Enantioselective Heterocyclic Synthesis of Spiro Chromanone-Thiochroman Complexes Catalyzed by a Bifunctional Indene Catalyst

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1. General Information

Chemicals and solvents were purchased from commercial suppliers and used as received. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker ACF300 (300 MHz) or AMX500 (500 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform $\delta_{7.26}$), carbon (chloroform $\delta_{77.0}$) or tetramethylsilane (TMS $\delta_{0.00}$) was used as a reference. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), bs (broad singlet). Coupling constants were reported in Hertz (Hz). Low resolution mass spectra were obtained on a Finnigan/MAT LCQ spectrometer in ESI mode, and a Finnigan/MAT 95XL-T mass spectrometer in EI mode. All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with iodine, or ninhydrin followed by heating using a heat gun. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel. The enantiomeric excesses of products were determined by chiral phase HPLC analysis. Optical rotations were recorded on Jasco DIP-1000 polarimeter.
2. Preparation of the Catalysts

![Chemical Reaction Diagram]

Scheme 1, Synthetic route for catalyst 3a, 3b, and 3c
tert-butyl (1S,2R)-2-hydroxy-2,3-dihydro-1H-inden-1-ylcarbamate (b)\textsuperscript{1}. A solution of (Boc)\textsubscript{2}O (2.4 g, 11 mmol) in THF (5 ml) was added to the mixture of the amino alcohol a (1.5 g, 10 mmol) and sodium carbonate (2.12 g, 20 mmol) in THF/H\textsubscript{2}O (1:1, 60 ml) at 0\textdegree C. The mixture was stirred at 0\textdegree C for 1 h and then at room temperature for another 2 h (TLC was used to monitor the reaction). Water
(30 ml) was added to the mixture upon completion. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3 x 50 ml). The combined organic layers was washed with brine (60 ml) and dried with anhydrous MgSO₄ for 1h. It was then filtered and the solvent was removed under vacuum to give the product (2.5 g) with quantitative yield. It was sufficiently pure for the next step. The pure product was obtained by purification with silica gel chromatography. ¹H NMR (500 MHz, CDCl₃): δ = 7.3-7.29 (m, 1H), 7.24-7.22 (m, 3H), 5.11 (d, J = 28.7 Hz, 2H), 4.60 (s, 1H), 3.13 (dd, J = 16.6, 5.2 Hz, 1H), 2.93 (dd, J = 16.6, 1.7 Hz, 1H), 1.96 (s, 1H), 1.51 (s, 9H); ¹³C NMR (125 MHz, CDCl₃): δ = 156.30, 140.82, 139.82, 128.18, 127.12, 125.33, 124.47, 79.88, 73.65, 58.89, 39.41, 28.39; HRMS (ESI) calcd for C₁₄H₁₉NO₃ (M + H⁺) 249.1365, found 249.1367.

Diisopropyl azodicarboxylate (3.0 g, 15 mmol) was added to a stirred solution of compound b (2.5 g, 10 mmol) and triphenylphosphane (3.15 g, 12 mmol) in THF (50 mL) at 0 °C via syringe under nitrogen atmosphere. After 10 min, diphenylphosphoryl azide (DPPA) (4.1 g, 15 mmol) was added dropwise by syringe. The solution was stirred overnight at room temperature. After that, triphenylphosphane (5.3 g, 20 mmol) was added in one portion, and the solution was stirred at room temperature for 2 hours. Water (5 mL) was then added and the solution was heated at 50°C for 6 h. The reaction mixture was concentrated and the residue was purified by silica gel chromatography (eluting with 1:1 EtOAc-DCM then 1:10 methanol-DCM) to obtain the white solid product (1.57g, 63% yield, two steps). ¹H NMR (300 MHz, CDCl₃): δ = 7.20-7.19 (d, J = 5.9 Hz, 4H), 4.85-4.63 (m, 2H), 3.42 (dd, J = 14.8, 7.5 Hz, 1H), 3.19 (dd, 3.19 (dd,
$J = 15.6, 7.4$ Hz, 1H), 2.63 (dd, $J = 15.6, 8.2$ Hz, 1H), 1.75 (s, 2H), 1.49 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 156.29, 141.55, 140.60, 128.07, 126.94, 124.78, 123.80, 79.65, 64.52, 62.39, 39.25, 28.37$; HRMS (ESI) calcd for C$_{14}$H$_{21}$N$_2$O$_2$ (M + H$^+$) 249.1603, found 249.1601.

![tert-butyl (1S,2S)-2-(dimethylamino)-2,3-dihydro-1H-inden-1-ylcarbamate](image)

*tert*-butyl (1S,2S)-2-(dimethylamino)-2,3-dihydro-1H-inden-1-ylcarbamate (d)$^3$. To a solution of compound c (0.75 g, 3 mmol) in 15 mL CH$_3$CN was added aqueous formaldehyde (37% w/w, 1.2 mL, 15 mmol), the solution was stirred at room temperature for 15 minutes. After that, NaBH$_3$CN (0.38 g, 6 mmol) was added, followed 15 minutes stirring later by AcOH (1 mL). After 1 hour, the reaction mixture was dilute with 2% methanol-DCM (40 mL), washed with 1.0 M NaOH (3 x 30), dried by MgSO$_4$, and concentrated. The resulting residue was purified by silica gel chromatography (eluting with 1: 20 methanol-DCM) to afford the pure product (0.79 g, 95% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.26-7.15$ (m, 4H), 5.20 (t, $J = 8.4$ Hz, 1H), 4.77 (d, $J = 8.8$ Hz, 1H), 3.03 (m, 2H), 2.87 (dd, $J = 14.0, 7.4$ Hz, 1H), 2.40 (s, 6H), 1.49 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 155.49, 142.61, 139.71, 127.90, 126.96, 124.59, 124.13, 79.49, 74.59, 57.25, 42.94, 33.68, 28.43$; HRMS (ESI) calcd for C$_{16}$H$_{25}$N$_2$O$_2$ (M + H$^+$) 277.1916, found 277.1918.

![tert-butyl (1S,2S)-2-(pyrrolidin-1-yl)-2,3-dihydro-1H-inden-1-ylcarbamate](image)

*tert*-butyl (1S,2S)-2-(pyrrolidin-1-yl)-2,3-dihydro-1H-inden-1-ylcarbamate (e)$^4$. Compound 3c (0.75 g, 3 mmol), 1,4-dibromobutane (0.78 g, 3.6 mmol), potassium carbonate (1.08 g, 7.8 mmol),
potassium iodide (0.1 g, 0.6 mmol) and 10 mL iso-propanol were added into a sealed tube. The mixture was heated at 80 °C for 48 hrs and then allowed to cool to room temperature. The mixture was filtered and washing with DCM, the filtrate was concentrated and the resulting residue was purified by silica gel chromatography (eluting with 1:5 EtOAc- hexane then 1:10 methanol-DCM) to obtain the product 5 (0.64 g, 70% yield). 

$^1$H NMR (500 MHz, CDCl$_3$): δ = 7.26-7.16 (m, 4H), 5.25-5.22 (m, 1H), 4.81 (d, $J = 9.1$ Hz, 1H), 3.17 (dd, $J = 18.9, 11.0$ Hz, 1H), 3.01-2.98 (m, 2H), 2.80-2.75 (m, 4H), 1.85 (s, 4H), 1.49 (s, 9H); 

$^{13}$C NMR (75 MHz, CDCl$_3$): δ = 155.44, 142.25, 139.68, 128.06, 127.05, 124.56, 124.08, 79.61, 72.61, 59.61, 52.34, 36.24, 28.41, 23.36; HRMS (ESI) calcd for C$_{18}$H$_{27}$N$_2$O$_2$ (M + H$^+$) 303.2073, found 303.2062.

**tert-butyl (1S,2S)-2-(piperidin-1-yl)-2,3-dihydro-1H-inden-1-ylcarbamate (f)**. Compound c (0.75 g, 3 mmol), 1,5-dibromopentane (0.83 g, 3.6 mmol), potassium carbonate (1.08 g, 7.8 mmol), potassium iodide (0.1 g, 0.6 mmol) and 10 mL iso-propanol were added into a sealed tube. The mixture was heated at 80 °C for 48 hrs and then allowed to cool to room temperature. The mixture was filtered and washing with DCM, the filtrate was concentrated and the resulting residue was purified by silica gel chromatography (eluting with 1:10 EtOAc- hexane then 1:10 methanol-DCM) to obtain the product 5 (0.71 g, 75% yield). 

$^1$H NMR (500 MHz, CDCl$_3$): δ = 7.28-7.12 (m, 4H), 5.24 (dd, $J = 13.7, 5.2$ Hz, 1H), 4.89-4.87 (m, 1H), 3.05 (s, 2H), 2.87 (dd, $J = 18.6, 11.7$ Hz, 1H), 2.60 (dd, $J = 23.2, 4.9$ Hz, 4H), 1.61-1.59 (m, 4H), 1.48 (s, 11H); 

$^{13}$C NMR (125 MHz, CDCl$_3$): δ = 155.41, 142.52, 139.97, 127.85, 126.88, 124.50, 124.14, 79.44, 74.64, 56.53, 51.60, 33.81, 28.41, 26.13, 24.45; HRMS (ESI) calcd for C$_{19}$H$_{29}$N$_2$O$_2$ (M + H$^+$) 317.2229, found 317.2227.

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(1S,2S)-N\textsuperscript{2},N\textsuperscript{2}-dimethyl-2,3-dihydro-1\textsubscript{H}-indene-1,2-diamine (g). To a solution of compound d (0.7 g, 2.5 mmol) in 3 mL methanol was added 3 mL concentrated HCl solution. The mixture was stirred at room temperature for 5 hrs, then 40% NaOH solution was added until pH of mixture was 14. After extraction by DCM (5 x 10 mL), the organic layer was combined and dried by MgSO\textsubscript{4}, then concentrated. The pure product (0.41 g, 93% yield) was obtained by silica gel chromatography (very short column, eluting with 1:10 to 1:5 methanol-DCM). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): δ = 7.30 (d, \( J = 7.3 \) Hz, 1H), 7.23-7.16 (m, 3H), 4.23 (d, \( J = 7.3 \) Hz, 1H), 2.95 (dd, \( J = 13.4, 6.1 \) Hz, 1H), 2.89-2.80 (m, 2H), 2.40 (s, 6H), 1.81 (s, 2H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): δ = 145.30, 139.71, 127.30, 126.68, 124.59, 123.42, 77.76, 59.07, 43.02, 31.17; HRMS (ESI) calcd for C\textsubscript{11}H\textsubscript{17}N\textsubscript{2} (M + H\textsuperscript{+}) 177.1392, found 177.1391.

1-(3,5-bis(trifluoromethyl)phenyl)-3-((1S,2S)-2-(dimethylamino)-2,3-dihydro-1\textsubscript{H}-inden-1-yl)thiourea (3a). To a solution of compound g (0.4 g, 2.27 mmol) in 10 mL DCM was added 1-isothiocyanato-3,5-bis(trifluoromethyl)benzene (0.59 g, 2.16 mmol) dropwise. The mixture was stirred at room temperature for 30 min, reaction completed. The solvent was removed by rotary evaporation and pure product 3a (1.0 g, 98% yield) was obtained by silica gel chromatography (eluting with 1:5 EtOAc- hexane then 1:10 methanol-DCM). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): δ = 12.84 (s, 1H), 8.10 (s, 2H), 7.61 (s, 1H), 7.42-7.28 (m, 4H), 6.86 (d, \( J = 3.2 \) Hz, 1H), 5.22 (m, 1H), 3.75 (q, \( J = 8.5 \) Hz, 2H), 1.81 (s, 3H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): δ = 145.30, 139.71, 127.30, 126.68, 124.59, 123.42, 77.76, 59.07, 43.02, 31.17; HRMS (ESI) calcd for C\textsubscript{13}H\textsubscript{18}F\textsubscript{4}N\textsubscript{2}S (M + H\textsuperscript{+}) 303.1184, found 303.1181.
Hz, 1H), 3.08 (ddd, J = 44.1, 15.9, 9.0 Hz, 2H), 2.52 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 182.25,
141.95, 139.83, 137.38, 133.15, 132.06, 131.80, 131.53, 131.26, 129.35, 127.86, 125.57, 124.18,
123.46, 122.73, 122.01, 117.60, 74.45, 62.57, 40.75, 25.39; HRMS (ESI) calcd for C$_{20}$H$_{20}$F$_6$N$_3$S (M + 
H$^+$) 448.1282, found 448.1277.

