, 1H), 6.99–6.92 (m, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.42 (d, *J* = 2.5 Hz, 1H), 6.09 (s, 1H), 3.80 (s, 3H), 3.76 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  159.9, 159.5, 153.0, 136.0, 131.8, 129.7, 128.7, 123.24, 123.0, 122.6, 122.2, 118.0, 114.1, 114.0, 112.1, 79.5, 55.5, 55.5; these data are consistent with reported literature values.<sup>2</sup> HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 15/85, 1.0 mL/min, 254 nm), retention time: t<sub>minor</sub> = 9.263 min, t<sub>major</sub> = 11.143 min, ee = 91%; [ $\alpha$ ]p<sup>25</sup> = + 48.1 (c = 0.45, CHCl<sub>3</sub>).



#### (R)-6-(4-Ethoxyphenyl)-9-methoxy-6H-benzo[c]chromene (9a)

It was prepared following the general procedure B and purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **9a** (32.2mg, 97%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.69 (dd, J = 7.7, 1.0 Hz, 1H), 7.26–7.21 (m, 2H), 7.21–7.15 (m, 1H), 7.03–6.98 (m, 1H), 6.95 (d, J = 8.0 Hz, 1H), 6.84 (d, J = 8.6 Hz, 2H), 6.77–6.71 (m, 2H), 6.05 (s, 1H), 3.99 (q, J = 7.0 Hz, 2H), 3.84 (s, 3H), 1.37 (t, J = 7.0 Hz, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  160.0,

159.2, 154.0, 132.0, 131.6, 129.9, 129.7, 127.6, 127.1, 123.3, 122.9, 122.1, 118.1, 114.5, 113.2, 107.7, 79.4, 63.6, 55.6, 15.0; these data are consistent with reported literature values.<sup>2</sup> HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 215 nm), retention time:  $t_{minor} = 9.087$  min,  $t_{major} = 10.160$  min, ee = 97%;  $[\alpha]_D^{25} = +42.9$  (c = 0.35, CHCl<sub>3</sub>).



# (*R*)-tert-butyl(4-(9-methoxy-6*H*-benzo[*c*]chromen-6-yl)phenoxy)dimethylsilane (9b)

It was prepared following the general procedure B and purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **9b** (38.8mg, 93%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.72 (dd, J = 7.7, 1.1 Hz, 1H), 7.28 (d, J = 2.3 Hz, 1H), 7.25 (s, 1H), 7.25–7.19 (m, 2H), 7.07–7.01 (m, 1H), 6.99 (d, J = 8.1 Hz, 1H), 6.85–6.80 (m, 2H), 6.80–6.76 (m, 1H), 6.74 (d, J = 8.4 Hz, 1H), 6.06 (s, 1H), 3.87 (s, 3H), 0.99 (s, 9H), 0.20 (s, 6H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  160.0, 156.0, 154.1, 132.7, 131.6, 129.9, 129.7, 127.6, 127.3, 123.3, 123.0, 122.2, 120.2, 118.1, 113.2, 107.7, 79.5, 55.6, 25.9, 18.4, -4.2; these data are consistent with reported literature values.<sup>2</sup> HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 2/98, 1.0 mL/min, 254 nm), retention time: t<sub>minor</sub> = 6.083 min, t<sub>major</sub> = 6.587 min, ee = 97%; [ $\alpha$ ]<sub>D</sub><sup>25</sup> = + 18.4 (c = 0.63, CHCl<sub>3</sub>).



#### (*R*)-(4-(6*H*-benzo[*c*]chromen-6-yl)phenoxy)(tert-butyl)dimethylsilane (9c)

It was prepared following the general procedure B and purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **9c** (34.9mg, 90%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.82 (d, J = 7.7 Hz, 2H), 7.49–7.41 (m, 1H), 7.36–7.24 (m, 4H), 7.14–7.03 (m, 2H), 6.90 (d, J = 8.4 Hz, 3H), 6.18 (s, 1H), 1.07 (s, 9H), 0.28 (s, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  156.0, 153.9, 134.6, 132.5, 130.3, 129.7, 129.7, 128.6, 127.8, 126.4, 123.3, 123.0, 122.2, 120.2, 118.1, 79.7, 25.9, 18.4, -4.2; HRMS (EI) m/z [M + H]<sup>+</sup> calculated for C<sub>25</sub>H<sub>29</sub>O<sub>2</sub>Si :389.1931, found 389.1918; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 2/98, 1.0 mL/min, 215 nm), retention time: t<sub>minor</sub> = 4.190 min, t<sub>major</sub> = 5.197 min, ee = 91%; [ $\alpha$ ]p<sup>25</sup> = – 0.034 (c = 0.21, CHCl<sub>3</sub>).



