## Supporting Information

# Palladium-Catalyzed Asymmetric Allenylic Alkylation: Construction of Multiple Chiral Thiochromanone Derivatives 

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## 1. General and Materials

General: All reactions were carried out under an atmosphere of nitrogen using the standard Schlenk techniques, unless otherwise noted. Solvents were treated prior to use according to the standard methods. ${ }^{1} \mathrm{H}$ NMR, ${ }^{13} \mathrm{C}$ NMR and ${ }^{19} \mathrm{~F}$ NMR spectra were recorded at room temperature in $\mathrm{CDCl}_{3}$ on 400 MHz and 700 MHz instrument with TMS as internal standard. Enantiomeric excess was determined by HPLC analysis, using chiral column described below in detail. Optical rotations were measured by polarimeter. Flash column chromatography was performed on silica gel (200-300 mesh). The heat source for all heating reactions is the oil bath. High-resolution mass spectrometry (HRMS) was measured on an electrospray ionization (ESI) apparatus using the time-of-flight (TOF) mass spectrometry. All reactions were monitored by TLC analysis.

Materials: Commercially available reagents and solvents were used throughout without further purification.

## 2. Synthesis of Substrates

### 2.1. The Synthesis of Thiochromanone Derivatives

The thiochromanone derivatives 1a-c and $\mathbf{1 e - 1 p}$ were synthesized from (substituted) 2-mercaptobenzaldehydes and $\alpha, \beta$-unsaturated ester through two steps according to the known procedure, ${ }^{1}$ all of which are the new compounds. Firstly, the known 2-mercaptobenzaldehydes $\mathbf{S 1}$ underwent the organocatalytic domino sulfa-Michael-aldol reactions with $\alpha, \beta$-unsaturated ester $\mathbf{S} \mathbf{2}$ to provide the intermediate alcohols. Then, the desired thiochromanone derivatives $\mathbf{1}$ could be synthesized through the oxidation with PCC.

Besides, thiochromanone derivative with amide group 1d was synthesized through exchange from the thiochromanone $\mathbf{1 c}$ and piperidine according to the known procedure. ${ }^{2}$


General Procedure: To a solution of (substituted) 2-mercaptobenzaldehydes $\mathbf{S 1}$ (7.0 mmol) in dichloromethane ( 60 mL ) was added organocatalyst ( $1.4 \mathrm{mmol}, 20 \mathrm{~mol} \%$ ) and $\alpha, \beta$-unsaturated esters $\mathbf{S} 2(9.1 \mathrm{mmol})$ sequentially under nitrogen atmosphere. The reaction mixture was stirred at room temperature for about $48-120 \mathrm{~h}$. The reaction was complete as monitored by TLC. Then the reaction mixture was concentrated under the reduced pressure to obtain the crude residue. The residue was purified by flash chromatography on silica gel using hexanes/ethyl acetate (20/1-10/1) as eluent to give the intermediate alcohol compounds.

To a solution of pyridinium chlorochromate (PCC, 2.5 equiv.) in dichloromethane ( 0.1 M ) was added celite (equal in quality to PCC) and the obtained alcohol compounds at ambient temperature. TLC analysis indicated completion of the reactions after about 5-8 h . After filtration through celite, the volatiles were removed under the reduced pressure. The residue was purified by flash chromatography on silica gel using hexanes/ethyl acetate (50/1) as eluent to give the desirable thiochromanone derivatives $\mathbf{1}$.

3-Nitro-2-phenylthiochroman-4-one (1a):
$0.243 \mathrm{~g}, 30 \%$ yield (two steps), orange solid, mp 173-174 ${ }^{\circ} \mathrm{C}$, new compound, $\mathrm{R}_{\mathrm{f}}=0.05$ (hexanes/
 ethyl acetate $3 / 1$ ), keto. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.18(\mathrm{~d}, J=7.6 \mathrm{~Hz}$, $1 \mathrm{H}), 7.56-7.45(\mathrm{~m}, 3 \mathrm{H}), 7.42-7.34(\mathrm{~m}, 3 \mathrm{H}), 7.34-7.26(\mathrm{~m}, 2 \mathrm{H}), 6.13(\mathrm{~d}, J=$ $13.1 \mathrm{~Hz}, 1 \mathrm{H}), 5.27(\mathrm{~d}, J=13.1 \mathrm{~Hz}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 184.0$, $140.6,135.2,133.0,130.7,129.9,129.4,128.9,128.0,126.9,126.2,95.1,48.3$ HRMS Calculated for $\mathrm{C}_{15} \mathrm{H}_{12} \mathrm{NO}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+}$286.0532, found: 286.0533.

## 1-(4-Hydroxy-2-phenyl-2H-thiochromen-3-yl)ethan-1-one (1b):

$0.324 \mathrm{~g}, 41 \%$ yield (two steps), yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.79$ (hexanes/ethyl

acetate $3 / 1$ ), enol. ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.05(\mathrm{dd}, J=7.8,1.5 \mathrm{~Hz}$, $1 \mathrm{H}), 7.29-7.25(\mathrm{~m}, 1 \mathrm{H}), 7.25-7.15(\mathrm{~m}, 6 \mathrm{H}), 7.15-7.08(\mathrm{~m}, 1 \mathrm{H}), 4.99(\mathrm{~s}, 1 \mathrm{H})$, $2.18(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 198.2,173.9,142.0,134.5,132.3$, 129.3, 128.7, 128.0, 127.7, 127.5, 126.8, 125.9, 106.0, 42.0, 25.2. HRMS Calculated for $\mathrm{C}_{17} \mathrm{H}_{15} \mathrm{O}_{2} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+}$283.0787, found: 283.0788.

## Methyl 4-hydroxy-2-phenyl-2H-thiochromene-3-carboxylate (1c):

$1.126 \mathrm{~g}, 39 \%$ yield (two steps), pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.47$ (hexanes/
 ethyl acetate 20/1), enol/keto $=14.3 / 1$. The enol isomer: ${ }^{1} \mathrm{H}$ NMR $(400 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right) \delta 13.04(\mathrm{~s}, 1 \mathrm{H}), 8.01-7.92(\mathrm{~m}, 1 \mathrm{H}), 7.25-7.12(\mathrm{~m}, 8 \mathrm{H}), 5.12(\mathrm{~s}, 1 \mathrm{H})$, $3.77(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 171.8,166.1,142.7,134.2$, $131.4,128.5,127.8,127.4,126.6,126.5,125.6,96.9,52.3,39.6$. HRMS Calculated for $\mathrm{C}_{17} \mathrm{H}_{15} \mathrm{O}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+}$299.0736, found: 299.0742.

Methyl 4-hydroxy-2-(o-tolyl)-2H-thiochromene-3-carboxylate (1e):
0.701 g , $32 \%$ yield (two steps), pale yellow solid, $\mathrm{mp} 115-116{ }^{\circ} \mathrm{C}$, new compound, $\mathrm{R}_{\mathrm{f}}=0.62$
 (hexanes/ethyl acetate 20/1), enol/keto $=12.5 / 1$. The enol isomer: ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 13.08(\mathrm{~s}, 1 \mathrm{H}), 8.06-7.95(\mathrm{~m}, 1 \mathrm{H}), 7.24-7.19(\mathrm{~m}, 2 \mathrm{H})$, 7.17-7.14 (m, 1H), 7.12-7.04 (m, 2H), 6.98-6.89 (m, 2H), $5.32(\mathrm{~s}, 1 \mathrm{H}), 3.71$ $(\mathrm{s}, 3 \mathrm{H}), 2.49(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 171.8,166.6,139.8$, $134.3,133.9,131.4,130.8,128.6,128.1,127.4,126.5,126.2,126.1,125.7,96.5,52.4,35.7,19.7$. HRMS Calculated for $\mathrm{C}_{18} \mathrm{H}_{17} \mathrm{O}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+}$313.0893, found: 313.0890.

Methyl 4-hydroxy-2-(m-tolyl)-2H-thiochromene-3-carboxylate (1f):
$0.575 \mathrm{~g}, 26 \%$ yield (two steps), pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.62$ (hexanes/
 ethyl acetate $20 / 1$ ), enol/keto $=14.3 / 1$. The enol isomer: ${ }^{1} \mathrm{H}$ NMR ( 400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 13.05(\mathrm{~s}, 1 \mathrm{H}), 8.03-7.87(\mathrm{~m}, 1 \mathrm{H}), 7.25-7.14(\mathrm{~m}, 3 \mathrm{H}), 7.11-$ $6.94(\mathrm{~m}, 4 \mathrm{H}), 5.09(\mathrm{~s}, 1 \mathrm{H}), 3.75(\mathrm{~s}, 3 \mathrm{H}), 2.24(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 100 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 171.9,166.1,142.6,138.1,134.2,131.4,128.5,128.3,128.3$, $127.8,127.4,126.5,125.6,123.7,96.8,52.3,39.6,21.5$. HRMS Calculated for $\mathrm{C}_{18} \mathrm{H}_{17} \mathrm{O}_{3} \mathrm{~S}$ $[\mathrm{M}+\mathrm{H}]^{+} 313.0893$, found: 313.0889.

Methyl 4-hydroxy-2-(p-tolyl)-2H-thiochromene-3-carboxylate (1g):
$0.362 \mathrm{~g}, 17 \%$ yield (two steps), pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.62$ (hexanes/
 ethyl acetate 20/1), enol/keto $=14.3 / 1$. The enol isomer: ${ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 13.03(\mathrm{~s}, 1 \mathrm{H}), 8.01-7.92(\mathrm{~m}, 1 \mathrm{H}), 7.24-7.14(\mathrm{~m}, 3 \mathrm{H}), 7.08$ $(\mathrm{d}, J=8.1 \mathrm{~Hz}, 2 \mathrm{H}), 6.99(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 5.10(\mathrm{~s}, 1 \mathrm{H}), 3.76(\mathrm{~s}, 3 \mathrm{H})$, $2.24(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 171.9,166.0,139.8,137.2$,
134.2, 131.4, 129.2, 128.5, 127.8, 126.5, 126.5, 125.6, 97.0, 52.3, 39.4, 21.1. HRMS Calculated for $\mathrm{C}_{18} \mathrm{H}_{17} \mathrm{O}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+} 313.0893$, found: 313.0891.