![Chemical Structure](image)

(1S,2S)-2-(pyrrolidin-1-yl)-2,3-dihydro-1H-inden-1-amine (h). To a solution of compound e (0.6 g,
2.0 mmol) in 3 mL methanol was added 3 mL concentrated HCl solution. The mixture was stirred at
room temperature for 5hrs, then 40% NaOH solution was added until pH of mixture was 14. After
extraction by DCM (5 x 10 mL), the organic layer was combined and dried by MgSO$_4$, then
concentrated. The pure product (0.36 g, 90% yield) was obtained by silica gel chromatography (very
short column, eluting with 1:10 to 1:5 methanol-DCM). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.31-7.16 (m,
4H), 4.35 (d, J = 7.3 Hz, 1H), 3.10 (dd, J = 15.3, 7.7 Hz, 1H), 2.94 (dd, J = 15.3, 9.0 Hz, 1H),
2.86-2.81 (m, 5H), 2.41 (s, 2H), 1.86 (dd, J = 9.0, 3.9 Hz, 4H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 145.37,
139.57, 127.40, 126.78, 124.37, 123.45, 75.99, 61.21, 52.62, 35.34, 23.23; HRMS (ESI) calcd for
C$_{13}$H$_{19}$N$_2$ (M + H$^+$) 203.1548, found 203.1543.

![Chemical Structure](image)

1-(3,5-bis(trifluoromethyl)phenyl)-3-((1S,2S)-2-(pyrrolidin-1-yl)-2,3-dihydro-1H-inden-1-yl)thiou
rea (3b). To a solution of compound e (0.36 g, 1.78 mmol) in 10 mL DCM was added 1-isothiocyanato-3,5-bis(trifluoromethyl)benzene (0.51 g, 1.87 mmol) dropwise. The mixture was stirred at room temperature for 30 min, reaction completed. The solvent was removed by rotary evaporation and pure product 3b (0.84 g, 95% yield) was obtained by silica gel chromatography (eluting with 1:5 EtOAc- hexane then 1: 10 methanol-DCM). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 12.82\) (s, 1H), 8.05 (s, 2H), 7.63 (s, 1H), 7.34 (ddd, \(J = 37.5, 21.3, 6.6\) Hz, 4H), 6.68 (s, 1H), 5.25-5.23 (m, 1H), 4.03 (q, \(J = 8.2\) Hz, 1H), 3.11 (dd, \(J = 8.7, 3.6\) Hz, 2H), 2.94-2.84 (m, 4H), 1.90 (s, 4H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 182.77, 141.97, 140.04, 137.91, 132.10, 131.83, 131.31, 129.36, 127.95, 125.62, 124.29, 123.49, 123.42, 122.12, 117.94, 77.25, 77.00, 76.75, 70.55, 63.20, 48.55, 26.86, 23.93; HRMS (ESI) calcd for C\(_{22}\)H\(_{22}\)F\(_6\)N\(_3\)S (M + H\(^+\)) 474.1439, found 474.1443.

(15,25)-2-(piperidin-1-yl)-2,3-dihydro-1H-inden-1-amine (i). To a solution of compound f (0.7 g, 2.2 mmol) in 3 mL methanol was added 3 mL concentrated HCl solution. The mixture was stirred at room temperature for 5 hrs, then 40% NaOH solution was added until pH of mixture was 14. After extraction by DCM (5 x 10 mL), the organic layer was combined and dried by MgSO\(_4\), then concentrated. The pure product (0.43 g, 90% yield) was obtained by silica gel chromatography (very short column, eluting with 1:10 to 1: 5 methanol-DCM). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.22\) (d, \(J = 7.3\) Hz, 1H), 7.14-7.07 (m, 3H), 4.25 (d, \(J = 6.9\) Hz, 1H), 2.92 (dd, \(J = 13.9, 6.6\) Hz, 1H), 2.81 (ddd, \(J = 21.8, 14.7, 8.2\) Hz, 2H), 2.53 (s, 4H), 2.15 (s, 2H), 1.58-1.53 (m, 4H), 1.40 (dt, \(J = 11.3, 5.8\) Hz, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 145.16, 139.87, 127.20, 126.56, 124.42, 123.38, 77.71, 58.33, 51.96, 31.95,
To a solution of compound \(i\) (0.4 g, 1.85 mmol) in 10 mL DCM was added 1-isothiocyanato-3,5-bis(trifluoromethyl)benzene (0.53 g, 1.95 mmol) dropwise. The mixture was stirred at room temperature for 30 min, reaction completed. The solvent was removed by rotary evaporation and pure product \(3c\) (0.87 g, 97% yield) was obtained by silica gel chromatography (eluting with 1:10 EtOAc-hexane then 1:10 methanol-DCM). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 12.20\) (s, 1H), 8.06 (s, 2H), 7.70 (s, 1H), 7.43-7.26 (m, 4H), 6.72 (s, 1H), 5.31 (m, 1H), 3.72 (q, \(J = 8.2\) Hz, 1H), 3.21 (dd, \(J = 16.1, 8.5\) Hz, 1H), 3.01 (dd, \(J = 16.1, 8.8\) Hz, 1H), 2.77-2.67 (m, 4H), 1.56 (dd, \(J = 44.8, 22.4\) Hz, 7H); \(^1\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 183.44, 141.53, 140.37, 137.76, 132.13, 131.85, 131.58, 131.31, 129.41, 127.85, 125.78, 125.58, 124.25, 123.61, 122.07, 118.82, 75.27, 62.04, 50.65, 26.33, 25.94, 23.84; HRMS (ESI) calcd for C\(_{23}\)H\(_{24}\)F\(_6\)N\(_3\)S (M + H\(^+\)) 488.1595, found 488.1598.

**tert-butyl (1S,2S)-2-hydroxy-2,3-dihydro-1H-inden-1-ylcarbamate (k)**. It was prepared by using the same procedure for synthesis of compound \(b\). Quantitative yield. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.18-7.11\) (m, 4H), 5.00 (s, 1H), 4.82 (t, \(J = 5.9\) Hz, 1H), 4.35-4.28 (m, 1H), 3.19 (dd, \(J = 15.8, 7.7\) Hz, 1H), 2.81 (dd, \(J = 15.8, 8.1\) Hz, 1H), 1.41 (s, 9H); \(^1\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 157.35, 140.12, 139.34, 128.40, 127.09, 125.09, 123.05, 81.82, 80.40, 63.98, 38.31, 28.31; HRMS (ESI) calcd for C\(_{14}\)H\(_{21}\)N\(_2\) (M + H\(^+\)) 217.1705, found 217.1708.
\[ \text{C}_{12}\text{H}_{19}\text{NO}_3 (M + H^+) \text{ 249.1365, found 249.1366.} \]

\[ \text{NHBoc} \]

**tert-butyl (1S,2R)-2-amino-2,3-dihydro-1H-inden-1-ylcarbamate (l)**. It was prepared by using the same procedure for synthesis of compound e (67% yield, two steps). \( ^1\text{H} \text{NMR (500 MHz, CDCl}_3\text{):} \delta = 7.29 (m, 1H), 7.21 (d, J = 2.2 \text{ Hz, 3H}), 5.23 (s, 1H), 5.03 (s, 1H), 3.82 (s, 1H), 3.12 (dd, J = 15.9, 6.1 \text{ Hz, 1H}), 2.69 (dd, J = 15.9, 3.3 \text{ Hz, 1H}), 1.73 (s, 2H), 1.49 (s, 9H); \] \( ^{13}\text{C} \text{NMR (125 MHz, CDCl}_3\text{):} \delta = 156.05, 141.43, 140.60, 128.00, 126.94, 125.20, 124.71, 79.53, 58.56, 54.70, 39.70, 28.38; \) HRMS (ESI) calcd for \( \text{C}_{14}\text{H}_{21}\text{N}_2\text{O}_2 (M + H^+) \text{ 249.1603, found 249.1606.} \]

\[ \text{NHBoc} \]

**tert-butyl (1S,2R)-2-(piperidin-1-yl)-2,3-dihydro-1H-inden-1-ylcarbamate (m)**. It was prepared by using the same procedure for synthesis of compound f (75% yield). \( ^1\text{H} \text{NMR (300 MHz, CDCl}_3\text{):} \delta = 7.58 (s, 1H), 7.21-7.14 (m, 3H), 5.81 (d, J = 5.3 \text{ Hz, 1H}), 4.90 (s, 1H), 3.02 (p, J = 7.4 \text{ Hz, 1H}), 2.92-2.89 (m, 2H), 2.42 (dd, J = 11.7, 6.2 \text{ Hz, 4H}), 1.58 (dt, J = 12.0, 6.1 \text{ Hz, 6H}), 1.46 (s, 9H); \] \( ^{13}\text{C} \text{NMR (75 MHz, CDCl}_3\text{):} \delta = 156.03, 143.35, 140.42, 127.83, 126.62, 125.95, 124.17, 78.75, 67.58, 54.81, 52.40, 34.51, 28.34, 25.76, 24.26; \) HRMS (ESI) calcd for \( \text{C}_{19}\text{H}_{29}\text{N}_2\text{O}_2 (M + H^+) \text{ 317.2229, found 317.2225.} \)
(1S,2R)-2-(piperidin-1-yl)-2,3-dihydro-1H-inden-1-amine (n). It was prepared by using the same procedure for synthesis of compound i (90% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.30\) (d, \(J = 6.3\) Hz, 1H), 7.14-7.08 (m, 3H), 4.15 (d, \(J = 5.4\) Hz, 1H), 2.80 (qd, \(J = 14.8, 8.5\) Hz, 2H), 2.72-2.68 (m, 1H), 2.48 (s, 2H), 2.38 (d, \(J = 3.8\) Hz, 2H), 2.30 (s, 2H), 1.56 (dt, \(J = 11.0, 5.7\) Hz, 4H), 1.42-1.40 (m, 2H); \(^13\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 144.85, 140.48, 127.51, 126.39, 124.44, 124.35, 69.87, 55.40, 52.58, 33.51, 25.53, 24.04\); HRMS (ESI) calcd for C\(_{14}\)H\(_{21}\)N\(_2\) (M + H\(^+\)) 217.1705, found 217.17010.

1-(3,5-bis(trifluoromethyl)phenyl)-3-((1S,2R)-2-(piperidin-1-yl)-2,3-dihydro-1H-inden-1-yl)thiourea (5). It was prepared by using the same procedure for synthesis of catalyst 3c (97% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 8.38\) (s, 1H), 7.78 (d, \(J = 51.1\) Hz, 3H), 7.60 (s, 1H), 7.15-7.05 (m, 3H), 5.53 (s, 1H), 3.06 (d, \(J = 6.6\) Hz, 1H), 2.89 (dd, \(J = 15.4\) Hz, 6.9, 1H), 2.79-2.74 (m, 1H), 2.31 (s, 4H), 1.25 (s, 6H); \(^13\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 180.13, 141.42, 140.74, 139.08, 133.36, 133.08, 132.81, 132.55, 128.71, 126.97, 126.83, 126.05, 124.47, 123.88, 123.71, 121.71, 119.54, 118.85, 68.02, 58.90, 52.26, 34.34, 25.63, 23.88\); HRMS (ESI) calcd for C\(_{23}\)H\(_{24}\)F\(_6\)N\(_3\)S (M + H\(^+\)) 488.1595, found 488.1590.
(1S,2S)-1-(piperidin-1-yl)-2,3-dihydro-1H-inden-2-ol (o)\(^4\). Compound j (0.75 g, 5 mmol), 1,5-dibromopentane (1.38 g, 6.0 mmol), potassium carbonate (1.80 g, 13 mmol), potassium iodide (0.17 g, 1.0 mmol) and 10 mL iso-propanol were added into a sealed tube. The mixture was heated at 80 °C for 48 hrs and then allowed to cool to room temperature. The mixture was filtered and washing with DCM, the filtrate was concentrated and the resulting residue was purified by silica gel chromatography (eluting with 1:5 EtOAc- hexane then 1:10 methanol-DCM) to obtain the product o (0.82 g, 75% yield). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.36-7.33\) (m, 1H), 7.12-7.16 (m, 3H), 4.66 (dd, \(J = 12.3, 5.3\) Hz, 1H), 4.08 (d, \(J = 4.8\) Hz, 1H), 3.25 (dd, \(J = 16.2, 7.1\) Hz, 1H), 2.80 (dd, \(J = 16.2, 5.5\) Hz, 1H), 2.62-2.61 (m, 4H), 1.58-1.54 (m, 4H), 1.46 (d, \(J = 5.3\) Hz, 2H); \(^1\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 140.62, 140.33, 127.66, 126.41, 125.82, 124.90, 78.49, 73.54, 50.79, 40.06, 26.51, 24.66\); HRMS (ESI) calcd for C\(_{14}\)H\(_{20}\)NO (M + H\(^+\)) 218.1545, found 218.1545.