#### (R)-9-Methoxy-6-(4-(methylthio)phenyl)-6H-benzo[c]chromene (9d)

It was prepared following the general procedure B and purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **9d** (32.1mg, 96%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.71 (dd, J = 7.8, 1.4 Hz, 1H), 7.31–7.27 (m, 3H), 7.24–7.20 (m, 3H), 7.04 (td, J = 7.6, 1.1 Hz, 1H), 6.98 (dd, J = 8.1, 0.9 Hz, 1H), 6.79 (d, J = 1.3 Hz, 2H), 6.09 (s, 1H), 3.88 (s, 3H), 2.47 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  160.1, 153.8, 138.9, 136.8, 131.5, 130.0, 128.8, 127.6,

126.6, 126.5, 123.3, 122.9, 122.3, 118.2, 113.2, 107.8, 79.2, 55.6, 15.9; these data are consistent with reported literature values.<sup>2</sup> HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 215 nm), retention time:  $t_{minor} = 11.460 \text{ min}$ ,  $t_{major} = 12.607 \text{ min}$ , ee = 97%;  $[\alpha]_D^{25} = +20.2$  (c = 0.31, CHCl<sub>3</sub>).



#### (*R*)-9-Methoxy-6-(p-tolyl)-6*H*-benzo[*c*]chromene (9e)

It was prepared following the general procedure B and purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **9e** (28.7mg, 95%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.72 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.28 (d, *J* = 5.2 Hz, 2H), 7.26–7.24 (m, 1H), 7.22 (td, *J* = 8.1, 1.5 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.04 (td, *J* = 7.6, 1.0 Hz, 1H), 7.01–6.97 (m, 1H), 6.77 (d, *J* = 1.3 Hz, 2H), 6.10 (s, 1H), 3.87 (s, 3H), 2.35 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  160.0, 154.0, 138.3, 137.1, 131.5, 129.9, 129.3, 128.3, 127.6, 127.0, 123.3, 122.9, 122.1, 118.1, 113.2, 107.7, 79.5, 55.6, 21.4; these data are consistent with reported literature values.<sup>2</sup> HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 5/95, 1.0 mL/min, 215 nm), retention time: t<sub>minor</sub> = 9.360 min, t<sub>major</sub> = 10.117 min, ee = 96%; [ $\alpha$ ]p<sup>25</sup> = + 26.9 (c = 0.25, CHCl<sub>3</sub>).



(*R*)-6-(P-tolyl)-6*H*-benzo[*c*]chromene (9f)

It was prepared following the general procedure B and purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **9f** (23.9mg, 88%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.87–7.77 (m, 2H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.38–7.21 (m, 6H), 7.14–7.02 (m, 2H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.21 (s, 1H), 2.41 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  153.9, 138.3, 136.8, 134.3, 130.2, 129.7, 129.3, 128.6, 128.3, 127.8, 126.4, 123.3, 123.0, 122.2, 122.2, 118.1, 79.7, 21.4; HRMS (EI) *m*/*z* [M + H]<sup>+</sup> calculated for C<sub>20</sub>H<sub>17</sub>O : 273.1274, found 273.1288; HPLC: the ee value was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/Hexane = 2/98, 1.0 mL/min, 215 nm), retention time: t<sub>major</sub> = 8.880 min, t<sub>minor</sub> = 11.030 min, ee = 92%; [ $\alpha$ ]p<sup>25</sup> = – 0.033 (c = 0.18, CHCl<sub>3</sub>).