## Methyl 2-(4-fluorophenyl)-4-hydroxy-2H-thiochromene-3-carboxylate (1h):

0.582 g , $26 \%$ yield (two steps), pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.50$ (hexanes/
 ethyl acetate 20/1), enol/keto $=20.0 / 1$. The enol isomer: ${ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 13.02(\mathrm{~s}, 1 \mathrm{H}), 8.00-7.93(\mathrm{~m}, 1 \mathrm{H}), 7.30-7.14(\mathrm{~m}, 5 \mathrm{H}), 6.90-$ $6.83(\mathrm{~m}, 2 \mathrm{H}), 5.10(\mathrm{~s}, 1 \mathrm{H}), 3.77(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ $171.7,166.1,162.1\left(\mathrm{~d},{ }^{1} J_{\mathrm{F}-\mathrm{C}}=246.0 \mathrm{~Hz}\right), 138.5\left(\mathrm{~d},{ }^{4} J_{\mathrm{F}-\mathrm{C}}=3.0 \mathrm{~Hz}\right), 133.9$, $131.5,128.4,128.2\left(\mathrm{~d},{ }^{3} J_{\mathrm{F}-\mathrm{C}}=8.3 \mathrm{~Hz}\right), 127.9,126.5,125.8,115.3\left(\mathrm{~d},{ }^{2} J_{\mathrm{F}-\mathrm{C}}=21.7 \mathrm{~Hz}\right), 97.0,52.4$, 39.0. ${ }^{19} \mathrm{~F}$ NMR ( $376 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$-115.11. HRMS Calculated for $\mathrm{C}_{17} \mathrm{H}_{14} \mathrm{FO}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+}$ 317.0642, found: 317.0643.

Methyl 2-(4-chlorophenyl)-4-hydroxy-2H-thiochromene-3-carboxylate (1i):
0.895 g , $38 \%$ yield (two steps), pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.50$ (hexanes/
 ethyl acetate $20 / 1$ ), enol/keto $=14.3 / 1$. The enol isomer: ${ }^{1} \mathrm{H}$ NMR $(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 13.02(\mathrm{~s}, 1 \mathrm{H}), 7.98-7.93(\mathrm{~m}, 1 \mathrm{H}), 7.29-7.20(\mathrm{~m}, 2 \mathrm{H}), 7.18-$ $7.09(\mathrm{~m}, 5 \mathrm{H}), 5.08(\mathrm{~s}, 1 \mathrm{H}), 3.77(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 171.6, 166.2, 141.2, 133.7, 133.2, 131.6, 128.6, 128.3, 128.0, 127.9, 126.6, 125.8, 96.7, 52.4, 39.0. HRMS Calculated for $\mathrm{C}_{17} \mathrm{H}_{14} \mathrm{ClO}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+} 333.0347\left({ }^{35} \mathrm{Cl}\right)$ and 335.0321 $\left({ }^{37} \mathrm{Cl}\right)$, found: $333.0350\left({ }^{35} \mathrm{Cl}\right)$ and $335.0324\left({ }^{37} \mathrm{Cl}\right)$.

Methyl 2-(4-bromophenyl)-4-hydroxy-2H-thiochromene-3-carboxylate (1j):
$1.272 \mathrm{~g}, 48 \%$ yield (two steps), pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.50$ (hexanes/
 ethyl acetate $20 / 1$ ), enol/keto $=25.0 / 1$. The enol isomer: ${ }^{1} \mathrm{H}$ NMR $(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 13.02(\mathrm{~s}, 1 \mathrm{H}), 8.02-7.87(\mathrm{~m}, 1 \mathrm{H}), 7.32-7.14(\mathrm{~m}, 5 \mathrm{H}), 7.12-$ $6.99(\mathrm{~m}, 2 \mathrm{H}), 5.06(\mathrm{~s}, 1 \mathrm{H}), 3.77(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 171.6, 166.2, 141.7, 133.7, 131.6, 131.6, 128.4, 128.3, 127.9, 126.6, 125.9, 121.4, 96.6, 52.4, 39.1. HRMS Calculated for $\mathrm{C}_{17} \mathrm{H}_{14} \mathrm{BrO}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+} 376.9842\left({ }^{79} \mathrm{Br}\right)$ and $378.9822\left({ }^{81} \mathrm{Br}\right)$, found: $376.9844\left({ }^{79} \mathrm{Br}\right)$ and $378.9832\left({ }^{81} \mathrm{Br}\right)$.

Methyl 4-hydroxy-2-(4-methoxyphenyl)-2H-thiochromene-3-carboxylate (1k):
$0.555 \mathrm{~g}, 34 \%$ yield (two steps, 1.0 equivalent amount of organocatalyst was used), light yellow liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.42$ (hexanes/ethyl acetate $20 / 1)$, enol/keto $=11.1 / 1$. The enol isomer: ${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$
 $13.01(\mathrm{~s}, 1 \mathrm{H}), 7.96(\mathrm{dd}, J=7.7,1.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.26-7.16(\mathrm{~m}, 3 \mathrm{H}), 7.14-7.07(\mathrm{~m}, 2 \mathrm{H}), 6.76-6.68(\mathrm{~m}$,
$2 \mathrm{H}), 5.09(\mathrm{~s}, 1 \mathrm{H}), 3.77(\mathrm{~s}, 3 \mathrm{H}), 3.71(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C} \mathrm{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 171.9,165.9,158.9$, $134.9,134.2,131.4,128.5,127.9,127.7,126.4,125.6,113.8,97.2,55.2,52.3,39.1$. HRMS Calculated for $\mathrm{C}_{18} \mathrm{H}_{16} \mathrm{NaO}_{4} \mathrm{~S}[\mathrm{M}+\mathrm{Na}]^{+} 351.0662$, found: 351.0665 .

## Methyl 4-hydroxy-2-methyl-2H-thiochromene-3-carboxylate (11):

$0.488 \mathrm{~g}, 42 \%$ yield (two steps), pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.67$ (hexanes/ OLOM ethyl acetate 20/1), enol/keto $=11.1 / 1$. The enol isomer: ${ }^{1} \mathrm{H}$ NMR $(400 \mathrm{MHz}$, $1 \mathrm{H}), 4.02(\mathrm{q}, J=6.9 \mathrm{~Hz}, 1 \mathrm{H}), 3.86(\mathrm{~s}, 3 \mathrm{H}), 1.35(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (100 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 171.6,164.5,134.6,131.1,128.2,128.0,126.5,125.4,100.0,52.1$, 31.9, 23.1. HRMS Calculated for $\mathrm{C}_{12} \mathrm{H}_{16} \mathrm{NO}_{3} \mathrm{~S}\left[\mathrm{M}+\mathrm{NH}_{4}\right]^{+}$254.0845, found: 254.0846.

## Methyl 4-hydroxy-6-nitro-2-phenyl-2H-thiochromene-3-carboxylate (1m):

$0.296 \mathrm{~g}, 12 \%$ yield (two steps), pale yellow solid, mp 182-183 ${ }^{\circ} \mathrm{C}$, new compound, $\mathrm{R}_{\mathrm{f}}=0.34$
 (hexanes/ethyl acetate 20/1), enol. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 13.04$ $(\mathrm{s}, 1 \mathrm{H}), 8.82(\mathrm{~d}, J=2.5 \mathrm{~Hz}, 1 \mathrm{H}), 8.08(\mathrm{dd}, J=8.7,2.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.30(\mathrm{~d}$, $J=8.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.25-7.08(\mathrm{~m}, 5 \mathrm{H}), 5.25(\mathrm{~s}, 1 \mathrm{H}), 3.80(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 171.3,163.8,145.7,143.3,141.8,128.8,128.7$, $128.2,128.0,126.5,125.4,121.7,97.6,52.7,40.1$. HRMS Calculated for $\mathrm{C}_{17} \mathrm{H}_{14} \mathrm{NO}_{5} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+}$ 344.0587, found: 344.0589.

## Methyl 4-hydroxy-6-methoxy-2-phenyl-2H-thiochromene-3-carboxylate (1n):

$0.092 \mathrm{~g}, 9 \%$ yield (two steps), pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.54$ (hexanes/
 ethyl acetate 20/1), enol/keto $=12.5 / 1$. The enol isomer: ${ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 13.07(\mathrm{~s}, 1 \mathrm{H}), 7.51(\mathrm{~d}, J=2.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.23-7.10(\mathrm{~m}$, $5 \mathrm{H}), 7.06(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.84(\mathrm{dd}, J=8.6,2.8 \mathrm{~Hz}, 1 \mathrm{H}), 5.09(\mathrm{~s}$, $1 \mathrm{H}), 3.82(\mathrm{~s}, 3 \mathrm{H}), 3.76(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 171.9$, $166.1,157.9,142.6,129.5,128.9,128.4,127.4,126.7,124.8,118.7,110.9,97.5,55.5,52.3,39.6$. HRMS Calculated for $\mathrm{C}_{18} \mathrm{H}_{16} \mathrm{NaO}_{4} \mathrm{~S}[\mathrm{M}+\mathrm{Na}]^{+} 351.0662$, found: 351.0657 .

## Methyl 4-hydroxy-6-methyl-2-phenyl-2H-thiochromene-3-carboxylate (10):

$0.994 \mathrm{~g}, 40 \%$ yield (two steps), pale yellow solid, $\mathrm{mp} 143-144^{\circ} \mathrm{C}$, new compound, $\mathrm{R}_{\mathrm{f}}=0.59$ (he-
 xanes/ethyl acetate 20/1), enol/keto $=11.1 / 1$. The enol isomer: ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 13.05(\mathrm{~s}, 1 \mathrm{H}), 7.78(\mathrm{~s}, 1 \mathrm{H}), 7.23-7.10(\mathrm{~m}, 5 \mathrm{H})$, 7.10-7.01 (m, 2H), $5.10(\mathrm{~s}, 1 \mathrm{H}), 3.76(\mathrm{~s}, 3 \mathrm{H}), 2.34(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 171.9,166.3,142.8,135.5,132.4,130.6,128.4$, $128.3,127.7,127.4,126.9,126.6,97.0,52.3,39.6,21.1$. HRMS Calculated for $\mathrm{C}_{18} \mathrm{H}_{17} \mathrm{O}_{3} \mathrm{~S}$ $[\mathrm{M}+\mathrm{H}]^{+} 313.0893$, found: 313.0892.