1-((1S,2R)-2-azido-2,3-dihydro-1H-inden-1-yl)piperidine (p)\(^5\). To a stirred solution of compound o (0.78 g, 3.6 mmol) and triethylamine (1.1 g, 10.8 mmol) in dry DCM (10 mL) at 0°C under nitrogen was added dropwise methanesulfonyl chloride (0.62 g, 5.4 mmol). The mixture was stirred for another 20 min at room temperature, and the solvent was evaporated under reduced pressure. The residue was extracted with DCM, washed successively with water, and brine, and dried over MgSO\(_4\). The organic
layer was concentrated to afford crude mesylate intermediate. Then the crude mesylate intermediate was redissolved in DMF (10 mL), followed by adding NaN₃ (1.87 g, 28.8 mmol). The mixture was heated under nitrogen at 70°C for 6 hrs. After the mixture was cooled, the solvent was evaporated under reduced pressure and the residue was extracted with EtOAc (25 mL x 3) and dried over MgSO₄. The organic layer was removed under reduced pressure, and the crude product was purified by silica gel chromatography (eluting with 1:10 EtOAc- hexane) to afford product p (0.48 g, 55% yield, two step). ¹H NMR (500 MHz, CDCl₃): δ = 7.26-7.10 (m, 4H), 4.63 (d, J = 6.9 Hz, 1H), 3.17 (td, J = 8.0 Hz, 1H), 3.03 (dd, J = 15.8, 7.9 Hz, 1H), 2.81 (dd, J = 15.8, 7.9 Hz, 1H), 2.48 (ddt, J = 38.5, 10.7, 5.2 Hz, 4H), 1.53 (dt, J = 11.3, 5.7 Hz, 4H), 1.39 (dd, J = 11.7, 6.0 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ = 140.43, 139.14, 128.56, 126.94, 124.71, 124.15, 72.82, 66.85, 51.91, 33.83, 25.94, 24.30; HRMS (ESI) calcd for C₁₄H₁₉N₄ (M + H⁺) 243.1610, found 243.1612.

(15,2R)-1-(piperidin-1-yl)-2,3-dihydro-1H-inden-2-amine (q). To a solution of compound p (0.46 g, 1.9 mmol) in 10 mL THF was added triphenylphosphane (1.5 g, 5.7 mmol). The mixture was stirred at room temperature for 3h, then added 3 mL water, heated at 60°C for 4 hrs. The solvent was removed by reduced pressure, and the resulting residue was purified by a very short silica gel column (eluting with 1:10 to 1:5 methanol-DCM) to afford compound q (0.39 g, 95% yield). ¹H NMR (500 MHz, CDCl₃): δ = 7.27 (t, J = 5.8 Hz, 1H), 7.19-7.11 (m, 3H), 4.31 (d, J = 6.9 Hz, 1H), 2.99-2.83 (m, 3H), 2.60-2.58(m, 4H), 2.45 (s, 2H), 1.64-1.59 (m, 4H), 1.45 (dt, J = 11.7, 5.8 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ = 144.92, 139.73, 127.18, 126.54, 124.36, 123.34, 77.45, 58.16, 51.84, 31.67, 25.82, 24.29; HRMS (ESI)
calcd for C_{14}H_{21}N_{2} (M + H\textsuperscript{+}) 217.1705, found 217.1708.

\[\text{1-(3,5-bis(trifluoromethyl)phenyl)-3-((1S,2R)-1-(piperidin-1-yl)-2,3-dihydro-1H-inden-2-yl)thiour}ea \ (4)\]. To a solution of compound q (0.39 g, 1.81 mmol) in 10 mL DCM was added 1-isothiocyanato-3,5-bis(trifluoromethyl)benzene (0.52 g, 1.90 mmol) dropwise. The mixture was stirred at room temperature for 30 min, reaction completed. The solvent was removed by rotary evaporation and pure product 4 (0.90 g, 97% yield) was obtained by silica gel chromatography (eluting with 1:10 EtOAc- hexane then 1: 10 methanol-DCM). \(^1\)H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta = 12.14 \) (s, 1H), 7.98 (s, 2H), 7.61 (s, 1H), 7.27 (dd, \(J = 20.9, 12.6, 4.3 \) Hz, 4H), 6.68 (s, 1H), 5.22 (m, 1H), 3.63 (dd, \(J = 6.2, 8.3 \) Hz, 1H), 3.13 (dd, \(J = 16.1, 8.6 \) Hz, 1H), 2.92 (dd, \(J = 16.2, 8.9 \) Hz, 1H), 2.68-2.60 (m, 4H), 1.56-1.44 (m, 6H); \(^{13}\)C NMR (75 MHz, CDCl\textsubscript{3}): \(\delta = 183.34, 141.50, 140.33, 137.67, 132.31, 131.87, 131.42, 130.98, 129.36, 127.78, 125.76, 125.53, 124.93, 123.58, 121.31, 118.75, 75.21, 62.01, 50.56, 26.29, 25.90, 23.78; HRMS (ESI) calcd for C_{23}H_{24}F_{6}N_{3}S (M + H\textsuperscript{+}) 488.1595, found 488.1587.
3. Representative Procedure

To a solution of 2-mercaptobenzaldehyde 6a (13.8 mg, 0.1 mmol, 1 equiv.) in 0.95 mL xylene was added (E)-3-benzylidenechroman-4-one 7a (20.4 mg, 0.1 mmol, 1 equiv.) at -30, followed by adding of 50 µL of pre-cooled catalyst 5 solution (2.6 mg in 50 µL xylene, 0.005 mmol, 0.05 equiv.). The mixture was stirred at -30 for 8 h. The crude product was purified by column chromatography on silica gel, eluted by hexane/EtOAc= 10:1 then 6:1 to afford 36 mg (96% yield) of the desired product 8a as white solid.

4. Analytical Data

(2'S,3'S,4'R)-4'-hydroxy-2'-phenylspiro[chroman-3,3'-thiochroman]-4-one (8a) (Table 2, entry 1).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.64-7.59 (m, 2H), 7.34-7.31 (m, 2H), 7.18-7.07 (m, 4H), 6.98-6.96 (m, 3H), 6.73 (t, $J = 7.5$ Hz, 1H), 6.50 (d, $J = 8.3$ Hz, 1H), 5.50 (d, $J = 6.7$ Hz, 1H), 5.00 (s, 1H), 4.77 (d, $J = 12.4$ Hz, 1H), 4.55 (d, $J = 12.6$ Hz, 1H), 2.78 (d, $J = 6.7$ Hz, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 195.32, 160.94, 136.09, 134.82, 133.23, 132.61, 129.50, 128.40, 127.82, 127.69, 127.17, 126.71, 125.19, 124.92, 121.58, 120.94, 117.55, 72.58, 66.86, 51.48, 51.37; HRMS (ESI) calcd for
C_{23}H_{18}O_3SNa (M + Na^+) 397.0874, found 397.0872; HPLC (Chiralpak IC, i-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm): t_{major} = 6.7 min, t_{minor} = 9.6 min, ee = 97%, dr = 8.0:1; [α]^{25}_D (major) = +162.8 (c = 1.07 in CHCl_3).

(2'S,3S,4'R)-2'-(4-chlorophenyl)-4'-hydroxyspiro[chroman-3,3'-thiochroman]-4-one (8b) (Table 2, entry 2). The title compound was prepared according the typical procedure, as described above in 98% yield. 1H NMR (300 MHz, CDCl_3): δ = 7.70-7.67 (m, 2H), 7.35-7.15 (m, 6H), 7.02-6.99 (m, 2H), 6.86-6.80 (m, 1H), 6.58 (d, J = 8.1 Hz, 1H), 5.56 (d, J = 6.4 Hz, 1H), 5.03 (s, 1H), 4.80 (d, J = 12.5 Hz, 1H), 4.61 (d, J = 12.5 Hz, 1H), 2.93 (d, J = 6.6 Hz, 1H); 13C NMR (125 MHz, CDCl_3): δ = 195.18, 160.85, 136.35, 134.19, 133.46, 133.06, 132.17, 130.85, 127.90, 127.78, 127.14, 126.68, 125.13, 125.07, 121.55, 121.22, 117.78, 72.85, 66.70, 51.40, 50.78; HRMS (EI) calcd for C_{23}H_{17}ClO_3S 408.0587, found 408.0573; HPLC (Chiralpak IC, i-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm): t_{major} = 6.1 min, t_{minor} = 8.2 min, ee = 95%, dr = 8.1:1; [α]^{25}_D (major) = +138.6 (c = 1.25 in CHCl_3).
(2'S,3'S,4'R)-2'-(3-chlorophenyl)-4'-hydroxyspiro[chroman-3,3'-thiochroman]-4-one (8c) (Table 2, entry 3). The title compound was prepared according the typical procedure, as described above in 96% yield. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.72-7.67$ (m, 2H), 7.48 (s, 1H), 7.29-7.19 (m, 5H), 7.02-6.92 (m, 2H), 6.84 (t, $J = 7.5$ Hz, 1H), 6.61 (d, $J = 8.2$ Hz, 1H), 5.58 (d, $J = 6.4$ Hz, 1H), 5.01 (s, 1H), 4.81 (d, $J = 12.6$ Hz, 1H), 4.62 (d, $J = 12.6$ Hz, 1H), 2.78 (dd, $J = 6.4$, 2.8 Hz, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 195.04$, 160.85, 136.96, 136.38, 133.64, 133.04, 132.02, 129.54, 128.79, 128.53, 127.90, 127.82, 127.17, 126.68, 125.17, 125.10, 121.54, 121.10, 117.66, 72.66, 66.59, 51.28, 50.95; HRMS (EI) calcd for C$_{23}$H$_{17}$O$_4$S 408.0587, found 408.0568; HPLC (Chiralpak IC, i-propanol/hexane = 10/90, flow rate 1.0 mL/min, $\lambda = 254$ nm): $t_{major} = 7.1$ min, $t_{minor} = 8.6$ min, $ee = 97$%, $dr = 7.6:1$; $[^{\alpha}]_{25}D^{(major)} = +140.4$ (c = 1.15 in CHCl$_3$).

(2'R,3'S,4'R)-2'-(2-bromophenyl)-4'-hydroxyspiro[chroman-3,3'-thiochroman]-4-one (8d) (Table 2, entry 4). The title compound was prepared according the typical procedure, as described above in 97% yield. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 8.00$ (d, $J = 7.9$ Hz, 1H), 7.75 (dd, $J = 7.9$, 1.5 Hz, 1H), 7.64 (d, $J = 7.3$ Hz, 1H), 7.23-7.09 (m, 7H), 6.90-6.79 (m, 2H), 6.57 (d, $J = 8.3$ Hz, 1H), 5.68 (d, $J =$
7.2 Hz, 2H), 4.81 (d, J = 12.6 Hz, 1H), 4.63 (d, J = 12.6 Hz, 1H), 3.09 (d, J = 5.8 Hz, 1H); 13C NMR (75 MHz, CDCl₃): δ = 193.88, 160.46, 136.17, 134.89, 133.36, 132.38, 132.23, 131.58, 129.74, 127.92, 127.38, 126.82, 125.43, 125.31, 124.94, 121.31, 120.93, 120.85, 117.42, 72.06, 66.95, 50.71, 48.35; HRMS (ESI) calcd for C₂₃H₁₇BrO₄SNa (M + Na⁺) 474.9979, found 474.9978; HPLC (Chiralpak IC, i-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm): tᵐajor = 6.5 min, tᵦminor = 10.2 min, ee = 95%, dr = 19.0:1; [α]²⁵ D (major) = +405.3 (c = 1.50 in CHCl₃).