#### (R)-6-([1,1'-Biphenyl]-4-yl)-9-methoxy-6H-benzo[c]chromene (9g)

It was prepared following the general procedure B and purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **9g** (34.6mg, 95%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.75 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 4H), 7.49–7.42 (m, 4H), 7.38–7.33 (m, 1H), 7.32 (d, *J* = 2.3 Hz, 1H), 7.27–7.23 (m, 1H), 7.10–7.05 (m, 1H), 7.05–7.02 (m, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.83–6.79 (m, 1H), 6.19 (s, 1H), 3.89 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  160.1, 154.0, 141.4, 140.9, 139.1, 131.5, 123.0, 129.0, 128.7, 127.7, 127.6, 127.4, 127.3, 126.7, 123.4, 122.9, 122.3, 118.2, 113.3, 107.9, 79.4, 55.6; these data are consistent with reported literature values.<sup>2</sup> HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 5/95, 1.0 mL/min, 215 nm), retention time: t<sub>minor</sub> = 12.997 min, t<sub>major</sub> = 15.420 min, ee = 97%; [ $\alpha$ ] $_D^{25}$  = + 6.6 (c = 0.48, CHCl<sub>3</sub>)



#### (*R*)-9-Methoxy-6-phenyl-6*H*-benzo[*c*]chromene (9h)

It was prepared following the general procedure B and purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **9h** (27.6mg, 96%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.73 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.41–7.32 (m, 5H), 7.30 (d, *J* = 2.1 Hz, 1H), 7.25–7.20 (m, 1H), 7.08–7.02 (m, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 6.81–6.74 (m, 2H), 6.13 (s, 1H), 3.88 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  160.1, 154.0, 140.1, 131.5, 129.9, 128.7, 128.6, 128.3, 127.7, 126.8, 123.3, 122.9, 122.2, 118.1, 113.2, 107.8, 79.7, 55.6; these data are consistent with reported literature values.<sup>2</sup> HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 3/97, 1.0 mL/min, 254 nm), retention time: t<sub>major</sub> = 10.873 min, t<sub>minor</sub> = 11.543 min, ee = 97%; [ $\alpha$ ] $_D^{25}$  = + 23.1 (c = 0.50, CHCl<sub>3</sub>).



#### (*R*)-6-(4-Bromophenyl)-9-methoxy-6*H*-benzo[*c*]chromene (9i)

It was prepared following the general procedure B and purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **9i** (34.1mg, 93%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.74–7.68 (m, 1H), 7.47 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 2.1 Hz, 1H), 7.26–7.21 (m, 3H), 7.07–7.02 (m, 1H), 6.98 (d, J = 8.1 Hz, 1H), 6.83–6.75 (m, 2H), 6.09 (s, 1H), 3.88 (s, 3H); <sup>13</sup>C NMR (126)

MHz, CDCl<sub>3</sub>)  $\delta$  160.2, 153.6, 139.1, 131.8, 131.4, 130.0, 130.0, 127.5, 126.1, 123.4, 122.8, 122.6, 122.4, 118.1, 113.3, 107.9, 78.8, 55.6; these data are consistent with reported literature values.<sup>2</sup> The ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 5/95, 1.0 mL/min, 215 nm), retention time: t<sub>minor</sub> = 10.563 min, t<sub>major</sub> = 12.120 min, ee = 98%; [ $\alpha$ ]<sub>D</sub><sup>25</sup> = + 19.0 (c = 0.15, CHCl<sub>3</sub>).



#### (R)-6-(4-Chlorophenyl)-9-methoxy-6H-benzo[c]chromene (9j)

It was prepared following the general procedure B and purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **9j** (29.0mg, 90%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.72 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.34–7.28 (m, 5H), 7.25–7.21 (m, 1H), 7.08–7.03 (m, 1H), 6.99 (dd, *J* = 8.1, 0.9 Hz, 1H), 6.84–6.76 (m, 2H), 6.11 (s, 1H), 3.88 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  160.2, 153.6, 138.6, 134.3, 131.4, 130.0, 129.7, 128.8, 127.5, 126.1, 123.4, 122.8, 122.4, 118.1, 113.3, 107.9, 78.8, 55.6; these data are consistent with reported literature values.<sup>2</sup> HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 5/95, 1.0 mL/min, 227 nm), retention time: t<sub>minor</sub> = 9.683 min, t<sub>major</sub> = 11.507 min, ee = 93%; [ $\alpha$ ]p<sup>25</sup> = + 17.7 (c = 0.35, CHCl<sub>3</sub>).