## tert-Butyl 4-hydroxy-2-phenyl-2H-thiochromene-3-carboxylate (1p):

$0.250 \mathrm{~g}, 8 \%$ yield (two steps), pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.62$ (hexanes/ ethyl acetate 20/1), enol/keto $=2.5 / 1$. The enol and keto mixture: ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $13.24(\mathrm{~s}, 1 \mathrm{H}$, enol), 8.15 (dd, $J=8.0,1.2 \mathrm{~Hz}, 1 \mathrm{H}$, keto), 7.95 (dd, $J=7.7,1.5 \mathrm{~Hz}, 1 \mathrm{H}$, enol),
7.45-7.16 (m, 16H, enol and keto), $5.05(\mathrm{~s}, 1 \mathrm{H}$, enol $), 4.93(\mathrm{~d}, J=12.6 \mathrm{~Hz}, 1 \mathrm{H}$, keto $), 4.19(\mathrm{~d}, J=$
 $12.6 \mathrm{~Hz}, 1 \mathrm{H}$, keto), 1.42 (s, 9H, enol), 1.23 (s, 9H, keto). ${ }^{13} \mathrm{C}$ NMR (100 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 190.9,171.3,166.9,165.3,143.5,141.5,136.5,134.0$, 133.9, 131.1, 129.9, 129.7, 128.8, 128.8, 128.7, 128.4, 128.3, 127.6, 127.3, $126.9,126.4,126.3,125.5,125.4,98.6,82.6,82.2,62.6,47.6,40.2,28.1$, 27.6. HRMS Calculated for $\mathrm{C}_{20} \mathrm{H}_{21} \mathrm{O}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+}$341.1206, found: 341.1203.

## Methyl 2-(benzofuran-2-yl)-4-hydroxy-2H-thiochromene-3-carboxylate (1q):

$0.732 \mathrm{~g}, 23 \%$ yield (two steps), yellow solid, $\mathrm{mp} 146-147^{\circ} \mathrm{C}$, new compound, $\mathrm{R}_{\mathrm{f}}=0.51$ (hexanes/
 ethyl acetate $20 / 1$ ), enol. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 13.03(\mathrm{~s}, 1 \mathrm{H})$, $7.98(\mathrm{dd}, J=7.3,1.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.38(\mathrm{dd}, J=18.4,8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.27-7.17$ $(\mathrm{m}, 4 \mathrm{H}), 7.14-7.09(\mathrm{~m}, 1 \mathrm{H}), 6.30(\mathrm{~s}, 1 \mathrm{H}), 5.31(\mathrm{~s}, 1 \mathrm{H}), 3.80(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (100 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 171.5,166.5,156.5,155.1,133.9,131.6,128.2$, $128.1,128.0,126.8,125.9,124.3,122.7,120.8,111.3,104.8,94.8,52.4$, 34.4. HRMS Calculated for $\mathrm{C}_{19} \mathrm{H}_{14} \mathrm{NaO}_{4} \mathrm{~S}[\mathrm{M}+\mathrm{Na}]^{+} 361.0505$, found: 361.0499 .


To a solution of thiochromanone derivative $\mathbf{1 c}(2.5 \mathrm{mmol}, 0.746 \mathrm{~g})$ in toluene $(25 \mathrm{~mL})$ was added the piperidine ( $5.0 \mathrm{mmol}, 0.426 \mathrm{~g}$ ) and 4-dimethylaminopyridine (DMAP) ( $1.0 \mathrm{mmol}, 0.122$ g) sequentially. The mixture was refluxed for 24 hours. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure to afford the crude residue. The residue was purified by flash chromatography on silica gel using hexanes/ethyl acetate/dichloromethane (20/1/1-3/1/1) as eluent to give the desirable thiochromanone derivative with amide $\mathbf{1 d}$.

## 2-Phenyl-3-(piperidine-1-carbonyl)thiochroman-4-one (1d):

$0.335 \mathrm{~g}, 38 \%$ yield, white solid, $\mathrm{mp} 202-203{ }^{\circ} \mathrm{C}$, new compound, $\mathrm{R}_{\mathrm{f}}=0.43$ (hexanes/ethyl acetate $3 / 1)$, keto. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.12(\mathrm{dd}, J=8.0,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.51-7.40(\mathrm{~m}, 3 \mathrm{H}), 7.38-$ $7.26(\mathrm{~m}, 4 \mathrm{H}), 7.25-7.18(\mathrm{~m}, 1 \mathrm{H}), 5.27(\mathrm{~d}, J=12.5 \mathrm{~Hz}, 1 \mathrm{H}), 4.54(\mathrm{~d}, J=12.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.71-3.55$ $(\mathrm{m}, 1 \mathrm{H}), 3.53-3.41(\mathrm{~m}, 1 \mathrm{H}), 3.39-3.30(\mathrm{~m}, 1 \mathrm{H}), 3.29-3.11(\mathrm{~m}, 1 \mathrm{H}), 1.65-1.37(\mathrm{~m}, 4 \mathrm{H}), 1.27-1.04$ (m, 2H). ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 192.0,166.0,141.5,137.3,133.9,130.5,129.9,128.8$, $128.5,128.1,127.2,125.5,58.5,48.5,47.5,43.1,26.3,25.5,24.5$. HRMS Calculated for $\mathrm{C}_{21} \mathrm{H}_{22} \mathrm{NO}_{2} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+}$352.1366, found: 352.1367.

### 2.2. Synthesis of Allenylic Carbonates

The allenylic carbonates $\mathbf{2 a - 2 m}$ could be conveniently synthesized from the commercially available propargyl alcohol and aldehydes through two steps according to the known procedure, ${ }^{3,4}$ all of which are new compounds. Firstly, the propargyl alcohol underwent copper-catalyzed reactions with aldehydes to provide the intermediate allenylic alcohols. ${ }^{3}$ Then, the allenylic carbonates 2 were prepared from the above allenylic alcohol intermediates according to the known literature procedure with slight modification. ${ }^{4}$ In addition, allenylic carbonate $\mathbf{2 n}$, a new compound, could be synthesized through two steps according to the known procedure. ${ }^{4,5}$ Firstly, the propargylic dioxolanone $\mathbf{S 1}$ underwent copper-catalyzed $\mathrm{S}_{\mathrm{N}} 2$, substitution with Grignard reagent to provide the intermediate $\alpha$-hydroxyallene. ${ }^{5}$ Then, the allenylic carbonate $\mathbf{2 n}$ was prepared from the above $\alpha$-hydroxyallene intermediate according to the known literature procedure with slight modification. ${ }^{4}$


General Procedure: To a dried Schlenk flask were sequentially added copper dibromide (1.787 $\mathrm{g}, 8.0 \mathrm{mmol}$ ), diphenyl(2-pyrrolidinyl)methanol ( $5.067 \mathrm{~g}, 20 \mathrm{mmol}$ ), 1,4-dioxane ( 40 mL ), aldehydes ( 30 mmol ), and propargyl alcohol ( $1.682 \mathrm{~g}, 30 \mathrm{mmol}$ ) under the nitrogen atmosphere. The mixture was stirred in an oil bath preheated at $70{ }^{\circ} \mathrm{C}$ or $130{ }^{\circ} \mathrm{C}$ for $12-20 \mathrm{~h}$. After cooling to room temperature, the resulting mixture was diluted with diethyl ether ( 60 mL ), which was washed with an aqueous solution of hydrochloric acid $(3.0 \mathrm{M}, 60 \mathrm{~mL})$. After separation, the aqueous layer was extracted with diethyl ether ( $60 \mathrm{~mL} \times 3$ ). The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under the reduced pressure. The residue was purified by flash chromatography on silica gel using hexanes/ethyl acetate (20/1-5/1) as eluent to afford the intermediate allenylic alcohols.

A solution of the above allenylic alcohols ( 9.7 mmol ) and pyridine ( $2.34 \mathrm{~mL}, 29.1 \mathrm{mmol}$ ) in dichloromethane ( 25 mL ) was cooled to $0^{\circ} \mathrm{C}$. The ethyl chloroformate ( $1.85 \mathrm{~mL}, 19.4 \mathrm{mmol}$ ) (or isopropyl chloroformate) was added dropwise over a period of 5 minutes. The reaction mixture was allowed to warm to room temperature. When the reaction was completed as monitored by TLC, the reaction mixture was acidified with the hydrogen chloride aqueous solution ( 3.0 M ) to pH 5-6 and extracted three times with dichloromethane. The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under the reduced pressure. The residue was purified by flash chroma- tography on silica gel using hexanes/ethyl acetate (50/1) as eluent to give the desirable allenylic carbonates $\mathbf{2}$.

## Ethyl (4-phenylbuta-2,3-dien-1-yl) carbonate (2a):

$0.184 \mathrm{~g}, 24 \%$ yield (two steps), yellow liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.49$ (hexanes/ethyl acetate
 10/1). ${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.33-7.28(\mathrm{~m}, 4 \mathrm{H}), 7.25-7.14(\mathrm{~m}$, $1 \mathrm{H}), 6.37-6.28(\mathrm{~m}, 1 \mathrm{H}), 5.84-5.68(\mathrm{~m}, 1 \mathrm{H}), 4.78-4.67(\mathrm{~m}, 2 \mathrm{H}), 4.20(\mathrm{q}, ~ J$ $=7.1 \mathrm{~Hz}, 2 \mathrm{H}), 1.29(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 206.7, 155.0, 133.2, 128.7, 127.4, 127.1, 96.7, 90.8, 65.1, 64.2, 14.3. HRMS Calculated for

## Isopropyl (4-phenylbuta-2,3-dien-1-yl) carbonate (2a"):

$1.120 \mathrm{~g}, 45 \%$ yield (two steps), yellow liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.56$ (hexanes/ethyl acetate 20/1). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.33-7.27(\mathrm{~m}, 4 \mathrm{H}), 7.25-7.19$ ( m , $1 \mathrm{H}), 6.37-6.26(\mathrm{~m}, 1 \mathrm{H}), 5.83-5.64(\mathrm{~m}, 1 \mathrm{H}), 4.92-4.83(\mathrm{~m}, 1 \mathrm{H})$, 4.76-4.66 (m, 2H), $1.30(\mathrm{~d}, J=6.3 \mathrm{~Hz}, 3 \mathrm{H}), 1.26(\mathrm{~d}, J=6.3 \mathrm{~Hz}, 3 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR (100 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 206.6,154.5,133.2,128.7,127.4,127.1,96.7,90.9,72.2,64.9$, 21.8, 21.7. HRMS Calculated for $\mathrm{C}_{14} \mathrm{H}_{16} \mathrm{NaO}_{3}[\mathrm{M}+\mathrm{Na}]^{+}$255.0992, found: 255.0993.