(2'S,3S,4'R)-4'-hydroxy-2'-(4-nitrophenyl)spiro[chroman-3,3'-thiochroman]-4-one (8e) (Table 2, entry 5). The title compound was prepared according the typical procedure, as described above in 97% yield. ¹H NMR (300 MHz, CDCl₃): δ = 7.85-7.67 (m, 3H), 7.31-7.17 (m, 4H), 6.94-6.84 (m, 2H), 6.65 (dd, J = 9.9, 1.9 Hz, 1H), 6.53 (d, J = 8.5 Hz, 1H), 5.65 (d, J = 5.8 Hz, 1H), 5.35 (s, 1H), 4.77 (d, J = 12.6 Hz, 1H), 4.60 (d, J = 12.7 Hz, 1H), 2.98 (d, J = 5.8 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 194.37, 160.58, 136.40, 134.88, 132.90, 131.89, 131.76, 127.86, 127.15, 126.68, 125.25, 125.20, 123.86, 121.16, 117.54, 115.25, 114.90, 71.91, 66.60, 50.61, 42.29; HRMS (EI) calcd for C₂₃H₁₇NO₅S 419.0827, found 419.0825; HPLC (Chiralpak IC, i-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm): tᵐajor = 11.4 min, tᵦminor = 14.0 min, ee = 97%, dr = 7.7:1; [α]²⁵ D (major) = +92.2 (c = 0.67 in CHCl₃).
(2'S,3S,4'R)-2'-(3,4-dichlorophenyl)-4'-hydroxyspiro[chroman-3,3'-thiochroman]-4-one (8f) (Table 2, entry 6). The title compound was prepared according the typical procedure, as described above in 97% yield. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.73-7.67 (m, 2H), 7.57 (d, $J$ = 2.2 Hz, 1H), 7.32-7.29 (m, 1H), 7.26-7.16 (m, 4H), 7.08 (d, $J$ = 8.5 Hz, 1H), 6.88-6.85 (m, 1H), 6.61 (d, $J$ = 8.5 Hz, 1H), 5.56 (s, 1H), 4.97 (s, 1H), 4.78 (d, $J$ = 12.6 Hz, 1H), 4.61 (d, $J$ = 12.3 Hz, 1H), 2.81 (s, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 194.94, 160.75, 136.54, 135.26, 132.92, 132.36, 131.83, 131.68, 131.37, 129.36, 128.91, 127.98, 127.17, 126.68, 125.23, 125.14, 121.51, 121.35, 117.68, 72.56, 66.51, 51.22, 50.40; HRMS (EI) calcd for C$_{23}$H$_{17}$Cl$_2$O$_3$S 442.0197, found 442.0117; HPLC (Chiralpak IC, i-propanol/hexane = 10/90, flow rate 1.0 mL/min, $\lambda$ = 254 nm): $t_{\text{major}}$ = 5.8 min, $t_{\text{minor}}$ = 6.9 min, ee = 95%, dr = 8.2:1; $[\alpha]_{D}^{25}$ (major) = +125.5 ($c$ = 1.40 in CHCl$_3$).

(2'R,3S,4'R)-2'-(4-chloro-2-fluorophenyl)-4'-hydroxyspiro[chroman-3,3'-thiochroman]-4-one (8g) (Table 2, entry 7). The title compound was prepared according the typical procedure, as described above in 95% yield. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.88 (t, $J$ = 7.1 Hz, 2H), 7.78 (d, $J$ = 8.0 Hz, 1H), 7.37-7.28 (m, 5H), 7.06-7.01 (m, 1H), 6.89 (t, $J$ = 7.4 Hz, 1H), 6.77 (d, $J$ = 8.5 Hz, 1H), 6.61 (d, $J$ = 8.5 Hz, 1H), 4.91 (s, 1H), 4.78 (d, $J$ = 12.5 Hz, 1H), 4.59 (d, $J$ = 12.3 Hz, 1H), 2.79 (s, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 194.90, 160.75, 136.54, 135.26, 132.92, 132.36, 131.83, 131.68, 131.37, 129.36, 128.91, 127.98, 127.17, 126.68, 125.23, 125.14, 121.51, 121.35, 117.68, 72.56, 66.51, 51.22, 50.40; HRMS (EI) calcd for C$_{23}$H$_{17}$Cl$_2$F$_2$O$_3$S 464.0427, found 464.0427; HPLC (Chiralpak IC, i-propanol/hexane = 10/90, flow rate 1.0 mL/min, $\lambda$ = 254 nm): $t_{\text{major}}$ = 5.8 min, $t_{\text{minor}}$ = 6.9 min, ee = 95%, dr = 8.2:1; $[\alpha]_{D}^{25}$ (major) = +125.5 ($c$ = 1.40 in CHCl$_3$).
1H), 7.73-7.69 (m, 1H), 7.59 (d, J = 8.8 Hz, 0H), 7.49 (t, J = 7.5 Hz, 1H), 7.39 (t, J = 7.4 Hz, 1H), 7.24 (t, J = 5.3 Hz, 1H), 6.84 (t, J = 7.6 Hz, 1H), 6.54 (d, J = 8.3 Hz, 0H), 5.61 (d, J = 6.0 Hz, 1H), 5.12 (s, 1H), 5.12 (s, 1H), 4.80 (d, J = 12.7 Hz, 1H), 4.62 (d, J = 12.7 Hz, 1H), 2.78 (d, J = 6.1 Hz, 1H); ^13^C NMR (75 MHz, CDCl3); δ = 191.78, 160.70, 142.76, 140.05, 136.73, 134.61, 134.25, 133.84, 132.91, 130.57, 128.05, 127.18, 126.73, 126.31, 125.38, 125.19, 122.63, 121.48, 117.71, 72.50, 66.57, 51.62, 50.97; HRMS (EI) calcd for C_{23}H_{16}ClFO_{3}S 426.0493, found 426.0475; HPLC (Chiralpak IC, i-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm): t_{major} = 7.1 min, t_{minor} = 8.6 min, ee = 97%, dr = 20.0:1; [α]^{25}_{D} (major) = +150.6 (c = 1.23 in CHCl3).

(2'S,3'S,4'R)-4'-hydroxy-2'-{(4-methoxyphenyl)spiro[chroman-3,3'-thiochroman]-4-one (8h) (Table 2, entry 8). The title compound was prepared according the typical procedure, as described above in 96% yield. ^1^H NMR (500 MHz, CDCl3); δ = 7.69-7.65 (m, 2H), 7.33-7.30 (m, 2H), 7.24-7.14 (m, 4H), 6.81-6.79 (m, 1H), 6.61-6.56 (m, 3H), 5.54 (d, J = 6.6 Hz, 1H), 5.05 (s, 1H), 4.83 (d, J = 12.6 Hz, 1H), 4.62 (d, J = 12.3 Hz, 1H), 3.64 (s, 3H), 2.88 (d, J = 6.6 Hz, 1H); ^1^C NMR (125 MHz, CDCl3): δ = 195.48, 160.93, 159.47, 136.02, 133.23, 132.80, 130.67, 127.77, 127.14, 126.68, 126.61, 125.07, 124.82, 121.65, 120.95, 117.74, 113.07, 73.05, 66.85, 55.18, 51.47, 50.74; HRMS (ESI) calcd for C_{24}H_{20}O_{4}SNa (M + Na) 427.0980, found 427.0991; HPLC (Chiralpak IC, i-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm): t_{major} = 9.6 min, t_{minor} = 14.1 min, ee = 96%, dr = 8.0:1; [α]^{25}_{D} (major) = +150.6 (c = 1.23 in CHCl3).
(major) = +116.4 (c = 1.17 in CHCl₃).

(2'S,3S,4'R)-2'-(4-(allyloxy)phenyl)-4'-hydroxyspiro[chroman-3,3'-thiochroman]-4-one (8i) (Table 2, entry 9). The title compound was prepared according the typical procedure, as described above in 96% yield. ¹H NMR (300 MHz, CDCl₃): δ = 7.71-7.65 (m, 2H), 7.32-7.17 (m, 6H), 6.83 (t, J = 7.5 Hz, 1H), 6.62-6.57 (m, 3H), 5.93 (ddd, J = 22.8, 10.6, 5.5 Hz, 1H), 5.55 (d, J = 6.6 Hz, 1H), 5.25 (m, 2H), 5.04 (s, 1H), 4.84 (d, J = 12.4 Hz, 1H), 4.62 (d, J = 12.4 Hz, 1H), 4.38 (d, J = 5.3 Hz, 2H), 2.70 (d, J = 6.9 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ = 195.45, 160.92, 158.45, 136.04, 133.16, 132.99, 132.78, 130.64, 127.79, 127.13, 126.75, 126.68, 125.08, 124.83, 121.63, 120.96, 117.77, 117.54, 113.91, 73.01, 68.64, 66.83, 51.44, 50.75; HRMS (ESI) calcd for C₂₆H₂₂O₄SNa (M + Na⁺) 453.1136, found 453.1119; HPLC (Chiralpak IC, i-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm):

*tm*ajor = 8.6 min, *t*m*inor = 12.7 min, ee = 96%, dr = 8.0:1; [α]$_D^{25}$ (major) = +227.3 (c = 1.17 in CHCl₃).
The title compound was prepared according the typical procedure, as described above in 98% yield. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.86 (dd, $J$ = 7.9 Hz, 1.6, 1H), 7.68-7.64 (m, 2H), 7.24-7.15 (m, 4H), 6.96-6.93 (m, 1H), 6.79-6.75 (m, 2H), 6.46 (d, $J$ = 8.2 Hz, 1H), 6.38 (d, $J$ = 8.2 Hz, 1H), 6.02 (dd, $J$ = 17.3, 10.4, 5.7, 5.0 Hz, 1H), 5.65 (s, 2H), 5.36 (dd, $J$ = 17.0, 3.0, 1.6 Hz, 1H), 5.27 (m, 1H), 4.69 (d, $J$ = 12.6 Hz, 1H), 4.55 (m, 1H), 4.26 (m, 1H), 4.17 (m, 1H), 3.22 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 194.48, 160.64, 155.65, 135.71, 133.47, 133.05, 132.96, 130.55, 129.21, 127.62, 127.02, 126.26, 125.51, 124.95, 124.15, 121.10, 120.36, 119.95, 117.52, 117.33, 110.28, 71.95, 68.87, 66.99, 50.82, 42.65; HRMS (ESI) calc for C$_{26}$H$_{22}$O$_4$SNa ($M^+$ Na$^+$) 453.1136, found 453.1141; HPLC (Chiralpak IC, $i$-propanol/hexane = 10/90, flow rate 1.0 mL/min, $\lambda$ = 254 nm): $t_{\text{major}}$ = 6.4 min, $t_{\text{minor}}$ = 7.3 min, ee = 99%, dr = 11.0:1; $[\alpha]_{D}^{25}$ (major) = +465.9 (c = 1.33 in CHCl$_3$).

(2'S,3S,4'R)-4'-hydroxy-2'- (3-phenoxyphenyl) spiro[chroman-3,3'-thiochroman]-4-one (8k) (Table 2, entry 11). The title compound was prepared according the typical procedure, as described above in 97% yield. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.73-7.65 (m, 2H), 7.31-7.98 (m, 10H), 6.87-6.84 (m, 1H), 6.77-6.75 (m, 2H), 6.69-7.63 (m, 2H), 5.55 (s, 1H), 5.02 (s, 1H), 4.81 (d, $J$ = 12.6 Hz, 1H), 4.61 (d, $J$ = 12.3 Hz, 1H), 3.09 (s, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 195.28, 161.03, 157.06, 156.24, 136.88, 136.19, 133.09, 132.30, 129.59, 128.93, 127.78, 127.14, 126.79, 125.11, 124.91, 124.63, 123.08, 121.56, 120.98, 120.35, 119.11, 118.42, 117.79, 72.75, 66.65, 51.54, 51.29; HRMS (ESI) calc for C$_{29}$H$_{22}$O$_4$SNa ($M^+$ Na$^+$) 489.1136, found 489.1143; HPLC (Chiralpak IC, $i$-propanol/hexane = 10/90, flow rate 1.0 mL/min, $\lambda$ = 254 nm): $t_{\text{major}}$ = 6.4 min, $t_{\text{minor}}$ = 7.3 min, ee = 99%, dr = 11.0:1; $[\alpha]_{D}^{25}$ (major) = +465.9 (c = 1.33 in CHCl$_3$).
10/90, flow rate 1.0 mL/min, \( \lambda = 254 \text{ nm} \): \( t_{\text{major}} = 6.5 \text{ min}, \ t_{\text{minor}} = 7.2 \text{ min}, \ ee = 98\%, \ dr = 11.0:1; \)

\([\alpha]_{25}^D\) (major) = +164.9 (c = 1.50 in CHCl₃).