(R)-9-Methoxy-6-(3-methoxyphenyl)-6H-benzo[c]chromene (9k)

It was prepared following the general procedure B and purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **9k** (29.6mg, 93%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.69 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.26–7.18 (m, 3H), 7.05–6.97 (m, 2H), 6.95–6.90 (m, 2H), 6.84 (dd, *J* = 7.3, 1.5 Hz, 1H), 6.79–6.73 (m, 2H), 6.07 (s, 1H), 3.84 (s, 3H), 3.74 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  160.1, 159.9, 154.0, 141.6, 131.5, 129.9, 129.6, 127.6, 126.7, 123.3, 122.9, 122.3, 120.7, 118.1, 114.1, 113.7, 113.2, 107.8, 79.5, 55.6, 55.4; these data are consistent with reported literature values.<sup>2</sup> HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 215 nm), retention time: t<sub>major</sub> = 10.530 min, t<sub>minor</sub> = 11.557 min, ee = 97%; [ $\alpha$ ]<sub>D</sub><sup>25</sup> = + 36.0 (c = 0.4, CHCl<sub>3</sub>).



#### (*R*)-9-Methoxy-6-(m-tolyl)-6*H*-benzo[*c*]chromene (9l)

It was prepared following the general procedure B and purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **9I** (28.4mg, 94%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.76 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.32 (d, *J* = 2.3 Hz, 1H), 7.31–7.26 (m, 2H), 7.26–7.24 (m, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.10–7.06 (m, 1H), 7.04 (d, *J* = 8.1 Hz, 1H), 6.83–6.75 (m, 2H), 6.11 (s, 1H), 3.90 (s, 3H), 2.38 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  160.0, 154.2, 139.9, 138.4, 131.5, 129.9, 129.4, 129.0, 128.5, 127.7, 127.0, 125.5, 123.3, 122.9, 122.2, 118.1, 113.2, 107.7, 79.8, 55.6, 21.7; these data are consistent with reported literature values.<sup>2</sup> HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 5/95, 1.0 mL/min, 215 nm), retention time: t<sub>major</sub> = 8.163 min, t<sub>minor</sub> = 9.547 min, ee = 96%; [ $\alpha$ ]D<sup>25</sup> = + 21.1 (c = 0.36, CHCl<sub>3</sub>).



#### (*R*)-9-Methoxy-6-(o-tolyl)-6*H*-benzo[*c*]chromene (9m)

It was prepared following the general procedure B and purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **9m** (27.2mg, 90%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.75 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.32–7.26 (m, 3H), 7.26–7.17 (m, 3H), 7.10–7.04 (m, 1H), 7.01–6.94 (m, 1H), 6.74 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 1H), 6.28 (s, 1H), 3.87 (s, 3H), 2.41 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  160.0, 154.6, 137.5, 137.1, 132.0, 130.9, 129.9, 128.9, 128.6, 127.1, 126.6, 126.4, 123.4, 123.1, 122.3, 117.9, 113.3, 107.8, 77.7, 55.6, 19.8; these data are consistent with reported literature values.<sup>2</sup> HPLC: the evalue was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 5/95, 1.0 mL/min, 274 nm), retention time: t<sub>major</sub> = 7.163 min, t<sub>minor</sub> = 7.850 min, ee = 89%; [\alpha]p<sup>25</sup> = -4.0 (c = 0.22, CHCl<sub>3</sub>).



#### (S)-9-Methoxy-6-(thiophen-2-yl)-6*H*-benzo[*c*]chromene (9n)

It was prepared following the general procedure B and purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **9n** (27.6mg, 94%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.73 (dd, J = 7.7, 1.2 Hz, 1H), 7.32 (d, J = 2.4 Hz, 1H), 7.29–7.26 (m, 1H), 7.26–7.22 (m, 1H), 7.09–7.00 (m, 3H), 6.93–6.89 (m, 1H), 6.89–6.84 (m, 2H), 6.45 (s, 1H), 3.91 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  160.3, 153.0, 144.2, 130.9, 130.0, 127.3, 127.1, 126.6, 126.5, 126.1, 123.3, 122.6, 122.4, 118.5, 113.4, 107.9, 74.9, 55.6; these data are consistent with

reported literature values.<sup>2</sup> HPLC: the ee value was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 215 nm), retention time:  $t_{major}$  = 7.620 min,  $t_{minor}$  = 13.467 min, ee = 94%; [ $\alpha$ ] $_{D}^{25}$  = + 98.1 (c = 0.38, CHCl<sub>3</sub>).