## Ethyl (4-(o-tolyl)buta-2,3-dien-1-yl) carbonate (2b):

$0.191 \mathrm{~g}, 4 \%$ yield (two steps), yellow liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.53$ (hexanes/ethyl acetate
 20/1). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.39-7.32$ (m 1H), 7.18-7.10 (m, $3 \mathrm{H}), 6.58-6.43(\mathrm{~m}, 1 \mathrm{H}), 5.72(\mathrm{q}, J=6.7 \mathrm{~Hz}, 1 \mathrm{H}), 4.77-4.69(\mathrm{~m}, 2 \mathrm{H})$, $4.21(\mathrm{q}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}), 2.36(\mathrm{~s}, 3 \mathrm{H}), 1.30(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 207.4,155.0,135.3,131.4,130.5,127.6,127.4,126.2,94.0,89.8,65.4,64.2$, 19.9, 14.3. HRMS Calculated for $\mathrm{C}_{14} \mathrm{H}_{17} \mathrm{O}_{3}[\mathrm{M}+\mathrm{H}]^{+}$233.1172, found: 233.1174.

## Ethyl (4-(m-tolyl)buta-2,3-dien-1-yl) carbonate (2c):

$1.212 \mathrm{~g}, 26 \%$ yield (two steps), yellow liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.53$ (hexanes/ethyl acetate
 20/1). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.20(\mathrm{t}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.13-7.07$ $(\mathrm{m}, 2 \mathrm{H}), 7.04(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 6.33-6.25(\mathrm{~m}, 1 \mathrm{H}), 5.80-5.69(\mathrm{~m}, 1 \mathrm{H})$, 4.77-4.68 (m, 2H), 4.20 (q, J=7.1 Hz, 2H), $2.33(\mathrm{~s}, 3 \mathrm{H}), 1.30(\mathrm{t}, J=7.1$ $\mathrm{Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 206.7,155.0,138.3,133.0$, $128.6,128.3,127.7,124.2,96.7,90.6,65.3,64.2,21.4,14.3$. HRMS Calculated for $\mathrm{C}_{14} \mathrm{H}_{16} \mathrm{NaO}_{3}$ $[\mathrm{M}+\mathrm{Na}]^{+} 255.0992$, found: 255.0994 .

## Ethyl (4-(p-tolyl)buta-2,3-dien-1-yl) carbonate (2d):

$1.571 \mathrm{~g}, 34 \%$ yield (two steps), yellow liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.53$ (hexanes/ethyl acetate
 20/1). ${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.19(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.12$ $(\mathrm{d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.35-6.21(\mathrm{~m}, 1 \mathrm{H}), 5.84-5.63(\mathrm{~m}, 1 \mathrm{H}), 4.77-$ $4.67(\mathrm{~m}, 2 \mathrm{H}), 4.20(\mathrm{q}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}), 2.33(\mathrm{~s}, 3 \mathrm{H}), 1.30(\mathrm{t}, J=7.1$ $\mathrm{Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (100 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 206.5,155.0,137.3,130.1,129.4,127.0,96.5,90.6,65.3$, 64.2, 21.3, 14.3. HRMS Calculated for $\mathrm{C}_{14} \mathrm{H}_{16} \mathrm{KO}_{3}[\mathrm{M}+\mathrm{K}]^{+} 271.0731$, found: 271.0732.

## Ethyl (4-(3-fluorophenyl)buta-2,3-dien-1-yl) carbonate (2e):

1.775 g , $38 \%$ yield (two steps), yellow liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.44$ (hexanes/ethyl acetate
 20/1). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.29-7.26(\mathrm{~m}, 1 \mathrm{H}), 7.06(\mathrm{~d}, J=$ $7.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.00(\mathrm{~d}, J=9.9 \mathrm{~Hz}, 1 \mathrm{H}), 6.96-6.86(\mathrm{~m}, 1 \mathrm{H}), 6.36-6.22$ $(\mathrm{m}, 1 \mathrm{H}), 5.90-5.64(\mathrm{~m}, 1 \mathrm{H}), 4.78-4.68(\mathrm{~m}, 2 \mathrm{H}), 4.20(\mathrm{q}, J=7.1 \mathrm{~Hz}$, $2 \mathrm{H}), 1.30(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $\left.100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 206.8,163.1\left(\mathrm{~d},{ }^{1} J_{\mathrm{F}-\mathrm{C}}=243.9 \mathrm{~Hz}\right)$, $154.9,135.7\left(\mathrm{~d},{ }^{3} J_{\mathrm{F}-\mathrm{C}}=7.9 \mathrm{~Hz}\right), 130.1\left(\mathrm{~d},{ }^{3} J_{\mathrm{F}-\mathrm{C}}=8.3 \mathrm{~Hz}\right), 122.8\left(\mathrm{~d},{ }^{4} J_{\mathrm{F}-\mathrm{C}}=2.7 \mathrm{~Hz}\right), 114.3\left(\mathrm{~d},{ }^{2} J_{\mathrm{F}-\mathrm{C}}\right.$ $=21.4 \mathrm{~Hz}), 113.6\left(\mathrm{~d},{ }^{2} J_{\mathrm{F}-\mathrm{C}}=22.12 \mathrm{~Hz}\right), 96.1\left(\mathrm{~d},{ }^{4} J_{\mathrm{F}-\mathrm{C}}=2.6 \mathrm{~Hz}\right), 91.2,64.8,64.3,14.3 .{ }^{19} \mathrm{~F} \mathrm{NMR}$
( $376 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$-113.32. The HRMS Calculated for $\mathrm{C}_{13} \mathrm{H}_{14} \mathrm{FO}_{3}[\mathrm{M}+\mathrm{H}]^{+}$237.0921, found: 237.0922.

## 4-(3-Chlorophenyl)buta-2,3-dien-1-yl ethyl carbonate (2f):

$2.096 \mathrm{~g}, 42 \%$ yield (two steps), yellow liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.39$ (hexanes/ethyl acetate
 20/1). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.28$ ( $\mathrm{s}, 1 \mathrm{H}$ ), 7.26-7.14 (m, $3 \mathrm{H}), ~ 6.31-6.23(\mathrm{~m}, 1 \mathrm{H}), 5.87-5.73(\mathrm{~m}, 1 \mathrm{H}), 4.77-4.69(\mathrm{~m}, 2 \mathrm{H}), 4.21$ $(\mathrm{q}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}), 1.30(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 100 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 206.8,154.9,135.3,134.6,129.9,127.4,126.9,125.2,95.9,91.3,64.7,64.3,14.3$. HRMS Calculated for $\mathrm{C}_{13} \mathrm{H}_{17} \mathrm{ClNO}_{3}\left[\mathrm{M}+\mathrm{NH}_{4}\right]^{+} 270.0891\left({ }^{35} \mathrm{Cl}\right)$ and $272.0866\left({ }^{37} \mathrm{Cl}\right)$, found: $270.0889\left({ }^{35} \mathrm{Cl}\right)$ and $272.0856\left({ }^{37} \mathrm{Cl}\right)$.

## 4-(3-Bromophenyl)buta-2,3-dien-1-yl ethyl carbonate (2g):

$2.252 \mathrm{~g}, 38 \%$ yield (two steps), yellow liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.38$ (hexanes/ethyl acetate
 20/1). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.43(\mathrm{~s}, 1 \mathrm{H}), 7.38-7.30(\mathrm{~m}, 1 \mathrm{H})$, 7.23-7.13 (m, 2H), 6.37-6.15 (m, 1H), 5.88-5.69 (m, 1H), 4.77-4.68 (m, $2 \mathrm{H}), 4.21(\mathrm{q}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}), 1.30(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR $(100$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 206.7,154.9,135.5,130.3,130.1,129.8,125.7,122.8$, 95.8, 91.4, 64.7, 64.3, 14.3. HRMS Calculated for $\mathrm{C}_{13} \mathrm{H}_{17} \mathrm{BrNO}_{3}\left[\mathrm{M}+\mathrm{NH}_{4}\right]^{+} 314.0386\left({ }^{79} \mathrm{Br}\right)$ and 316.0367 $\left({ }^{81} \mathrm{Br}\right)$, found: $314.0392\left({ }^{79} \mathrm{Br}\right)$ and $316.0374\left({ }^{81} \mathrm{Br}\right)$.

## Ethyl (4-(3-methoxyphenyl)buta-2,3-dien-1-yl) carbonate (2h):

$1.390 \mathrm{~g}, 28 \%$ yield (two steps), yellow liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.34$ (hexanes/ethyl acetate
 20/1). ${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.22(\mathrm{t}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H})$, 6.92-6.825 (m, 2H), 6.78 (dd, $J=8.2,2.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.33-6.22$ (m, $1 \mathrm{H}), 5.83-5.65(\mathrm{~m}, 1 \mathrm{H}), 4.77-4.68(\mathrm{~m}, 2 \mathrm{H}), 4.19(\mathrm{q}, J=7.1 \mathrm{~Hz}$, $2 \mathrm{H}), 3.81(\mathrm{~s}, 3 \mathrm{H}), 1.29(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 206.7,159.9,154.9$, 134.6, 129.6, 119.7, 113.3, 112.2, 96.7, 90.9, 65.1, 64.2, 55.2, 14.3. HRMS Calculated for $\mathrm{C}_{14} \mathrm{H}_{17} \mathrm{O}_{4}[\mathrm{M}+\mathrm{H}]^{+}$249.1121, found: 249.1119

## 4-(3,5-Dimethylphenyl)buta-2,3-dien-1-yl ethyl carbonate (2i):

$2.200 \mathrm{~g}, 45 \%$ yield (two steps), pale yellow liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.45$ (hexanes/ethyl
 acetate 20/1). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 6.91$ ( $\mathrm{s}, 2 \mathrm{H}$ ), 6.86 ( s , $1 \mathrm{H}), 6.27-6.20(\mathrm{~m}, 1 \mathrm{H}), 5.83-5.62(\mathrm{~m}, 1 \mathrm{H}), 4.75-4.68(\mathrm{~m}, 2 \mathrm{H})$, 4.24-4.16 (m, 2H), $2.29(\mathrm{~s}, 6 \mathrm{H}), 1.30(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 206.7,155.0,138.2,132.9,129.2,124.9,96.7$, 90.5, 65.3, 64.2, 21.2, 14.3. HRMS Calculated for $\mathrm{C}_{15} \mathrm{H}_{19} \mathrm{O}_{3}[\mathrm{M}+\mathrm{H}]^{+} 247.1329$, found: 247.1328.