(2'S,3S,4'R)-4'-hydroxy-2'- (4-isopropylphenyl)spiro[chroman-3,3′-thiochroman]-4-one (8l) (Table 2, entry 12). The title compound was prepared according the typical procedure, as described above in 97% yield. ¹H NMR (500 MHz, CDCl₃): \( \delta = 7.68-7.65 \text{ (m, 2H)}, 7.29 \text{ (d, } J = 8.2 \text{ Hz, 2H)}, 7.21-7.14 \text{ (m, 4H)}, 6.86 \text{ (d, } J = 8.2 \text{ Hz, 2H)}, 6.78-6.75 \text{ (m, 1H)}, 6.52 \text{ (d, } J = 8.2 \text{ Hz, 1H)}, 5.58 \text{ (d, } J = 6.3 \text{ Hz, 1H)}, 5.03 \text{ (s, 1H)}, 4.85 \text{ (d, } J = 12.3 \text{ Hz, 1H)}, 4.61 \text{ (d, } J = 12.3 \text{ Hz, 1H}), 2.93 \text{ (d, } J = 6.6 \text{ Hz, 1H}), 2.67 \text{ (dt, } J = 13.9, 6.9 \text{ Hz, 1H}), 1.04 \text{ (dd, } J = 6.9, 0.9 \text{ Hz, 6H}); ¹³C NMR (125 MHz, CDCl₃): \( \delta = 195.44, 160.84, 149.17, 135.88, 133.17, 132.71, 131.87, 129.35, 127.74, 127.19, 126.67, 125.56, 125.15, 124.81, 121.53, 120.66, 117.64, 72.67, 66.70, 51.32, 51.14, 33.67, 23.68, 23.66; HRMS (ESI) calcd for C₂₆H₂₄O₃SNa (M + Na⁺) 439.1344, found 439.1321; HPLC (Chiralpak IC, \( \beta \)-propanol/hexane = 10/90, flow rate 1.0 mL/min, \( \lambda = 254 \text{ nm} \): \( t_{\text{major}} = 7.0 \text{ min}, \ t_{\text{minor}} = 10.9 \text{ min}, \ ee = 97\%, \ dr = 8.0:1; \ [\alpha]_{25}^D\) (major) = +150.5 (c = 1.00 in CHCl₃).
(2'R,3S,4'R)-2'-(5-bromobenzo[d][1,3]dioxol-4-yl)-4'-hydroxy-spiro[chroman-3,3'-thiochroman]-4-one (8m) (Table 2, entry 13). The title compound was prepared according the typical procedure, as described above in 98% yield. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.76-7.74 (m, 1H), 7.63 (d, $J$ = 7.6 Hz, 1H), 7.47 (s, 1H), 7.31-7.17 (m, 4H), 6.86-6.83 (m, 1H), 6.68 (d, $J$ = 8.2 Hz, 1H), 6.63 (s, 1H), 5.84 (dd, $J$ = 38.0, 1.4 Hz, 2H), 5.63 (d, $J$ = 24.0 Hz, 2H), 4.79 (d, $J$ = 12.6 Hz, 1H), 4.64 (d, $J$ = 12.6 Hz, 1H), 3.12 (s, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 193.85, 160.42, 148.04, 146.88, 136.10, 133.29, 132.31, 127.92, 127.59, 127.43, 126.82, 125.39, 125.27, 121.03, 120.93, 117.34, 115.76, 111.72, 110.92, 101.80, 71.95, 66.75, 50.66, 48.47; HRMS (ESI) calcd for C$_{24}$H$_{17}$BrO$_5$SNa (M + Na$^+$) 518.9878, found 518.9897; HPLC (Chiralpak IC, i-propanol/hexane = 10/90, flow rate 1.0 mL/min, $\lambda$ = 254 nm): $t_{\text{major}}$ = 8.6 min, $t_{\text{minor}}$ = 13.0 min, ee = 98%, dr = 17.0:1; $[\alpha]^{22}_D$(major) = +147.3 (c = 1.23 in CHCl$_3$).

(2'R,3S,4'R)-4'-hydroxy-2'-{(5-methylfuran-2-yl)spiroadan-3,3'-thiochroman]-4-one (8n) (Table 2, entry 14). The title compound was prepared according the typical procedure, as described above in 96% yield. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.82 (dd, $J$ = 7.9 Hz, 1.6, 1H), 7.65 (d, $J$ = 7.6 Hz, 1H), 7.37 (ddd, $J$ = 8.8, 7.3, 1.9 Hz, 1H), 7.20-7.15 (m, 3H), 6.94-6.90 (m, 1H), 6.78 (m,
1H), 6.20 (d, J = 3.2 Hz, 1H), 5.67 (m, 1H), 5.41 (d, J = 6.3 Hz, 1H), 5.09 (s, 1H), 4.70 (d, J = 12.6 Hz, 1H), 4.59 (d, J = 12.3 Hz, 1H), 3.01 (d, J = 7.3 Hz, 1H), 1.98 (s, 3H); 13C NMR (126 MHz, CDCl3): δ = 194.92, 161.35, 152.20, 146.68, 136.00, 133.47, 131.97, 127.82, 127.40, 127.03, 125.24, 125.06, 121.36, 121.14, 117.74, 111.00, 106.21, 72.50, 67.37, 51.10, 43.26, 13.19; HRMS (ESI) calcd for C22H18O4SNa (M + Na+) 401.0823, found 401.0825; HPLC (Chiralpak IC, i-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm): t_major = 7.8 min, t_minor = 9.1 min, ee = 96%, dr = 8.4:1; [α]25D (major) = +80.1 (c = 1.33 in CHCl3).

(2'R,3S,4'R)-4'-hydroxy-2'-(thiophen-2-yl)spiro[chroman-3,3'-thiochroman]-4-one (8o) (Table 2, entry 15). The title compound was prepared according to the typical procedure, as described above in 98% yield. 1H NMR (500 MHz, CDCl3): δ = 7.78-7.76 (m, 2H), 7.34-7.31 (m, 1H), 7.25-7.16 (m, 3H), 7.04 (dd, J = 8.0 Hz, 4.3, 2H), 6.88 (t, J = 7.1 Hz, 1H), 6.72 (dd, J = 5.0, 3.5 Hz, 2H), 5.46-5.43 (m, 2H), 4.80 (d, J = 12.3 Hz, 1H), 4.63 (d, J = 12.3 Hz, 1H), 2.99 (d, J = 7.9 Hz, 1H); 13C NMR (125 MHz, CDCl3): δ = 195.23, 161.28, 137.75, 136.18, 133.41, 132.33, 128.52, 127.91, 127.17, 126.96, 126.31, 125.57, 125.15, 124.87, 122.00, 121.34, 117.88, 73.68, 67.16, 51.67, 45.56; HRMS (ESI) calcd for C21H16O4S2Na (M + Na+) 403.0439, found 403.0420; HPLC (Chiralpak IC, i-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm): t_major = 7.6 min, t_minor = 9.3 min, ee = 97%, dr = 8.3:1; [α]25D (major) = +129.2 (c = 1.40 in CHCl3).
(2'S,3S,4'R)-4'-hydroxy-2'-isopropylspiro[chroman-3,3'-thiochroman]-4-one (8q) (Table 2, entry 17). The title compound was prepared according the typical procedure, as described above in 96% yield. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.93-7.90 (m, 1H), 7.61-7.45 (m, 2H), 7.19-6.92 (m, 5H), 5.24
(d, J = 7.3 Hz, 1H), 4.50 (q, J = 12.4 Hz, 2H), 4.03 (d, J = 4.7 Hz, 1H), 2.84 (d, J = 7.3 Hz, 1H), 2.02-1.91 (m, 1H), 1.07 (d, J = 6.6 Hz, 3H), 0.97 (d, J = 6.7 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta =$ 196.70, 161.62, 136.41, 133.86, 132.66, 127.64, 127.09, 126.34, 125.49, 124.56, 122.70, 121.81, 118.25, 75.26, 66.93, 54.81, 51.77, 30.03, 24.24, 19.27; HRMS (ESI) calcd for C$_{20}$H$_{20}$O$_3$SNa (M + Na$^+$) 363.1031, found 363.1038; HPLC (Chiralpak IC, i-propanol/hexane = 10/90, flow rate 1.0 mL/min, $\lambda =$ 254 nm): t$_{\text{major}}$ = 7.3 min, t$_{\text{minor}}$ = 8.6 min, ee = 95%, dr = 57.0:1; $[\alpha]^{25}_D$ (major) = +48.4 (c = 1.03 in CHCl$_3$).

$^{1}$H NMR (300 MHz, CDCl$_3$): $\delta =$ 7.92 (dd, J = 7.9 Hz, 1.6, 1H), 7.60-7.46 (m, 2H), 7.17-6.93 (m, 5H), 5.20 (d, J = 7.2 Hz, 1H), 4.50 (q, J = 12.3 Hz, 2H), 4.00 (d, J = 4.9 Hz, 1H), 2.77 (d, J = 7.6 Hz, 1H), 2.04 (d, J = 12.7 Hz, 1H), 1.70-1.43 (m, 4H), 1.26-0.83 (m, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta =$ 196.45, 161.53, 136.29, 134.04, 132.84, 127.64, 127.10, 126.27, 125.42, 124.58, 122.81, 121.83, 118.13, 110.18, 75.48, 67.20, 53.86, 51.31, 40.16, 34.34, 30.27, 26.63, 26.32, 25.85; HRMS (ESI) calcd for C$_{23}$H$_{24}$O$_3$SNa (M + Na$^+$) 403.1344, found 403.1345; HPLC (Chiralpak IC, i-propanol/hexane = 10/90, flow rate 1.0 mL/min, $\lambda =$ 254 nm): t$_{\text{major}}$ = 5.7 min, t$_{\text{minor}}$ = 6.3 min, ee = 96%, dr = 24.0:1; $[\alpha]^{25}_D$ (major) = +103.7 (c = 1.05 in CHCl$_3$).
(25,2'S,4'R)-4'-hydroxy-2'-phenyl-3,4-dihydro-1H-spiro[naphthalene-2,3'-thiochroman]-1-one (8s)

(Table 2, entry 19). The title compound was prepared according the typical procedure, as described above in 96% yield. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.79-7.77 (m, 1H), 7.64 (d, $J = 7.6$ Hz, 1H), 7.44-7.42 (m, 2H), 7.29-7.10 (m, 8H), 6.94 (d, $J = 7.6$ Hz, 1H), 5.47 (s, 1H), 5.38 (d, $J = 6.3$ Hz, 1H), 2.98 (d, $J = 6.6$ Hz, 1H), 2.93-2.87 (m, 1H), 2.39-2.33 (m, 1H), 2.18-2.03 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 202.37, 144.23, 136.57, 135.20, 133.71, 133.68, 133.50, 129.88, 128.17, 128.07, 128.05, 127.33, 127.12, 126.28, 126.14, 125.12, 124.52, 77.38, 52.58, 52.57, 25.94, 22.02; HRMS (ESI) calcd for C$_{24}$H$_{20}$O$_2$SNa (M + Na$^+$) 395.1082, found 395.1088; HPLC (Chiralpak IC, $i$-propanol/hexane = 10/90, flow rate 1.0 mL/min, $\lambda$ = 254 nm): $t_{\text{major}}$ = 7.1 min, $t_{\text{minor}}$ = 8.2 min, $ee = 95\%$, dr = 10.0:1; $[\alpha]^{25}_{D}$ (major) = + 49.0 (c = 1.20 in CHCl$_3$).