#### (R)-6-(2,2-Diphenylvinyl)-9-methoxy-6*H*-benzo[*c*]chromene (90)

It was prepared following the general procedure B and purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **90** (35.5mg, 91%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.73–7.69 (m, 1H), 7.41–7.35 (m, 5H), 7.34–7.28 (m, 5H), 7.26 (d, *J* = 2.5 Hz, 1H), 7.25–7.22 (m, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.07–7.03 (m, 2H), 6.86 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.42 (d, *J* = 9.6 Hz, 1H), 5.63 (d, *J* = 9.6 Hz, 1H), 3.88 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  160.1, 154.2, 146.5, 141.8, 139.0, 131.3, 129.9, 129.9, 128.6, 128.4, 128.2, 128.1, 128.0, 126.7, 126.6, 125.8, 123.4, 122.9, 122.1, 118.0, 113.4, 108.0, 75.3, 55.6; these data are consistent with reported literature values.<sup>2</sup> HPLC: the ee value was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/Hexane = 15/85, 1.0 mL/min, 254 nm), retention time: t<sub>minor</sub> = 7.663 min, t<sub>major</sub> = 13.947 min, ee = 96%; [ $\alpha$ ]p<sup>25</sup> = + 32.0 (c = 0.35, CHCl<sub>3</sub>).



(R)-9-Methoxy-6-(phenylethynyl)-6*H*-benzo[*c*]chromene (9p)

It was prepared following the general procedure A and purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **9p** (28.7mg, 92%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.74 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.50–7.44 (m, 3H), 7.35–7.26 (m, 5H), 7.26–7.25 (m, 1H), 7.14–7.08 (m, 2H), 6.91 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.06 (s, 1H), 3.89 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  160.5, 153.6, 132.2, 131.1, 130.0, 129.0, 128.5, 126.6, 124.3, 123.5, 122.9, 122.8, 122.3, 118.2, 113.5, 108.2, 87.9, 85.7, 68.7, 55.7; these data are consistent with reported literature values.<sup>2</sup> HPLC: the ee value was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/Hexane = 5/95, 1.0 mL/min, 215 nm), retention time: t<sub>minor</sub> = 18.503 min, t<sub>major</sub> = 20.887 min, ee = 87%; [ $\alpha$ ]p<sup>25</sup> = + 6.1 (c = 0.30, CHCl<sub>3</sub>).



#### (*R*)-9-Methoxy-6-methyl-6*H*-benzo[*c*]chromene (9q)

It was prepared following the general procedure A and purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **9q** (21.7mg, 96%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.72 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.29–7.26 (m, 1H), 7.26–7.24 (m, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 7.08–7.04 (m, 1H), 7.02 (dd, *J* = 8.1, 1.0 Hz, 1H), 6.86 (dd, *J* = 8.4, 2.5 Hz, 1H), 5.25 (q, *J* = 6.5 Hz, 1H), 3.87 (s, 3H), 1.63 (d, *J* = 6.5 Hz, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  159.7, 153.9, 130.8, 129.7, 128.6, 125.3, 123.3, 122.7, 121.9, 117.9, 113.3, 107.8, 73.5, 55.5, 20.4; these data are consistent with reported literature values.<sup>2</sup> HPLC: the ee value was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 254 nm), retention time: t<sub>major</sub> = 9.653 min, t<sub>minor</sub> = 11.207 min, ee = 93%; [ $\alpha$ ]p<sup>25</sup> = – 22.8 (c = 0.28, CHCl<sub>3</sub>).



#### (*R*)-6-Isopropyl-9-methoxy-6*H*-benzo[*c*]chromene (9r)

It was prepared following the general procedure A and purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **9r** (11.7mg, 92%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.91 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.51–7.43 (m, 2H), 7.28–7.20 (m, 3H), 7.06 (dd, *J* = 8.3, 2.5 Hz, 1H), 4.93 (d, *J* = 8.4 Hz, 1H), 4.10 (s, 3H), 2.28–2.17 (m, 1H), 1.27 (d, *J* = 6.6 Hz, 3H), 1.09 (d, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  159.7, 153.3, 130.6, 129.8, 127.7, 126.3, 123.1, 122.9, 121.7, 118.0, 112.9, 107.7, 83.2, 55.6, 32.0, 19.1, 18.8; these data are consistent with reported literature values.<sup>2</sup> HPLC: the ee value was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 254 nm), retention time: t<sub>major</sub> = 6.770 min, t<sub>minor</sub> = 12.690 min, ee = 86%; [ $\alpha$ ] $p^{25}$  = – 22.6 (c = 0.46, CHCl<sub>3</sub>).