4-([1,1'-Biphenyl]-4-yl)buta-2,3-dien-1-yl ethyl carbonate (2j):

$2.123 \mathrm{~g}, 36 \%$ yield (two steps), yellow liquid, new compound,
$\mathrm{R}_{\mathrm{f}}=0.32$ (hexanes/ethyl acetate 20/1). ${ }^{1} \mathrm{H}$ NMR ( 400 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta$ 7.60-7.53 (m, 4H), 7.45-7.41 (m, 2H), 7.38-7.31 (m, $3 \mathrm{H}), ~ 6.38-6.33(\mathrm{~m}, 1 \mathrm{H}), 5.86-5.69(\mathrm{~m}, 1 \mathrm{H}), 4.79-4.69(\mathrm{~m}, 2 \mathrm{H})$,
4.24-4.17 (m, 2H), $1.30(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 206.9,155.0,140.7$, 140.3, 132.2, 128.8, 127.5, 127.4, 127.4, 127.0, 96.4, 90.9, 65.1, 64.2, 14.3. HRMS Calculated for $\mathrm{C}_{19} \mathrm{H}_{19} \mathrm{O}_{3}[\mathrm{M}+\mathrm{H}]^{+} 295.1329$, found: 295.1327 .

## Ethyl (4-(naphthalen-2-yl)buta-2,3-dien-1-yl) carbonate (2k):

$1.834 \mathrm{~g}, 34 \%$ yield (two steps), pale yellow liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.57$ (hexanes/ethyl
 acetate $20 / 1$ ). ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.82-7.73(\mathrm{~m}, 3 \mathrm{H}), 7.65$ $(\mathrm{s}, 1 \mathrm{H}), 7.48-7.38(\mathrm{~m}, 3 \mathrm{H}), 6.57-6.42(\mathrm{~m}, 1 \mathrm{H}), 5.94-5.67(\mathrm{~m}, 1 \mathrm{H})$, 4.81-4.71 (m, 2H), 4.25-4.14 (m, 2H), $1.28(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 207.2,155.0,133.6,132.9,130.7,128.4$, 127.8, 127.8, 126.4, 126.1, 125.9, 124.7, 97.1, 91.1, 65.2, 64.2, 14.3. HRMS Calculated for $\mathrm{C}_{17} \mathrm{H}_{20} \mathrm{NO}_{3}\left[\mathrm{M}+\mathrm{NH}_{4}\right]^{+}$286.1438, found: 286.1437.

## Ethyl (4-(thiophen-3-yl)buta-2,3-dien-1-yl) carbonate (21):

$1.726 \mathrm{~g}, 38 \%$ yield (two steps), yellow liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.62$ (hexanes/ethyl acetate

$20 / 1) .{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.27-7.25(\mathrm{~m}, 1 \mathrm{H}), 7.11(\mathrm{~d}, J=2.8$
$\mathrm{Hz}, 1 \mathrm{H}), 7.09-7.02(\mathrm{~m}, 1 \mathrm{H}), 6.45-6.33(\mathrm{~m}, 1 \mathrm{H}), 5.77-5.59(\mathrm{~m}, 1 \mathrm{H})$,
4.74-4.65 (m, 2H), $4.19(\mathrm{q}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}), 1.29(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H})$. ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 207.0,154.9,134.3,126.4,126.1,121.7,91.3,90.0,65.1,64.2$, 14.3. HRMS Calculated for $\mathrm{C}_{11} \mathrm{H}_{12} \mathrm{NaO}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{Na}]^{+}$247.0399, found: 247.0401.

## Ethyl penta-2,3-dien-1-yl carbonate ( 2 m ):

$0.408 \mathrm{~g}, 13 \%$ yield (two steps), colorless liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.58$ (hexanes/ethyl acetate 20/1). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 5.41-5.10(\mathrm{~m}, 2 \mathrm{H}), 4.63-4.56(\mathrm{~m}$, $2 \mathrm{H}), 4.20(\mathrm{q}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}), 1.68(\mathrm{dd}, J=5.7,4.5 \mathrm{~Hz}, 3 \mathrm{H}), 1.31(\mathrm{t}, J=$ $7.1 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 206.5,155.0,87.7,85.9$, 66.0, 64.0, 14.3, 13.8. HRMS Calculated for $\mathrm{C}_{8} \mathrm{H}_{13} \mathrm{O}_{3}[\mathrm{M}+\mathrm{H}]^{+}$157.0859, found: 157.0859.


To a dried Schlenk flask were sequentially added catalyst $\mathrm{Cu}(\mathrm{MeCN})_{4} \mathrm{BF}_{4}(0.189 \mathrm{~g}, 0.6 \mathrm{mmol})$, $(n-\mathrm{BuO})_{3} \mathrm{P}(0.32 \mathrm{~mL}, 1.2 \mathrm{mmol})$ and dichloromethane $(10 \mathrm{~mL})$ under the nitrogen atmosphere. The mixture was stirred at room temperature for 1 h . After cooling to $-10^{\circ} \mathrm{C}$, the methylmagnesium bromide ( $12 \mathrm{~mL}, 1.0 \mathrm{M}$ in tetrahydrofuran, 12 mmol ) was added and the reaction was stirred for 30 min at $-10^{\circ} \mathrm{C}$. Then, a solution of the dioxolanone $\mathbf{S 1}(1.129 \mathrm{~g}, 6 \mathrm{mmol})$ in dichloromethane $(5.0 \mathrm{~mL})$ was added and the reaction mixture was stirred at $-10{ }^{\circ} \mathrm{C}$ for 22 h . Afterwards, the reaction mixture was quenched with ammonium chloride saturated solution. After separation, the aqueous layer was extracted with diethyl ether ( $20 \mathrm{~mL} \times 3$ ). The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under the reduced pressure. The residue was purified by flash chromatography on silica gel using hexanes/ethyl
acetate (20/1-10/1) as eluent to afford the intermediate $\alpha$-hydroxyallene.
A solution of the above $\alpha$-hydroxyallene ( $0.343 \mathrm{~g}, 2.1 \mathrm{mmol}$ ) and pyridine ( $0.51 \mathrm{~mL}, 6.3 \mathrm{mmol}$ ) in dichloromethane $(10 \mathrm{~mL})$ was cooled to $0^{\circ} \mathrm{C}$. The ethyl chloroformate $(0.40 \mathrm{~mL}, 4.2 \mathrm{mmol})$ was added dropwise over a period of 5 minutes. The reaction mixture was allowed to warm to room temperature. When the reaction was completed as monitored by TLC, the reaction mixture was acidified with the hydrogen chloride aqueous solution $(3.0 \mathrm{M})$ to $\mathrm{pH} 5-6$ and extracted three times with dichloromethane. The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under the reduced pressure. The residue was purified by flash chromatography on silica gel using hexanes/ethyl acetate (50/1) as eluent to give the desirable allenylic carbonate $\mathbf{2 n}$.

## Ethyl (4-phenylpenta-2,3-dien-1-yl) carbonate (2n):

$0.451 \mathrm{~g}, 33 \%$ yield (two steps), pale yellow liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.67$ (hexanes/ethyl acetate 20/1). ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.42-7.37(\mathrm{~m}, 2 \mathrm{H}), 7.35-7.29(\mathrm{~m}, 2 \mathrm{H}), 7.25-7.19(\mathrm{~m}$, $1 \mathrm{H}), 5.73-5.57(\mathrm{~m}, 1 \mathrm{H}), 4.70(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 4.20(\mathrm{q}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}), 2.12(\mathrm{~d}, J=2.8 \mathrm{~Hz}, 3 \mathrm{H})$, $1.30(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 205.8,155.0,136.0,128.4,127.1,125.9$, 102.9, 88.7, 65.7, 64.1, 16.8, 14.3. HRMS Calculated for $\mathrm{C}_{14} \mathrm{H}_{20} \mathrm{NO}_{3}\left[\mathrm{M}+\mathrm{NH}_{4}\right]^{+} 250.1438$, found: 250.1443 .

## 3. Palladium-Catalyzed Asymmetric Allenylic Alkylation



The metal precursor $\operatorname{Pd}(\mathrm{dba})_{2}(0.02 \mathrm{mmol}, 11.5 \mathrm{mg}, 10 \mathrm{~mol} \%)$, ligand ( $R$ )-DTB-BIPHEP (L4) ( $0.022 \mathrm{mmol}, 22.7 \mathrm{mg}, 11 \mathrm{~mol} \%$ ) and tetrahydrofuran $(1.5 \mathrm{~mL})$ were placed in a dried Schlenk tube under nitrogen atmosphere. The mixture was stirred at $30^{\circ} \mathrm{C}$ for 30 min . Then the mixture was cooled to $-20^{\circ} \mathrm{C}$. Thereafter, the thiochromanone derivatives $1(0.2 \mathrm{mmol}), 5 \AA \mathrm{MS}(50.0 \mathrm{mg})$ and 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) $(35.9 \mu \mathrm{~L}, 0.24 \mathrm{mmol})$ were added and the reaction was stirred at $-20^{\circ} \mathrm{C}$ for 10 minutes. Sequentially, the allenylic carbonates $2(0.3 \mathrm{mmol})$ and tetrahydrofuran $(0.5 \mathrm{~mL})$ were added slowly. The mixture was stirred at $-20^{\circ} \mathrm{C}$ for $72-168 \mathrm{~h}$. After the completion of the reaction, the volatiles were directly removed under the reduced pressure. The residue was quickly purified by column chromatography on silica gel (hexanes/ethyl acetate/dichloromethane 100/1/2-100/3/6) to give the desirable allenylic alkylation products 3 .