(2'S,3'S,4'R)-4'-hydroxy-2'-phenyl-3,3'-spirobi[thiochroman]-4-one (8t)

(Table 2, entry 20). The title compound was prepared according the typical procedure, as described above in 97% yield. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.97-7.96 (m, 1H), 7.69-7.68 (m, 1H), 7.50-7.48 (m, 1H), 7.29-7.09 (m, 9H), 5.52 (s, 1H), 5.30 (d, $J = 11.0$ Hz, 1H), 3.54 (dd, $J = 14.2$, 1.3 Hz, 1H), 3.48 (d, $J = 11.0$ Hz, 1H),
3.27 (d, J = 14.2 Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 196.36, 139.71, 135.69, 135.22, 133.21,
133.03, 132.88, 130.24, 130.12, 128.41, 128.18, 127.91, 127.66, 126.39, 125.79, 125.30, 125.03, 78.40,
51.67, 51.36, 28.02; HRMS (EI) calcd for C$_{23}$H$_{18}$O$_2$S$_2$ 390.0748, found 390.0730; HPLC (Chiralpak IC,
i-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm): t$_{major}$ = 14.3 min, t$_{minor}$ = 15.6 min, ee =
96%, dr = 1.2:1; [$\alpha$]$_{25}^D$ (major) = -55.4 (c = 0.93 in CHCl$_3$).

(2'S,3S,4'R)-4'-hydroxy-6-methyl-2'-phenylspiro[chroman-3,3'-thiochroman]-4-one (8u) (Table 2, entry 21). The title compound was prepared according the typical procedure, as described above in
98% yield. $^1$H NMR (500 MHz, CDCl$_3$): δ = 7.69-7.67 (m, 1H), 7.44-7.39 (m, 3H), 7.21 (t, J = 3.8 Hz,
2H), 7.18-7.14 (m, 1H), 7.06-7.01 (m, 4H), 6.47 (d, J = 8.5 Hz, 1H), 5.54 (d, J = 6.9 Hz, 1H), 5.09 (s,
1H), 4.79 (d, J = 12.6 Hz, 1H), 4.60 (d, J = 12.3 Hz, 1H), 3.15 (d, J = 6.6 Hz, 1H), 2.13 (s, 3H); $^{13}$C
NMR (125 MHz, CDCl$_3$): δ = 195.51, 159.12, 137.28, 134.96, 133.44, 132.67, 130.33, 129.54, 128.32,
127.74, 127.68, 127.14, 126.19, 125.14, 124.86, 121.23, 117.43, 73.19, 66.86, 51.55, 51.29, 20.24;
HRMS (ESI) calcd for C$_{24}$H$_{20}$O$_3$SNa (M + Na$^+$) 411.1031, found 411.1018; HPLC (Chiralpak IC,
i-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm): t$_{major}$ = 7.3 min, t$_{minor}$ = 13.2 min, ee =
97%, dr = 16.0:1; [$\alpha$]$_{25}^D$ (major) = +109.5 (c = 1.57 in CHCl$_3$).
(2'S,3S,4'R)-6-chloro-4'-hydroxy-2'-phenylspiro[chroman-3,3'-thiochroman]-4-one (8v) (Table 2, entry 22). The title compound was prepared according the typical procedure, as described above in 97% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 7.65 (dd, $J$=9.6, 5.2, 2H), 7.38 (dd, $J$=6.6, 2.8, 2H), 7.23-7.15 (m, 2H), 7.08-7.06 (m, 2H), 6.53 (d, $J$=9.1, 1H), 5.57 (d, $J$=6.0, 1H), 5.05 (s, 1H), 4.86 (d, $J$=12.6, 1H), 4.61 (d, $J$=12.6, 1H), 2.81 (d, $J$=6.3, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 194.71, 159.42, 135.89, 134.42, 132.93, 132.41, 129.42, 128.58, 127.86, 127.75, 127.17, 126.37, 125.75, 125.13, 124.94, 122.02, 119.41, 72.74, 66.88, 51.51, 51.46; HRMS (EI) calcd for C$_{23}$H$_{17}$ClO$_3$S 431.0485, found 431.0466; HPLC (Chiralpak IC, $i$-propanol/hexane = 10/90, flow rate 1.0 mL/min, $\lambda$ = 254 nm): $t_{\text{major}}$ = 5.6 min, $t_{\text{minor}}$ = 7.1 min, ee = 98%, dr = 11.0:1; $[\alpha]^{25}_{D}$ (major) = +205.2 ($c$ = 1.33 in CHCl$_3$).

(2'S,3S,4'R)-4'-hydroxy-6'-methyl-2'-phenylspiro[chroman-3,3'-thiochroman]-4-one (8w) (Table 2, entry 23). The title compound was prepared according the typical procedure, as described above in 96% yield. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.71-7.69 (m, 1H), 7.48 (s, 1H), 7.40-7.38 (m, 2H), 7.26-7.22 (m, 2H), 7.11 (d, $J$ = 8.2 Hz, 1H), 7.05 (d, $J$ = 6.6 Hz, 4H), 6.81 (t, $J$ = 7.6 Hz, 1H), 6.58 (d, $J$ = 6.3 Hz, 1H), 4.59 (d, $J$ = 12.6, 1H), 4.40 (d, $J$ = 12.6, 1H), 2.22 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 190.28, 159.42, 134.42, 132.93, 132.41, 129.42, 128.58, 127.86, 127.75, 127.17, 126.37, 125.75, 125.13, 124.94, 122.02, 119.41, 72.74, 66.88, 51.51, 51.46; HRMS (EI) calcd for C$_{23}$H$_{19}$O$_3$S 417.0468, found 417.0450; HPLC (Chiralpak IC, $i$-propanol/hexane = 10/90, flow rate 1.0 mL/min, $\lambda$ = 254 nm): $t_{\text{major}}$ = 6.3 min, $t_{\text{minor}}$ = 7.1 min, ee = 96%, dr = 11.0:1; $[\alpha]^{25}_{D}$ (major) = +205.2 ($c$ = 1.33 in CHCl$_3$).
= 8.5 Hz, 1H), 5.54 (d, J = 6.6 Hz, 1H), 5.05 (s, 1H), 4.83 (d, J = 12.3 Hz, 1H), 4.62 (d, J = 12.6 Hz, 1H), 2.72 (d, J = 6.9 Hz, 1H), 2.34 (s, 3H); "C NMR (125 MHz, CDCl3): δ = 195.32, 160.96, 136.04, 135.04, 134.73, 133.07, 129.48, 128.96, 128.75, 128.34, 127.75, 127.69, 126.75, 125.21, 121.59, 120.93, 117.71, 73.02, 67.04, 51.72, 51.23, 21.12; HRMS (ESI) calcd for C_{24}H_{20}O_{3}SNa (M + Na⁺) 411.1031, found 411.1011; HPLC (Chiralpak IC, i-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm): t_{major} = 6.7 min, t_{minor} = 11.4 min, ee = 96%, dr = 9.0:1; [α]_{D}^{25} (major) = +85.5 (c = 1.33 in CHCl₃).

(2'S,3'S,4'R)-4'-hydroxy-6'-methoxy-2'-phenylspiro[chroman-3,3'-thiochroman]-4-one (8x) (Table 2, entry 24). The title compound was prepared according the typical procedure, as described above in 97% yield. "H NMR (500 MHz, CDCl3): δ = 7.70-7.68 (m, 1H), 7.39-7.37 (m, 2H), 7.26-7.22 (m, 2H), 7.13 (d, J = 8.5 Hz, 1H), 7.06-7.03 (m, 3H), 6.82 (m, 2H), 6.58 (d, J = 8.2 Hz, 1H), 5.53 (d, J = 6.6 Hz, 1H), 5.05 (s, 1H), 4.80 (d, J = 12.6 Hz, 1H), 4.61 (d, J = 12.3 Hz, 1H), 3.81 (s, 3H), 2.82 (d, J = 6.9 Hz, 1H); "C NMR (125 MHz, CDCl3): δ = 195.33, 160.97, 157.65, 136.08, 135.15, 134.78, 129.42, 128.32, 127.69, 126.75, 126.45, 123.17, 121.53, 120.94, 117.70, 114.59, 112.53, 73.11, 67.02, 51.89, 51.28; HRMS (ESI) calcd for C_{24}H_{20}O_{3}SNa (M + Na⁺) 427.0980, found 427.0989; HPLC (Chiralpak IC, i-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm): t_{major} = 9.9 min, t_{minor} = 18.2 min, ee = 95%, dr = 15.0:1; [α]_{D}^{25} (major) = +59.5 (c = 1.10 in CHCl₃).

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(2'S,3'S,4'R)-6'-chloro-4'-hydroxy-2'-phenylspiro[chroman-3,3'-thiochroman]-4-one (8y) (Table 2, entry 25). The title compound was prepared according the typical procedure, as described above in 93% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 7.70-7.68 (m, 2H), 7.39-7.37 (m, 2H), 7.21 (ddddd, $J$=29.0, 27.4, 17.0, 5.0, 3H), 7.06-7.04 (m, 3H), 6.83-6.80 (m, 1H), 6.56 (d, $J$=8.5, 1H), 5.54 (d, $J$=6.6, 1H), 5.05 (s, 1H), 4.81 (d, $J$=12.3, 1H), 4.60 (d, $J$=12.6, 1H), 2.78 (d, $J$=6.6, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 195.03, 160.90, 136.25, 134.88, 134.41, 131.12, 130.83, 129.46, 128.56, 128.01, 127.72, 127.35, 126.68, 126.34, 121.48, 121.02, 117.74, 72.61, 66.56, 51.54, 51.14; HRMS (EI) calcd for C$_{23}$H$_{17}$ClO$_3$S 408.0587, found 408.0569; HPLC (Chiralpak IC, $i$-propanol/hexane = 10/90, flow rate 1.0 mL/min, $\lambda$ = 254 nm): $t_{major}$ = 5.9 min, $t_{minor}$ = 22.2 min, ee = 92%, dr = 8.0:1; [$\alpha$]$^D_{25}$ (major) = +37.9 ($c$ = 0.93 in CHCl$_3$).

5. Oxidation of Compound 8a

To a solution of 8a (37.5 mg, 0.1 mmol) in 2 mL DMSO was added 2-Iodoxybenzoic acid (IBX, 84 mg, 0.3 mmol). The mixture was stirred at room temperature for 4h, reaction completed. The mixture was diluted with 10 mL water, extracted with EtOAc (3x 20 mL), the organic layers were combined, dried
and concentrated. The crude product was purified by silica gel chromatography (eluting with 1:6 EtOAc-hexane) to give product 9a (34.6 mg, 93% yield).\(^6\) \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 8.11\) (dd, \(J = 7.9\) Hz, 1.3, 1H), 7.90 (dd, \(J = 7.9\) Hz, 1.9, 1H), 7.52-7.44 (m, 2H), 7.37 (dd, \(J = 7.1, 2.4\) Hz, 2H), 7.27-7.24 (m, 5H), 7.04 (m, 2H), 5.00-4.97 (m, 2H), 4.44 (d, \(J = 12.3\) Hz, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 192.54, 189.85, 160.74, 140.52, 136.33, 136.18, 133.89, 130.87, 129.24, 128.79, 128.74, 128.59, 128.01, 126.88, 125.30, 122.06, 120.43, 117.62, 69.20, 57.88, 47.57\); HRMS (ESI) calcd for C\(_{23}\)H\(_{16}\)O\(_3\)SNa (M + Na\(^+\)) 395.0718, found 395.0689; HPLC (Chiralpak IC, \(i\)-propanol/hexane = 10/90, flow rate 1.0 mL/min, \(\lambda = 254\) nm): \(t_{\text{major}} = 10.8\) min, \(t_{\text{minor}} = 17.7\) min, \(ee = 97\%\), \(dr = 8.0:1\); \([\alpha]^{25}_D\) (major) = −300.2 (c = 1.07 in CHCl\(_3\)).