#### (R)-1,3-Diphenyl-1*H*-isochromene (11a)

It was prepared following the general procedure C and purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **11a** (26.7mg, 94%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.74 (d, *J* = 7.5 Hz, 2H), 7.20–7.15 (m, 2H), 7.13–7.07 (m, 2H), 7.03–6.98 (m, 1H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 7.4 Hz, 1H), 6.33 (s, 1H), 5.16 (q, *J* = 6.5 Hz, 1H), 1.44 (d, *J* = 6.5 Hz, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  152.7, 140.0, 134.5, 132.0, 130.6, 129.0, 128.7, 128.6, 128.5, 128.5, 128.1, 126.7, 125.6, 125.4, 124.0, 101.3, 80.3; these data are consistent with reported literature values.<sup>2</sup> HPLC: the ee value was determined by

HPLC analysis (Chiralcel OD-H, *i*-PrOH/Hexane = 2/98, 1.0 mL/min, 322 nm), retention time:  $t_{minor} = 7.371$  min,  $t_{major} = 8.010$  min, ee = 89%;  $[\alpha]_D^{25} = -44.1$  (c = 0.30, CHCl<sub>3</sub>).



#### (R)-1-Methyl-3-phenyl-1*H*-isochromene (11b)

It was prepared following the general procedure C and purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (15:85) as eluent to afford **11b** (20.9mg, 95%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.74 (d, *J* = 7.5 Hz, 2H), 7.20–7.15 (m, 2H), 7.13–7.07 (m, 2H), 7.03–6.98 (m, 1H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 7.4 Hz, 1H), 6.33 (s, 1H), 5.16 (q, *J* = 6.5 Hz, 1H), 1.44 (d, *J* = 6.5 Hz, 3H); <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  152.8, 135.3, 132.9, 131.7, 128.9, 128.6, 128.1, 126.8, 125.5, 124.2, 123.5, 101.0, 74.5, 19.6; these data are consistent with reported literature values.<sup>2</sup> HPLC: the ee value was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/Hexane = 1/99, 1.0 mL/min, 331 nm), retention time: t<sub>minor</sub> = 6.763 min, t<sub>major</sub> = 7.390 min, ee = 91%; [ $\alpha$ ]p<sup>25</sup> = – 33.1 (c = 0.20, CHCl<sub>3</sub>).

### **References:**

- 1. S. Dasgupta, T. Rivas, M. P. Watson, Angew. Chem. Int. Ed. 2015, 54, 14154.
- 2. M. Wan, S. Sun, Y. Li, L. Liu, Angew. Chem. Int. Ed. 2017, 56, 5116.

## <sup>1</sup>H and <sup>13</sup>C NMR spectra



















































































































## HPLC data





**Integration Results** Retention No. Amount Peak Name Time Area **Relative Area** 1 7.707 809.698 49.18 n.a. 2 836.590 **1646.289** 50.82 100.00 9.167 n.a. Total:



Integration Results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		7.660	8.991	3.01	n.a.		
2		9.117	289.949	96.99	n.a.		
Total:			298.939	100.00			





## Integration Results

No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		10.493	634.646	50.36	n.a.		
2		11.287	625.683	49.64	n.a.		
Total:			1260.329	100.00			



Integration Results								
No.	Peak Name	Retention Time	Area	Relative Area	Amount			
		min	mAU*min	%	n.a.			
1		10.447	7.770	4.00	n.a.			
2		11.237	186.400	96.00	n.a.			
Total:			194.170	100.00				





Integration Results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		8.340	855.540	49.67	n.a.		
2		8.917	866.784	50.33	n.a.		
Total:			1722.323	100.00			



Integration Results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		8.340	3.231	2.40	n.a.		
2		8.923	131.116	97.60	n.a.		
Total:			134.347	100.00			





Integration Results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		7.067	399.309	50.11	n.a.		
2		8.357	397.516	49.89	n.a.		
Total:			796.825	100.00			