The racemates were prepared by running reactions with an achiral 1,3-bis(diphenylphosphino)propane ligand at $30^{\circ} \mathrm{C}$. It was worth noting that the products $\mathbf{3}$ were sensitive to water or alcohol, which would lead to partial decrease of dr value.
(-)-Methyl 4-oxo-2-phenyl-3-(4-phenylbuta-2,3-dien-1-yl)thiochromane-3-carboxylate (3ca):
The reaction was conducted at $-20^{\circ} \mathrm{C}$ for $72 \mathrm{~h} .78 .5 \mathrm{mg}, 92 \%$ yield, pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.28$ (hexanes/ethyl acetate 20/1), 32.3:1 dr, $99 \%$ ee (major diastereoisomer), $[\alpha]^{20}{ }_{\mathrm{D}}=-209.67\left(c 0.63, \mathrm{CHCl}_{3}\right)$. The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.17$
 (d, $J=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.43-7.31(\mathrm{~m}, 6 \mathrm{H}), 7.27-7.22(\mathrm{~m}, 4 \mathrm{H}), 7.20-7.10$ $(\mathrm{m}, 3 \mathrm{H}), 6.22-5.96(\mathrm{~m}, 1 \mathrm{H}), 5.66-5.43(\mathrm{~m}, 1 \mathrm{H}), 4.98(\mathrm{~s}, 1 \mathrm{H}), 3.65(\mathrm{~s}$, $3 \mathrm{H}), 3.22-3.02(\mathrm{~m}, 1 \mathrm{H}), 2.73-2.51(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 100 MHz , $\mathrm{CDCl}_{3}$ ) $\delta 207.4,192.4,169.7,141.5,135.6,133.9,133.2,130.8$, $130.5,129.2,128.9,128.6,128.5,127.3,127.1,126.8,125.5,95.5,89.9,62.7,52.4,51.1,32.5$. HPLC: Chiralpak IC column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}, n-\mathrm{Hexane} / i-\mathrm{PrOH}=95 / 5$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 15.0 min (minor) and 16.0 min (major). HRMS Calculated for the $\mathrm{C}_{27} \mathrm{H}_{23} \mathrm{O}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+}$ 427.1362, found: 427.1372.

The mixtrue with low 2.3:1 dr: ${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.17$ (d, $J=7.9 \mathrm{~Hz}, 1 \mathrm{H}$, major),