6. Preparation of Compound 12 for X-ray Crystallographic analysis

![Diagram of synthesis](image)

To a stirred mixture of compound 8e (210 mg, 0.5 mmol) and water (6 mL), NH\(_4\)Cl (214 mg, 4 mmol) and zinc metal powder (490 mg, 7.5 mmol) were added at room temperature. After the reaction mixture was stirred for 1 hour at 80 °C, the mixture was extracted with EtOAc (3 x 20 mL). The combined organic layer was dried by MgSO\(_4\) and concentrated, the resulting residue was purified by silica gel chromatography (eluting with EtOAc/hexane = 1/2) to give intermediate product 8z (107 mg, 55% yield).\(^7\)

The intermediate product 8z (98 mg, 0.25 mmol) was dissolved in 2 mL dried pyridine. Then
naphthalene-1-sulfonyl chloride (170 mg, 0.75 mmol) was added into the mixture. The reaction mixture was stirred at room temperature overnight. After that, 10 mL 1.0 M HCl solution was added and the resulting mixture was extracted with EtOAc (3 x 20 mL). The combined organic layer was dried by MgSO₄ and concentrated, the resulting residue was purified by silica gel chromatography (eluting with EtOAc/Hexane = 1/3) to give product 12 (123 mg, 85% yield). ¹H NMR (500 MHz, CDCl₃): δ = 8.57 (d, J = 8.5 Hz, 1H), 8.08 (dd, J = 7.6, 0.9 Hz, 1H), 8.03 (d, J = 8.2 Hz, 1H), 7.93 (d, J = 7.6 Hz, 1H), 7.65-7.58 (m, 4H), 7.42 (t, J = 7.7 Hz, 1H), 7.18-7.13 (m, 5H), 7.05-7.01 (m, 1H), 6.72-6.68 (m, 2H), 6.62 (d, J = 8.5 Hz, 2H), 6.40 (d, J = 8.5 Hz, 1H), 5.47 (d, J = 6.6 Hz, 1H), 4.93 (s, 1H), 4.67 (d, J = 12.6 Hz, 1H), 4.52 (d, J = 12.6 Hz, 1H), 2.67 (d, J = 6.9 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ = 195.12, 160.74, 136.29, 136.10, 134.68, 134.16, 133.88, 133.07, 132.25, 131.68, 130.43, 130.34, 129.23, 128.56, 128.04, 127.85, 127.08, 126.97, 126.55, 125.10, 125.01, 124.07, 124.01, 121.45, 120.98, 119.93, 117.58, 72.86, 66.69, 51.34, 50.59; HRMS (ESI) calcd for C₃₃H₂₄NO₅S₂ (M–H⁺) 578.1096, found 578.1110.

7. Preparation of the compound 11

To a solution of malononitrile 10 (10mg, 0.15mmol, 1.5equiv.) in 0.5mL toluene was added (E)-3-benzylidenechroman-4-one 7a (24mg, 0.1mmol, 1equiv.) at room temperature, followed by adding catalyst IV (4.88mg, 0.01mmol, 0.1equiv.). The mixture was stirred at room temperature. Upon completion, the crude product was purified by column chromatography on silica gel, eluted by
hexane/EtOAc=8:1 then 4:1 to afford the desired product 11 (27.4 mg, 91% yield) as primrose yellow solid. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.39 – 7.32 (m, 3H), 7.27 (q, $J$ = 6.0 Hz, 3H), 7.23 – 7.15 (m, 1H), 6.95 (t, $J$ = 7.5 Hz, 1H), 6.79 (d, $J$ = 8.1 Hz, 1H), 4.64 (s, 2H), 4.63 (d, $J$ = 13.2 Hz, 1H), 4.43 (d, $J$ = 13.8 Hz, 1H), 4.03 (s, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 158.77, 154.12, 140.87, 138.01, 130.30, 129.02, 127.92, 127.88, 121.26, 121.04, 119.26, 116.66, 115.94, 105.05, 66.48, 61.16, 39.71; HRMS (EI) calcd for C$_{19}$H$_{14}$O$_2$N$_2$ 302.1055, found 302.1048; HPLC (Chiralpak IC, $i$-propanol/hexane = 10/90, flow rate 1.0 mL/min, $\lambda$ = 254 nm): $t_{\text{major}}$ = 15.7 min, $t_{\text{minor}}$ = 27.0 min, $ee$ = 96%, $[\alpha]^{20}_{30}$ (major) = -64.1 ($c$ = 0.98 in CHCl$_3$).

Reference:

Compound b
Compound e

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Compound d
Compound g
Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2010

Compound e

- NHBoc

S43
Supplementary Material (ESI) for Chemical Communications
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Compound h
## Compound 3b

### NMR Spectra

**Chemical Shifts (ppm)**

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**Integral Values**

| 0.01 | 0.02 | 0.03 | 0.04 | 0.05 | 0.06 | 0.07 | 0.08 | 0.09 | 0.10 | 0.11 | 0.12 | 0.13 | 0.14 | 0.15 | 0.16 | 0.17 | 0.18 |
|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|

**Chemical Structure**

![Chemical Structure of Compound 3b](image-url)
Compound f
Compound i

![Chemical structure of Compound i]

S47
Compound 3c
Compound k
Compound I

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Compound m

\[
\begin{align*}
\text{Integral} & = 7.5810, 7.2600, 7.2118, 7.2036, 7.1926, 7.1838, 7.1740, 7.1581, 7.1433, 5.8170, 5.7994, 4.9015, 3.0662, 3.0415, 3.0147, 2.9928, 2.9155, 2.8953, 2.8860, 2.4553, 2.4290, 2.4110, 1.6171, 1.5996, 1.5826, 1.5656, 1.4604.
\end{align*}
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Compound n

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\]
Compound 5
Compound o
Compound p
Compound q
Compound 4
Compound 8a

[Chemical structure image]

[1H NMR spectrum image]

[13C NMR spectrum image]
Compound 8c
Compound 8e

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Compound 8f
Compound 8h

Supplementary Material (ESI) for Chemical Communications
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Compound 8i
### Compound 8j

#### NMR Spectra

The NMR spectra for Compound 8j are shown below. The spectra include proton and carbon chemical shifts, integral information, and structure representation.

#### NMR Data

**Integral Values:**

**Chemical Shifts (ppm):**
- Protons: $0.00, 0.51, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 9.5$
- Carbon: $194.47, 160.64, 155.65, 135.71, 133.47, 133.05, 132.95, 130.55, 129.21, 127.63, 127.02, 126.26, 125.51, 124.96, 124.15, 121.10, 120.36, 119.94, 117.52, 117.33, 110.27, 77.26, 77.00, 76.74, 71.94, 68.87, 66.99, 50.82, 42.65.$

**Structure Representation:**

The molecular structure of Compound 8j is also depicted, showing the presence of oxygen (O), sulfur (S), and hydroxyl (OH) groups.
Compound 8k
Compound 8m

(Chemical structures and spectra are shown.)
Compound 8n
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Compound 80
Compound 8p
Compound 8q
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Compound 8r
Compound 8s
Compound 8t
Compound 8u
Compound 8w
Compound 8x
Compound 11

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S84
Compound 12
Racemic 8a

=== Shimadzu LC solution Analysis Report ===

Acquired by: Admin
Sample Name: GB036P1
Sample ID: GYJ
Data File Name: G089.lcd
Method File Name: 10%IPA, 1ml-min, 60min.lcm
Batch File Name: Default.lcr
Report File Name: IC column with guard column, 10%IPA
Description: Recemic

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Enantiomeric enriched 8a

=== Shimadzu LC solution Analysis Report ===

Acquired by: Admin
Sample Name: GB044P1-xylene
Sample ID: GYJ
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Method File Name: 10%IPA, 1ml-min, 60min.lcm
Batch File Name: Default.lcr
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Racemic 8b

### Shimadzu LC solution Analysis Report ###

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- **Sample Name**: GB069P1 recemic
- **Sample ID**: GYJ
- **Data File Name**: G115.lcd
- **Method File Name**: 10%IPA, 1ml-min, 60min.lcm
- **Batch File Name**: 
- **Report File Name**: Default.lcr
- **Description**: IC column with guard column, 10%IPA.

![Chromatogram of Racemic 8b](image)

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Enantiomeric enriched 8b

### Shimadzu LC solution Analysis Report ###

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- **Sample ID**: GYJ
- **Data File Name**: G122.lcd
- **Method File Name**: 10%IPA, 1ml-min, 60min.lcm
- **Batch File Name**: 
- **Report File Name**: Default.lcr
- **Description**: IC column with guard column, 10%IPA.

![Chromatogram of Enantiomeric enriched 8b](image)

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S87
Racemic 8c

--- Shimadzu LC solution Analysis Report ---

Acquired by: Admin
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Data File Name: G172.lcd
Method File Name: 10%IPA, 1ml-min, 40min.lcm
Batch File Name:
Report File Name: Default.lcr
Description: IC column with guard column, 10%IPA

Chromatogram

GB114P1 racemic C:/Users/User/Desktop/LC data/Gao Yaqion/G172.lcd

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Enantiomeric enriched 8c

--- Shimadzu LC solution Analysis Report ---

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Racemic 8d

--- Shimadzu LCsolution Analysis Report ---

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Sample Name: GB115P1 recemic
Sample ID: GYJ
Data File Name: G173.lcd
Method File Name: 10%IPA, 1ml-min, 40min lcm
Batch File Name:
Report File Name: Default.lcr
Description: IC column with guard column, 10%IPA

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Enantiomeric enriched 8d

--- Shimadzu LCsolution Analysis Report ---

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Description: IC column with guard column, 10%IPA

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Supplementary Material (ESI) for Chemical Communications
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Racemic 8e

=== Shimadzu LCsolution Analysis Report ===

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Sample ID: GYJ
Data File Name: G178.lcd
Method File Name: 10%IPA, 1m-ml, 40min.lcm
Batch File Name:
Report File Name: Default.lcr
Description: IC column with guard column

Chromatogram

Peak Table

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Enantiomeric enriched 8e

=== Shimadzu LCsolution Analysis Report ===

Acquired by: Admin
Sample Name: go027
Sample ID: GYJ
Data File Name: G274.lcd
Method File Name: 10%IPA, 1ml-ml, 60min.lcm
Batch File Name:
Report File Name: Default.lcr
Description: IC column with guard column, 10%IPA

Chromatogram

Peak Table

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<tr>
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S90
Racemic 8f

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Enantiomeric enriched 8f
Racemic 8g

--- Shimadzu LC solution Analysis Report ---

Acquired by: Admin
Sample Name: GB116P1 racemic
Sample ID: GYJ
Data File Name: G176.lcd
Method File Name: 10%IPA, 1ml/min, 40min.lcm
Batch File Name: :
Report File Name: Default.lcr
Description: IC column with guard column, 10%IPA

Chromatogram

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Enantiomeric enriched 8g

--- Shimadzu LC solution Analysis Report ---

Acquired by: Admin
Sample Name: GB127P1
Sample ID: GYJ
Data File Name: G199.lcd
Method File Name: 10%IPA, 1ml/min, 40min.lcm
Batch File Name: :
Report File Name: Default.lcr
Description: IC column with guard column, 10%IPA

Chromatogram

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S92
Racemic 8h

== Shimadzu LCsolution Analysis Report ==

Acquired by : Admin
Sample Name : GB093P1
Sample ID : GYJ
Data File Name : G142.lcd
Method File Name : 10%IPA, 1ml-min, 40min.icm
Batch File Name : 
Report File Name : Default.lcr
Description : IC column with guard column, 10%IPA

Chromatogram

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Enantiomeric enriched 8h

== Shimadzu LCsolution Analysis Report ==

Acquired by : Admin
Sample Name : GB108P1
Sample ID : GYJ
Data File Name : G158.lcd
Method File Name : 10%IPA, 1ml-min, 40min.icm
Batch File Name : 
Report File Name : Default.lcr
Description : IC column with guard column, 10%IPA

Chromatogram

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</table>
Racemic 8i

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Enantiomeric enriched 8i

Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2010
Racemic 8j

--- Shimadzu LC solution Analysis Report ---

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Enantiomeric enriched 8j

--- Shimadzu LC solution Analysis Report ---

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Racemic 8k

Enantiomeric enriched 8k
**Racemic 8l**

--- Shimadzu LCsolution Analysis Report ---

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<td>10%IPA, 1ml-min, 40min.lcm</td>
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<td>Description</td>
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**Enantiomeric enriched 8l**

--- Shimadzu LCsolution Analysis Report ---

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<tr>
<td>Description</td>
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<table>
<thead>
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Racemic 8m

==== Shimadzu LC solution Analysis Report ====

Acquired by : Admin
Sample Name : GB089P1 racemic
Sample ID : GYJ
Data File Name : G140.lcd
Method File Name : 10\%IPA, 1ml-min, 40min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : IC column with guard column, 10\%IPA

Chromatogram

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</thead>
<tbody>
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Enantiomeric enriched 8m