Inte	gration	Results

No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		7.110	4.003	3.52	n.a.		
2		8.410	109.641	96.48	n.a.		
Total:			113.644	100.00			





Integration Results								
No.	Peak Name	Retention Time	Area	Relative Area	Amount			
		min	mAU*min	%	n.a.			
1		11.033	133.261	49.92	n.a.			
2		11.987	133.691	50.08	n.a.			
Total:			266.952	100.00				



Integration Results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		11.247	2.615	0.67	n.a.		
2		12.250	388.984	99.33	n.a.		
Total:			391.599	100.00			





integration results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		9.283	319.992	49.84	n.a.		
2		11.117	322.066	50.16	n.a.		
Tatal			0.40 0.50	400.00			



Integration Results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		9.263	1.947	4.42	n.a.		
2		11.143	42.139	95.58	n.a.		
Total:			44.086	100.00			





No.	Peak Name	Retention Time	Area	Relative Area	Amount			
		min	mAU*min	%	n.a.			
1		9.050	233.646	50.05	n.a.			
2		10.127	233.212	49.95	n.a.			
Tatal			100.070	100.00				



Integration Results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		9.087	14.977	1.37	n.a.		
2		10.160	1077.915	98.63	n.a.		
Total:			1092.892	100.00			





Integration Results								
No.	Peak Name	Retention Time	Area	Relative Area	Amount			
		min	mAU*min	%	n.a.			
1		6.087	156.850	50.01	n.a.			
2		6.607	156.762	49.99	n.a.			
Total			313 612	100 00				



integration results								
No.	Peak Name	Retention Time	Area	Relative Area	Amount			
		min	mAU*min	%	n.a.			
1		6.083	2.272	1.51	n.a.			
2		6.587	147.877	98.49	n.a.			
Total:			150.149	100.00				





Integration Results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		4.240	696.600	50.28	n.a.		
2		5.210	688.898	49.72	n.a.		
Total:			1385.498	100.00			



Integration Results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		4.190	6.481	4.42	n.a.		
2		5.197	140.224	95.58	n.a.		
Total:			146.705	100.00			





Integration Results								
No.	Peak Name	Retention Time	Area	Relative Area	Amount			
		min	mAU*min	%	n.a.			
1		11.423	83.545	50.05	n.a.			
2		12.550	83.391	49.95	n.a.			
Total			166 027	100.00				



Integratio	n Results

No.	Peak Name	Retention Time	Area	Relative Area	Amount
		min	mAU*min	%	n.a.
1		11.460	14.148	1.29	n.a.
2		12.607	1084.288	98.71	n.a.
Total:			1098.436	100.00	





Integration Results								
No.	Peak Name	Retention Time	Area	Relative Area	Amount			
		min	mAU*min	%	n.a.			
1		9.163	315.893	50.31	n.a.			
2		9.953	312.048	49.69	n.a.			
Total			607 044	100.00				



Integration Results								
No.	Peak Name	Retention Time	Area	Relative Area	Amount			
		min	mAU*min	%	n.a.			
1		9.360	3.944	2.10	n.a.			
2		10.177	183.769	97.90	n.a.			
Total:			187.713	100.00				





Integration Results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		9.173	166.695	50.05	n.a.		
2		11.380	166.393	49.95	n.a.		
Total:			333.088	100.00			



Integration Results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		8.880	443.200	95.92	n.a.		
2		11.030	18.873	4.08	n.a.		
Total:			462.073	100.00			





Integration Results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		12.717	88.683	49.77	n.a.		
2		14.780	89.497	50.23	n.a.		
Total:			178.180	100.00			



Integration Results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		12.997	11.264	1.45	n.a.		
2		15.420	765.019	98.55	n.a.		
Total:			776.283	100.00			





Integration Results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		10.797	114.658	49.87	n.a.		
2		11.460	115.242	50.13	n.a.		
Total:			229 900	100 00			



Integration Results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		10.873	96.193	98.51	n.a.		
2		11.543	1.455	1.49	n.a.		
Total:			97.648	100.00			





Integration Results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		10.587	985.597	49.71	n.a.		
2		12.140	996.951	50.29	n.a.		
Total:			1982.548	100.00			



Integration Results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		10.563	9.108	1.18	n.a.		
2		12.120	759.975	98.82	n.a.		
Total:			769.083	100.00			



No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		9.533	1069.043	49.72	n.a.		
2		10.940	1080.913	50.28	n.a.		