major

minor 7.88 (d, $J=7.9 \mathrm{~Hz}, 1 \mathrm{H}$, minor), 7.40-7.12 (m, 26H, major + minor), 6.16-6.01 ( $\mathrm{m}, 2 \mathrm{H}$, major + minor), 5.62-5.45 (m, 2H, major + minor), $5.09(\mathrm{~s}, 1 \mathrm{H}$, minor), $4.98(\mathrm{~s}, 1 \mathrm{H}$, major), $3.65(\mathrm{~s}, 6 \mathrm{H}$, major + minor), 3.18-3.04 ( $\mathrm{m}, 2 \mathrm{H}$, major + minor), 2.67-2.53 ( $\mathrm{m}, 2 \mathrm{H}$, major + minor). ${ }^{13} \mathrm{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 207.4,207.2,192.4,192.2,169.7,169.7,141.5,141.0$, $135.7,135.6,133.9,133.8,133.2,133.0,130.8,130.8,130.5,130.4,129.2,129.0,128.9,128.8$, $128.6,128.5,128.5,128.4,127.3,127.2,127.1,127.0,126.9,126.8,125.5,125.4,95.9,95.5,90.0$,
(-)-Methyl 4-oxo-3-(4-phenylbuta-2,3-dien-1-yl)-2-(o-tolyl)thiochromane-3-carboxylate (3ea): The reaction was conducted at $-20^{\circ} \mathrm{C}$ for $120 \mathrm{~h} .71 .9 \mathrm{mg}, 82 \%$ yield, pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.36$ (hexanes/ethyl acetate $20 / 1$ ), 24.0:1 dr, $98 \%$ ee (major diastereoisomer), $[\alpha]^{20}{ }_{\mathrm{D}}=-25.30\left(c \quad 0.83, \mathrm{CHCl}_{3}\right)$. The major diastereoisomer: ${ }^{1} \mathrm{H}$
 NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.20(\mathrm{dd}, J=8.0,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.52(\mathrm{~d}, J$ $=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.42-7.34(\mathrm{~m}, 1 \mathrm{H}), 7.29-7.09(\mathrm{~m}, 10 \mathrm{H}), 6.00-5.85(\mathrm{~m}$, $1 \mathrm{H}), 5.65-5.43(\mathrm{~m}, 1 \mathrm{H}), 5.04(\mathrm{~s}, 1 \mathrm{H}), 3.62(\mathrm{~s}, 3 \mathrm{H}), 3.15-3.00(\mathrm{~m}$, $1 \mathrm{H}), 2.84-2.69(\mathrm{~m}, 1 \mathrm{H}), 2.41(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ $207.0,192.1,170.1,141.3,136.4,134.9,134.1,133.2,130.9,130.8,130.5,128.5,128.5,128.1$, 127.1, 127.0, 126.9, 126.4, 125.4, 94.9, 89.9, 62.0, 52.5, 47.0, 32.8, 20.3. HPLC: Chiralpak ID column, $254 \mathrm{~nm}, 30{ }^{\circ} \mathrm{C}, n$-Hexane $/ i-\mathrm{PrOH}=97 / 3$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 13.9 min (major) and 16.6 min. HRMS Calculated for $\mathrm{C}_{28} \mathrm{H}_{24} \mathrm{NaO}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{Na}]^{+} 463.1338$, found: 463.1341 .
(-)-Methyl 4-oxo-3-(4-phenylbuta-2,3-dien-1-yl)-2-(m-tolyl)thiochromane-3-carboxylate(3fa): The reaction was conducted at $-20^{\circ} \mathrm{C}$ for $120 \mathrm{~h} .78 .1 \mathrm{mg}, 89 \%$ yield, pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.36$ (hexanes/ethyl acetate $20 / 1$ ), $32.3: 1 \mathrm{dr}, 99 \%$ ee (major diastereoisomer),
 $[\alpha]^{20}{ }_{\mathrm{D}}=-241.32\left(c \quad 0.90, \mathrm{CHCl}_{3}\right)$. The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.24-8.10(\mathrm{~m}, 1 \mathrm{H}), 7.42-7.37(\mathrm{~m}, 1 \mathrm{H})$, 7.27-7.13 (m, 10H), 6.19-6.00 (m, 1H), 5.60-5.41 (m, 1H), $4.97(\mathrm{~s}$, $1 \mathrm{H}), 3.65(\mathrm{~s}, 3 \mathrm{H}), 3.22-3.03(\mathrm{~m}, 1 \mathrm{H}), 2.69-2.52(\mathrm{~m}, 1 \mathrm{H}), 2.33(\mathrm{~s}, 3 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 207.5,192.5,169.7,141.7,138.1$, $135.3,134.0,133.2,130.8,130.5,130.1,129.7,128.6,128.4,127.3,127.1,126.8,126.1,125.5$, 95.5, 90.0, 62.7, 52.3, 51.1, 32.4, 21.5. HPLC: Chiralcel OD-3 column, $254 \mathrm{~nm}, 3{ }^{\circ} \mathrm{C}, n$-Hexane/ $i-\mathrm{PrOH}=95 / 5$, flow $=0.8 \mathrm{~mL} / \mathrm{min}$, retention time 10.2 min and 23.6 min (major). HRMS Calculated for $\mathrm{C}_{28} \mathrm{H}_{24} \mathrm{NaO}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{Na}]^{+} 463.1338$, found: 463.1342.
(-)-Methyl 4-oxo-3-(4-phenylbuta-2,3-dien-1-yl)-2-(p-tolyl)thiochromane-3-carboxylate(3ga):
The reaction was conducted at $-20^{\circ} \mathrm{C}$ for $120 \mathrm{~h} .79 .3 \mathrm{mg}, 90 \%$ yield, pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.36$ (hexanes/ethyl acetate 20/1), $32.3: 1 \mathrm{dr}, 99 \%$ ee (major diastereoisomer),
 $[\alpha]^{20}{ }_{\mathrm{D}}=-226.76\left(c \quad 0.93, \mathrm{CHCl}_{3}\right)$. The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 8.31-8.04 (m, 1H), 7.43-7.37 (m, 1H), 7.27-7.22 (m, 6H), 7.20-7.11 (m, 5H), 6.21-6.00 (m, 1H), 5.61-5.41 $(\mathrm{m}, 1 \mathrm{H}), 4.96(\mathrm{~s}, 1 \mathrm{H}), 3.65(\mathrm{~s}, 3 \mathrm{H}), 3.16-3.03(\mathrm{~m}, 1 \mathrm{H}), 2.64-2.55(\mathrm{~m}$, $1 \mathrm{H}), 2.34(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 207.4,192.6$, $169.8,141.7,138.8,134.0,133.2,132.4,130.9,130.5,129.2,129.0,128.6,127.3,127.0,126.9$, 125.5, 95.5, 89.9, 62.8, 52.4, 50.9, 32.4, 21.2. HPLC: Chiralpak IA, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}$, $n$-Hexane $/ i-$ $\mathrm{PrOH}=95 / 5$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 13.6 min and 17.4 min (major). HRMS Calculated for $\mathrm{C}_{28} \mathrm{H}_{24} \mathrm{NaO}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{Na}]^{+}$463.1338, found: 463.1340 .
(-)-Methyl 2-(4-fluorophenyl)-4-oxo-3-(4-phenylbuta-2,3-dien-1-yl)thiochromane-3-carboxylate (3ha): The reaction was conducted at $-20^{\circ} \mathrm{C}$ for 120 hours. $83.4 \mathrm{mg}, 94 \%$ yield, pale yellow
viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.40$ (hexanes/ethyl acetate 20/1), 49.0:1 dr, $99 \%$ ee (major diastereoisomer), $[\alpha]^{20}{ }_{\mathrm{D}}=-215.33\left(c \quad 0.73, \mathrm{CHCl}_{3}\right)$. The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR (400
 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.17(\mathrm{dd}, J=8.0,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.44-7.34(\mathrm{~m}, 3 \mathrm{H})$, 7.27-7.22 (m, 4H), 7.20-7.12 (m, 3H), 7.07-6.96 (m, 2H), 6.18-5.97 $(\mathrm{m}, 1 \mathrm{H}), 5.63-5.41(\mathrm{~m}, 1 \mathrm{H}), 4.95(\mathrm{~s}, 1 \mathrm{H}), 3.65(\mathrm{~s}, 3 \mathrm{H}), 3.17-3.04(\mathrm{~m}$, $1 \mathrm{H}), 2.63-2.50(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 207.4,192.1$, $169.7,162.8\left(\mathrm{~d},{ }^{1} J_{\mathrm{F}-\mathrm{C}}=248.6 \mathrm{~Hz}\right), 141.2,133.8,133.3,131.4(\mathrm{~d}$, $\left.{ }^{4} J_{\mathrm{F}-\mathrm{C}}=3.4 \mathrm{~Hz}\right), 131.0,131.0,130.8,130.5,128.6,127.2\left(\mathrm{~d},{ }^{3} J_{\mathrm{F}-\mathrm{C}}=8.9 \mathrm{~Hz}\right), 126.8,125.7,115.5(\mathrm{~d}$, $\left.{ }^{2} J_{\mathrm{F}-\mathrm{C}}=21.6 \mathrm{~Hz}\right), 95.6,89.8,62.6,52.4,50.3,32.4 .{ }^{19} \mathrm{~F}$ NMR ( $376 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta-112.38 . \mathrm{HPLC}:$ Chiralcel OD-H column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}, n-\mathrm{Hexane} / i-\mathrm{PrOH}=95 / 5$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 9.6 min and 15.7 min (major). HRMS Calculated for $\mathrm{C}_{27} \mathrm{H}_{21} \mathrm{FNaO}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{Na}]^{+} 467.1088$, found: 467.1087.
(-)-Methyl 2-(4-chlorophenyl)-4-oxo-3-(4-phenylbuta-2,3-dien-1-yl)thiochromane-3-carboxylate (3ia): The reaction was conducted at $-20^{\circ} \mathrm{C}$ for 120 hours. $88.3 \mathrm{mg}, 96 \%$ yield, pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.40$ (hexanes/ethyl acetate 20/1), 49.0:1 dr, $99 \%$ ee (major
 diastereoisomer), $[\alpha]^{20}{ }_{\mathrm{D}}=-200.57\left(c \quad 1.03, \mathrm{CHCl}_{3}\right)$. The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.17(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H})$, 7.44-7.38 (m, 1H), 7.35-7.28 (m, 4H), 7.27-7.21 (m, 4H), 7.19-7.13 $(\mathrm{m}, 3 \mathrm{H}), 6.19-5.99(\mathrm{~m}, 1 \mathrm{H}), 5.60-5.40(\mathrm{~m}, 1 \mathrm{H}), 4.93(\mathrm{~s}, 1 \mathrm{H}), 3.64(\mathrm{~s}$, $3 \mathrm{H}), 3.17-3.04(\mathrm{~m}, 1 \mathrm{H}), 2.64-2.53(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 100 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 207.4,192.0,169.6,141.0,134.8,134.1,133.8,133.4,130.8,130.6,130.5,128.7,128.6$, 127.3, 127.2, 126.9, 125.7, $95.6,89.8,62.5,52.5,50.5,32.5$. HPLC: Chiralcel OD-H column, 254 $\mathrm{nm}, 30^{\circ} \mathrm{C}, n-\mathrm{Hexane} / i-\mathrm{PrOH}=95 / 5$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 10.2 min and 16.5 min (major). HRMS Calculated for $\mathrm{C}_{27} \mathrm{H}_{21} \mathrm{ClNaO}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{Na}]^{+} 483.0792\left({ }^{35} \mathrm{Cl}\right)$ and $485.0773\left({ }^{37} \mathrm{Cl}\right)$, found: $483.0793\left({ }^{35} \mathrm{Cl}\right)$ and $485.0792\left({ }^{37} \mathrm{Cl}\right)$.
(-)-Methyl 2-(4-bromophenyl)-4-oxo-3-(4-phenylbuta-2,3-dien-1-yl)thiochromane-3-carboxylate (3ja): The reaction was conducted at $-20^{\circ} \mathrm{C}$ for 120 hours. $94.5 \mathrm{mg}, 93 \%$ yield, pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.40$ (hexanes/ethyl acetate 20/1), 49.0:1 dr, $99 \%$ ee (major
 diastereoisomer $),[\alpha]^{20}{ }_{\mathrm{D}}=-186.71\left(c \quad 1.10, \mathrm{CHCl}_{3}\right)$. The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.17(\mathrm{dd}, J=8.0,1.2 \mathrm{~Hz}$, $1 \mathrm{H}), 7.51-7.35(\mathrm{~m}, 3 \mathrm{H}), 7.28-7.21(\mathrm{~m}, 6 \mathrm{H}), 7.19-7.13(\mathrm{~m}, 3 \mathrm{H}), 6.14-$ $6.00(\mathrm{~m}, 1 \mathrm{H}), 5.57-5.44(\mathrm{~m}, 1 \mathrm{H}), 4.91(\mathrm{~s}, 1 \mathrm{H}), 3.64(\mathrm{~s}, 3 \mathrm{H}), 3.17-$ $3.04(\mathrm{~m}, 1 \mathrm{H}), 2.62-2.52(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 207.4, 192.0, 169.6, 141.0, 134.6, 133.8, 133.4, 131.7, 130.9, 130.7, 130.5, 128.6, 127.3, 127.2, 126.9, 125.7, 123.0, $95.6,89.8,62.5,52.5,50.5,32.5$. HPLC: Chiralcel OD-H column, $254 \mathrm{~nm}, 30$ ${ }^{\circ} \mathrm{C}, n$-Hexane $/ i-\mathrm{PrOH}=95 / 5$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 11.1 min (minor) and 17.2 min (major). HRMS Calculated for $\mathrm{C}_{27} \mathrm{H}_{21} \mathrm{BrNaO}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{Na}]^{+} 527.0287\left({ }^{79} \mathrm{Br}\right)$ and $529.0270\left({ }^{81} \mathrm{Br}\right.$ ), found: $527.0292\left({ }^{79} \mathrm{Br}\right)$ and $529.0275\left({ }^{81} \mathrm{Br}\right)$.
(-)-Methyl 2-(4-methoxyphenyl)-4-oxo-3-(4-phenylbuta-2,3-dien-1-yl)thiochromane-3-carboxylate (3ka): The reaction was conducted at $-20^{\circ} \mathrm{C}$ for $72 \mathrm{~h} .76 .9 \mathrm{mg}, 84 \%$ yield, pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.23$ (hexanes/ethyl acetate 20/1), $32.3: 1 \mathrm{dr}, 99 \%$ ee (major
diastereoisomer), $[\alpha]^{20}{ }_{\mathrm{D}}=-208.12\left(c\right.$ 1.07, $\left.\mathrm{CHCl}_{3}\right)$. The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 8.21-8.09 (m, 1H), 7.43-7.34 (m, 1H), 7.33-7.27 (m, 2H), 7.26-7.20 (m, 4H),
 7.19-7.13 (m, 3H), 6.89-6.81 (m, 2H), 6.15-6.00 (m, 1H), 5.59-5.43 $(\mathrm{m}, 1 \mathrm{H}), 4.93(\mathrm{~s}, 1 \mathrm{H}), 3.79(\mathrm{~s}, 3 \mathrm{H}), 3.65(\mathrm{~s}, 3 \mathrm{H}), 3.15-3.01(\mathrm{~m}, 1 \mathrm{H})$, 2.65-2.52 (m, 1H). ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 207.4$, 192.6, $169.8,159.8,141.8,134.0,133.2,130.8,130.5,130.4,128.6,127.4$, $127.2,127.0,126.9,125.5,113.8,95.4,89.9,62.8,55.3,52.4,50.5$, 32.4. HPLC: Chiralcel OD-H column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}, n-\mathrm{Hexane} / i-\mathrm{PrOH}=94 / 6$, flow $=1.0 \mathrm{~mL} /$ min, retention time 13.3 min (minor) and 26.0 min (major). HRMS Calculated for $\mathrm{C}_{28} \mathrm{H}_{24} \mathrm{NaO}_{4} \mathrm{~S}$ $[\mathrm{M}+\mathrm{Na}]^{+} 479.1288$, found: 479.1291.
(-)-Methyl 2-methyl-4-oxo-3-(4-phenylbuta-2,3-dien-1-yl)thiochromane-3-carboxylate (3la):
The reaction was conducted at $-20^{\circ} \mathrm{C}$ for $72 \mathrm{~h} .68 .2 \mathrm{mg}, 94 \%$ yield, pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.45$ (hexanes/ethyl acetate 20/1), $9.0: 1 \mathrm{dr}, 99 \%$ ee (major diastereoisomer), $[\alpha]^{20}{ }_{\mathrm{D}}=-87.47\left(c \quad 0.95, \mathrm{CHCl}_{3}\right)$. The major diastereoisomer: ${ }^{1} \mathrm{H}$
 NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.16(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.41-7.34(\mathrm{~m}$, $1 \mathrm{H}), 7.30-7.14(\mathrm{~m}, 7 \mathrm{H}), 6.29-5.97(\mathrm{~m}, 1 \mathrm{H}), 5.65-5.35(\mathrm{~m}, 1 \mathrm{H}), 3.84$ (q, $J=6.9 \mathrm{~Hz}, 1 \mathrm{H}), 3.63(\mathrm{~s}, 3 \mathrm{H}), 3.39-3.24(\mathrm{~m}, 1 \mathrm{H}), 2.92-2.77(\mathrm{~m}$, $1 \mathrm{H}), 1.61(\mathrm{~d}, J=7.0 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 207.1,191.7,170.2,141.3,134.0$, 133.0, 130.7, 130.4, 128.6, 127.2, 127.1, 126.9, 125.3, 95.0, 89.3, 61.7, 52.4, 41.8, 31.1, 15.6. HPLC: Chiralpak IC column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}, n-\mathrm{Hexane} / i-\mathrm{PrOH}=99 / 1$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 19.7 min (major) and 22.0 min . HRMS Calculated for $\mathrm{C}_{22} \mathrm{H}_{21} \mathrm{O}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+} 365.1206$, found: 365.1209 .
(-)-Methyl 6-nitro-4-oxo-2-phenyl-3-(4-phenylbuta-2,3-dien-1-yl)thiochromane-3-carboxylate (3ma): The reaction was conducted at $-20^{\circ} \mathrm{C}$ for $120 \mathrm{~h} .86 .1 \mathrm{mg}, 91 \%$ yield, pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.18$ (hexanes/ethyl acetate 20/1), 49.0:1 dr, $99 \%$ ee (major
 diastereoisomer), $[\alpha]^{20}{ }_{\mathrm{D}}=-207.17$ (c 1.10, $\mathrm{CHCl}_{3}$ ). The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.94(\mathrm{~d}, J=2.5$ $\mathrm{Hz}, 1 \mathrm{H}), 8.16(\mathrm{dd}, J=8.7,2.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.40-7.32(\mathrm{~m}, 6 \mathrm{H})$, 7.24-7.19 (m, 2H), 7.18-7.08 (m, 3H), 6.15-5.99 (m, 1H), 5.62$5.48(\mathrm{~m}, 1 \mathrm{H}), 5.07(\mathrm{~s}, 1 \mathrm{H}), 3.66(\mathrm{~s}, 3 \mathrm{H}), 3.22-3.07(\mathrm{~m}, 1 \mathrm{H}), 2.63-2.52(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (100 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 207.5,190.5,168.9,149.7,145.6,134.2,133.6,130.9,129.4,129.2,128.8,128.6$, 128.1, 127.2, 126.7, 126.7, 125.7, 96.2, 89.3, 62.1, 52.6, 51.0, 32.0. HPLC: Chiralpak IB column, $254 \mathrm{~nm}, 30{ }^{\circ} \mathrm{C}, n$-Hexane $/ i-\mathrm{PrOH}=85 / 15$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 11.4 min and 18.6 min (major). HRMS Calculated for $\mathrm{C}_{27} \mathrm{H}_{22} \mathrm{NO}_{5} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+} 472.1213$, found: 472.1218 .
(-)-Methyl 6-methoxy-4-oxo-2-phenyl-3-(4-phenylbuta-2,3-dien-1-yl)thiochromane-3-carboxylate (3na): The reaction was conducted at $-20^{\circ} \mathrm{C}$ for $120 \mathrm{~h} .78 .8 \mathrm{mg}, 86 \%$ yield, yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.21$ (hexanes/ethyl acetate $20 / 1$ ), $32.3: 1 \mathrm{dr}, 99 \%$ ee (major diastereoisomer), $[\alpha]^{20}{ }_{\mathrm{D}}=-234.07\left(c \quad 0.93, \mathrm{CHCl}_{3}\right)$. The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.65(\mathrm{~d}, J=2.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.39-7.29(\mathrm{~m}, 5 \mathrm{H}), 7.25-7.21(\mathrm{~m}, 2 \mathrm{H}), 7.19-7.09(\mathrm{~m}$, 4H), 7.05-6.98 (m, 1H), 6.15-6.04 (m, 1H), 5.59-5.43 (m, 1H), $4.96(\mathrm{~s}, 1 \mathrm{H}), 3.84(\mathrm{~s}, 3 \mathrm{H}), 3.65(\mathrm{~s}$, $3 \mathrm{H}), 3.19-3.06(\mathrm{~m}, 1 \mathrm{H}), 2.66-2.54(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (100 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 207.4,192.5,169.8$,