==== Shimadzu LC solution Analysis Report ====

Acquired by : Admin
Sample Name : GB107P1
Sample ID : GYJ
Data File Name : G159.lcd
Method File Name : 10\%IPA, 1ml-min, 40min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : IC column with guard column, 10\%IPA

Chromatogram

<table>
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Racemic 8n

==== Shimadzu LC solution Analysis Report ====  
Acquired by: Admin
Sample Name: GB122P1 racemic
Sample ID: GYJ
Data File Name: G186.lcd
Method File Name: 10%IPA, 1ml-min, 40min.lcm
Batch File Name: 
Report File Name: Default.lcr
Description: IC column with guard column, 10%IPA

Chromatogram

SPD-20A Ch1 254nm
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Enantiomeric enriched 8n

==== Shimadzu LC solution Analysis Report ====  
Acquired by: Admin
Sample Name: GB133P1
Sample ID: GYJ
Data File Name: G208.lcd
Method File Name: 10%IPA, 1ml-min, 40min.lcm
Batch File Name: 
Report File Name: Default.lcr
Description: IC column with guard column, 10%IPA

Chromatogram

SPD-20A Ch1 254nm
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Racemic 8o

#### Shimadzu LC solution Analysis Report ####

Chromatogram

Chromatogram

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Enantiomeric enriched 8o

#### Shimadzu LC solution Analysis Report ####

Chromatogram

Chromatogram

Supplementary Material (ESI) for Chemical Communications
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**Racemic 8p**

**Shimadzu LCsolution Analysis Report**

- **Acquired by**: Admin
- **Sample Name**: GB120P1 recemic
- **Sample ID**: GYJ
- **Data File Name**: G183.lcd
- **Method File Name**: 10%IPA, 1ml-min, 40min.lcm
- **Batch File Name**: Default.lcr
- **Report File Name**: Default.lcr
- **Description**: IC column with guard column, 10%IPA

**Chromatogram**

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**Enantiomeric enriched 8p**

**Shimadzu LCsolution Analysis Report**

- **Acquired by**: Admin
- **Sample Name**: GB131P1
- **Sample ID**: GYJ
- **Data File Name**: G206.lcd
- **Method File Name**: 10%IPA, 1ml-min, 40min.lcm
- **Batch File Name**: Default.lcr
- **Report File Name**: Default.lcr
- **Description**: IC column with guard column, 10%IPA

**Chromatogram**

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Racemic 8q

==== Shimadzu LC solution Analysis Report ====

Acquired by: Admin
Sample Name: gb156p1 recemic
Sample ID: gyj
Date File Name: G228.lcd
Method File Name: 5%IPA, 1ml-min, 60min.lcm
Batch File Name: 
Report File Name: Default.lcr
Description: 1b column with guard column, 5%IPA

Chromatogram:

SPD-20A Ch1 254mm

Peak Table

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Enantiomeric enriched 8q

==== Shimadzu LC solution Analysis Report ====

Acquired by: Admin
Sample Name: gb156p1
Sample ID: gyj
Date File Name: G229.lcd
Method File Name: 5%IPA, 1ml-min, 60min.lcm
Batch File Name: 
Report File Name: Default.lcr
Description: 1b column with guard column, 5%IPA

Chromatogram:

SPD-20A Ch1 254mm

Peak Table

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Racemic 8r

#### Shimadzu LC Solution Analysis Report ####

- **Acquired by**: Admin
- **Sample Name**: gb157p1 racemic
- **Sample ID**: gjj
- **Data File Name**: G225.lcd
- **Method File Name**: 10%IPA, 1ml/min, 40min.lcm
- **Batch File Name**: Default.lcr
- **Description**: IC column with guard column, 10%IPA

![Chromatogram](image)

**PeakTable**

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Enantiomeric enriched 8r

#### Shimadzu LC Solution Analysis Report ####

- **Acquired by**: Admin
- **Sample Name**: gb159p1
- **Sample ID**: gjj
- **Data File Name**: G226.lcd
- **Method File Name**: 10%IPA, 1ml/min, 40min.lcm
- **Batch File Name**: Default.lcr
- **Description**: IC column with guard column, 10%IPA

![Chromatogram](image)

**PeakTable**

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Racemic 8s

--- Shimadzu LCsolution Analysis Report ---

Acquired by : Admin
Sample Name : GB072P1 recemic
Sample ID : GYJ
Data File Name : G125.lcd
Method File Name : 10%IPA, 1ml-min, 60min,lcm
Batch File Name :
Report File Name : Default.lcr
Description : IC column with guard column, 10%IPA

Chromatogram
GB072P1 recemic C:\Users\User\Desktop\LC data\Gao Yaqun\G125.lcd

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Enantiomeric enriched 8s

--- Shimadzu LCsolution Analysis Report ---

Acquired by : Admin
Sample Name : GB104P1
Sample ID : GYJ
Data File Name : G168.lcd
Method File Name : 10%IPA, 1ml-min, 40min,lcm
Batch File Name :
Report File Name : Default.lcr
Description : IC column with guard column, 10%IPA

Chromatogram
GB104P1 C:\Users\User\Desktop\LC data\Gao Yaqun\G168.lcd

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Racemic 8t

==== Shimadzu LCsolution Analysis Report ====

Acquired by : Admin
Sample Name : GB073P1 racemic
Sample ID : GYJ
Data File Name : G129.lcd
Method File Name : 5%IPA, 1ml-min, 60min.lcm
Batch File Name : 
Report File Name : Default.lcr
Description : IC column with guard column, 5%IPA

Chromatogram
GB073P1 racemic C:/Users/User/Desktop/LC data/Gao Yaojun/G129.lcd

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Enantiomeric enriched 8t

==== Shimadzu LCsolution Analysis Report ====

Acquired by : Admin
Sample Name : GB105P1
Sample ID : GYJ
Data File Name : G171.lcd
Method File Name : 5%IPA, 1ml-min, 60min.lcm
Batch File Name : 
Report File Name : Default.lcr
Description : IC column with guard column, 5%IPA

Chromatogram
GB105P1 C:/Users/User/Desktop/LC data/Gao Yaojun/G171.lcd

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Racemic 8u

--- Shimadzu LC solution Analysis Report ---

Acquired by: Admin
Sample Name: GB09SP1
Sample ID: GYJ
Data File Name: G146.lcd
Method File Name: 10%IPA, 1ml-min, 40min.lcm
Batch File Name: 
Report File Name: Default.lcr
Description: IC column with guard column, 10%IPA

Chromatogram

Peak Table

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Enantiomeric enriched 8u

--- Shimadzu LC solution Analysis Report ---

Acquired by: Admin
Sample Name: GB110P1
Sample ID: GYJ
Data File Name: G184.lcd
Method File Name: 10%IPA, 1ml-min, 40min.lcm
Batch File Name: 
Report File Name: Default.lcr
Description: IC column with guard column, 10%IPA

Chromatogram

Peak Table

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S106
Racemic 8v

==== Shimadzu LC solution Analysis Report====

Acquired by: Admin
Sample Name: GB124p1 racemic
Sample ID: GYJ
Data File Name: G191.lcd
Method File Name: 10%IPA, 1ml-min, 40min.lcm
Batch File Name: 
Report File Name: Default.lcr
Description: IC column with guard column, 10%IPA

Chromatogram

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Enantiomeric enriched 8v

==== Shimadzu LC solution Analysis Report====

Acquired by: Admin
Sample Name: GB135p1
Sample ID: GYJ
Data File Name: G210.lcd
Method File Name: 10%IPA, 1ml-min, 40min.lcm
Batch File Name: 
Report File Name: Default.lcr
Description: IC column with guard column, 10%IPA

Chromatogram

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Racemic 8w

==== Shimadzu LCsolution Analysis Report ====

Acquired by: Admin  
Sample Name: GB099P1  
Sample ID: GYJ  
Data File Name: G150.lcd  
Method File Name: 10%IPA, 1ml-min, 40min.lcm  
Batch File Name: Default.lcr  
Report File Name: GC column with guard column, 10%IPA  
Description: 

Chromatogram

 SPD-20A Ch1 254nm

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Enantiomeric enriched 8w

==== Shimadzu LCsolution Analysis Report ====

Acquired by: Admin  
Sample Name: GB111P1  
Sample ID: GYJ  
Data File Name: G165.lcd  
Method File Name: 10%IPA, 1ml-min, 40min.lcm  
Batch File Name: Default.lcr  
Report File Name: GC column with guard column, 10%IPA  
Description: 

Chromatogram

 SPD-20A Ch1 254nm

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Racemic 8x

--- Shimadzu LCsolution Analysis Report ---

Acquired by: Admin
Sample Name: GB101P1
Sample ID: GYJ
Data File Name: G155.lcd
Method File Name: 10%IPA, 1ml-min, 40min.lcm
Batch File Name: 
Report File Name: Default.lcr
Description: IC column with guard column, 10%IPA

Chromatogram

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Enantiomeric enriched 8x

--- Shimadzu LCsolution Analysis Report ---

Acquired by: Admin
Sample Name: GB113P1
Sample ID: GYJ
Data File Name: G167.lcd
Method File Name: 10%IPA, 1ml-min, 40min.lcm
Batch File Name: 
Report File Name: Default.lcr
Description: IC column with guard column, 10%IPA

Chromatogram

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Racemic 8v

==== Shimadzu LCsolution Analysis Report ====  
Acquired by: Admin  
Sample Name: GB100P1  
Sample ID: GYJ  
Data File Name: G154.lcd  
Method File Name: 10%IPA, 1ml-min, 40min.lcm  
Batch File Name:  
Report File Name: Default.lcr  
Description: IC column with guard column, 10%IPA  

Chromatogram  

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Enantiomeric enriched 8v

==== Shimadzu LCsolution Analysis Report ====  
Acquired by: Admin  
Sample Name: GB112P1  
Sample ID: GYJ  
Data File Name: G166.lcd  
Method File Name: 10%IPA, 1ml-min, 40min.lcm  
Batch File Name:  
Report File Name: Default.lcr  
Description: IC column with guard column, 10%IPA  

Chromatogram  

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Racemic 9

== Shimadzu LCsolution Analysis Report ==

Acquired by : Admin
Sample Name : gc070
Sample ID : gyl
Data File Name : G288.lcd
Method File Name : 10%IPA, 1ml-min, 60min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : IC column with guard column, 10%IPA

Chromatogram

gc070 C:\Users\User\Desktop\LC data\Gao Yaojun\G288.lcd

PeakTable

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Enantiomeric enriched 9

== Shimadzu LCsolution Analysis Report ==

Acquired by : Admin
Sample Name : GC072
Sample ID : gyl
Data File Name : G290.lcd
Method File Name : 10%IPA, 1ml-min, 60min.lcm
Batch File Name :
Report File Name : Default.lcr
Description : IC column with guard column, 10%IPA

Chromatogram

GC072 C:\Users\User\Desktop\LC data\Gao Yaojun\G290.lcd

PeakTable

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</table>
Supplementary Material (ESI) for Chemical Communications
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Racemic 11

Shimadzu LC solution Analysis Report

Acquired by: Admin
Sample Name: GB025 P2
Sample ID: GYJ
Data File Name: G063.lcd
Method File Name: 10%IPA, 1ml-min, 40min.lcm
Batch File Name:
Report File Name: Default.lcr
Description: LC column with guard column

Chromatogram
GB025 P2 C:\Users\User\Desktop\LC data\Gao Yaqun\G063.lcd

Enantiomeric enriched 11

Shimadzu LC solution Analysis Report

Acquired by: Admin
Sample Name: R154-p2
Sample ID: rq
Data File Name: rq052.lcd
Method File Name: 10%IPA, 1ml-min, 40min.lcm
Batch File Name:
Report File Name: Default.lcr
Description: LC column with guard column, 10%IPA

Chromatogram
R154-p2 C:\Users\User\Desktop\LC data\Ren Qiao\rq052.lcd

PeakTable

<table>
<thead>
<tr>
<th>Peak#</th>
<th>Ret. Time</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
<th>Height %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15,307</td>
<td>24124559</td>
<td>790994</td>
<td>49.993</td>
<td>61.630</td>
</tr>
<tr>
<td>2</td>
<td>26,192</td>
<td>24131021</td>
<td>455860</td>
<td>30.007</td>
<td>38.370</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>48255580</td>
<td>1135934</td>
<td>100.000</td>
<td>100.000</td>
</tr>
</tbody>
</table>

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