Integration Results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		9.683	5.417	3.57	n.a.		
2		11.507	146.410	96.43	n.a.		
Total:			151.827	100.00			





No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		10.110	575.315	49.18	n.a.		
2		11.007	594.391	50.82	n.a.		
Total			1169 706	100 00			



Integrati	on R	esu	lts
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No.	Peak Name	Retention Time	Area	Relative Area	Amount
		min	mAU*min	%	n.a.
1		10.530	403.866	98.31	n.a.
2		11.557	6.927	1.69	n.a.
Total:			410.793	100.00	





Integration Results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		8.163	441.638	49.86	n.a.		
2		9.517	444.170	50.14	n.a.		



Integration Results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		8.163	799.829	98.03	n.a.		
2		9.547	16.058	1.97	n.a.		
Total:			815.888	100.00			





Integration Results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		7.203	61.420	49.83	n.a.		
2		7.863	61.827	50.17	n.a.		
Total:			123 248	100 00			



Inte	gratio	n Re	sults
	0		

<u> </u>					1
No.	Peak Name	Retention Time	Area	Relative Area	Amount
		min	mAU*min	%	n.a.
1		7.163	366.496	94.46	n.a.
2		7.850	21.500	5.54	n.a.
Total:			387.996	100.00	





Integration Results						
No.	Peak Name	Retention Time	Area	Relative Area	Amount	
		min	mAU*min	%	n.a.	
1		7.593	573.902	49.92	n.a.	
2		13.273	575.670	50.08	n.a.	
				400.00		



Integrati	ion	Result	S

No.	Peak Name	Retention Time	Area	Relative Area	Amount
		min	mAU*min	%	n.a.
1		7.620	773.509	97.12	n.a.
2		13.467	22.968	2.88	n.a.
Total:			796.477	100.00	





Integration Results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		7.770	31.646	49.17	n.a.		
2		14.083	32.717	50.83	n.a.		



integration results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		7.663	14.770	1.98	n.a.		
2		13.947	730.832	98.02	n.a.		
Total:			745.603	100.00			





Integration Results						
No.	Peak Name	Retention Time	Area	Relative Area	Amount	
		min	mAU*min	%	n.a.	
1		18.077	246.366	49.62	n.a.	
2		20.680	250.152	50.38	n.a.	





Integration Results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		18.503	30.954	6.29	n.a.		
2		20.887	461.332	93.71	n.a.		
Total:			492.286	100.00			



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Integration Results									
No.	Peak Name	Retention Time	Area	Relative Area	Amount				
		min	mAU*min	%	n.a.				
1		9.730	234.518	49.89	n.a.				
2		11.043	235.542	50.11	n.a.				





Integration Results									
No.	Peak Name	Retention Time	Area	Relative Area	Amount				
		min	mAU*min	%	n.a.				
1		9.653	294.879	96.43	n.a.				
2		11.207	10.910	3.57	n.a.				
Total:			305.790	100.00					




Integration Results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		6.667	371.722	49.65	n.a.		
2		12.007	376.916	50.35	n.a.		

Total: 748.639



Integration Results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		6.770	47.976	93.11	n.a.		
2		12.690	3.549	6.89	n.a.		
Total:			51.525	100.00			



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integration results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		6.717	135.792	49.84	n.a.		
2		8.603	136.676	50.16	n.a.		



Integration Results						
No.	Peak Name	Retention Time	Area			
		min	mAU*min			
1		7 3 1 7	22 777			

2		8.010	386.469	94.43	n.a.
1		7.317	22.777	5.57	n.a.
110.		min	mAU*min	%	n.a.
No.	Peak Name	Retention Time	Area	Relative Area	Amount



Integration Results							
No.	Peak Name	Retention Time	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		6.660	129.319	50.42	n.a.		
2		7.250	127.151	49.58	n.a.		
Total			256 460	100.00			



Integration Results							
No.	Peak Name	<b>Retention Time</b>	Area	Relative Area	Amount		
		min	mAU*min	%	n.a.		
1		6.763	21.202	4.31	n.a.		
2		7.390	470.182	95.69	n.a.		
Total:			491.385	100.00			