157.8, 135.7, 133.9, 133.0, 131.6, 129.1, 128.8, 128.6, 128.6, $128.5,127.1,126.9,122.3,112.6,95.5,89.9,62.8,55.6,52.4$, 51.5, 32.5. HPLC: Chiral- pak AD-3, $254 \mathrm{~nm}, 30{ }^{\circ} \mathrm{C}$, $n$-Hexane $/ i-\mathrm{PrOH}=90 / 10$, flow $=0.8 \mathrm{~mL} / \mathrm{min}$, retention time 18.2 min and 19.4 min (major). HRMS Calculated for $\mathrm{C}_{28} \mathrm{H}_{25} \mathrm{O}_{4} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+} 457.1468$, found: 457.1466.
(-)-Methyl 6-methyl-4-oxo-2-phenyl-3-(4-phenylbuta-2,3-dien-1-yl)thiochromane-3-carboxylate (30a): The reaction was conducted at $-20^{\circ} \mathrm{C}$ for 120 hours. $82.9 \mathrm{mg}, 94 \%$ yield, pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.31$ (hexanes/ethyl acetate 20/1), 32.3:1 dr, $99 \%$ ee (major
 diastereoisomer), $[\alpha]^{20}{ }_{\mathrm{D}}=-225.21\left(c \quad 0.88, \mathrm{CHCl}_{3}\right)$. The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.00-7.94$ (m, $1 \mathrm{H}), 7.39-7.30(\mathrm{~m}, 5 \mathrm{H}), 7.26-7.21(\mathrm{~m}, 3 \mathrm{H}), 7.20-7.11(\mathrm{~m}, 4 \mathrm{H})$, 6.15-6.02 (m, 1H), 5.59-5.45 (m, 1H), $4.96(\mathrm{~s}, 1 \mathrm{H}), 3.64(\mathrm{~s}, 3 \mathrm{H})$, 3.17-3.06 (m, 1H), 2.64-2.55 (m, 1H), $2.36(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (100 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 207.4,192.7,169.8,138.2,135.7,135.5,134.4,134.0,130.6,129.1,128.8$, 128.5, 128.5, 127.2, 127.0, 126.9, 95.4 89.9, 62.8, 52.3, 51.3, 32.5, 21.0. HPLC: Chiralpak AD-H column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}, n$-Hexane $/ i-\mathrm{PrOH}=96 / 4$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 22.0 min and 25.0 min (major). HRMS Calculated for $\mathrm{C}_{28} \mathrm{H}_{25} \mathrm{O}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+} 441.1519$, found: 441.1516.
(-)-t-Butyl 4-oxo-2-phenyl-3-(4-phenylbuta-2,3-dien-1-yl)thiochromane-3-carboxylate (3pa): The reaction was conducted at $-20^{\circ} \mathrm{C}$ for $120 \mathrm{~h} .88 .7 \mathrm{mg}, 95 \%$ yield, pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.40$ (hexanes/ethyl acetate $20 / 1$ ), $32.3: 1 \mathrm{dr}, 99 \%$ ee (major diastereoisomer),
 $[\alpha]^{20}{ }_{\mathrm{D}}=-182.51\left(c \quad 1.03, \mathrm{CHCl}_{3}\right)$. The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.18(\mathrm{dd}, J=8.2,1.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.50-7.43$ $(\mathrm{m}, 2 \mathrm{H}), 7.40-7.31(\mathrm{~m}, 4 \mathrm{H}), 7.26-7.13(\mathrm{~m}, 7 \mathrm{H}), 6.17-6.01(\mathrm{~m}, 1 \mathrm{H})$, $5.56-5.41(\mathrm{~m}, 1 \mathrm{H}), 4.92(\mathrm{~s}, 1 \mathrm{H}), 3.19-3.03(\mathrm{~m}, 1 \mathrm{H}), 2.62-2.41(\mathrm{~m}$, $1 \mathrm{H}), 1.32(\mathrm{~s}, 9 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 207.4,192.4$, $168.1,141.7,135.5,134.2,132.8,131.2,130.3,129.6,128.8,128.5,128.4,126.9,126.9,126.8$, $125.2,95.2,90.1,83.2,62.2,51.3,32.0,27.7$. HPLC: Chiralpak AD-3 column, $254 \mathrm{~nm}, 30{ }^{\circ} \mathrm{C}$, $n$-Hexane $/ i-\mathrm{PrOH}=96 / 4$, flow $=0.8 \mathrm{~mL} / \mathrm{min}$, the retention time 11.2 min and 13.5 min (major). HRMS Calculated for $\mathrm{C}_{30} \mathrm{H}_{28} \mathrm{NaO}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{Na}]^{+} 491.1651$, found: 491.1656.
(+)-Methyl 2-(benzofuran-2-yl)-4-oxo-3-(-4-phenylbuta-2,3-dien-1-yl)thiochromane-3-carboxylate (3qa): The reaction was conducted at $-20^{\circ} \mathrm{C}$ for $72 \mathrm{~h} .79 .1 \mathrm{mg}, 85 \%$ yield, pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.32$ (hexanes/ethyl acetate $20 / 1$ ), $5.7: 1 \mathrm{dr}, 97 \%$ ee (major
 diastereoisomer), $[\alpha]^{20}{ }_{\mathrm{D}}=+33.29\left(c \quad 0.82, \mathrm{CHCl}_{3}\right)$. The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.21(\mathrm{dd}, J=8.0,1.1 \mathrm{~Hz}$, $1 \mathrm{H}), 7.53-7.47(\mathrm{~m}, 1 \mathrm{H}), 7.43-7.37(\mathrm{~m}, 2 \mathrm{H}), 7.28-7.16(\mathrm{~m}, 9 \mathrm{H}), 6.75$ $(\mathrm{s}, 1 \mathrm{H}), 6.14-6.01(\mathrm{~m}, 1 \mathrm{H}), 5.65-5.52(\mathrm{~m}, 1 \mathrm{H}), 5.14(\mathrm{~s}, 1 \mathrm{H}), 3.65(\mathrm{~s}$, $3 \mathrm{H})$, 3.28-3.16 (m, 1H), 2.97-2.85 (m, 1H). ${ }^{13} \mathrm{C}$ NMR ( 100 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 207.7,190.9,169.5,154.3,152.6,139.9,133.8,133.5,130.5,130.4,128.6,128.0,127.3$, 127.1, 126.9, 125.8, 124.7, 123.0, 121.3, 111.2, 106.1, 95.3, 89.2, 61.3, 52.7, 44.6, 32.9. HPLC: Chiralpak AD-H column, $254 \mathrm{~nm}, 30{ }^{\circ} \mathrm{C}, n$-Hexane $/ i-\mathrm{PrOH}=93 / 7$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, the
retention time 19.8 min and 22.3 min (major). HRMS Calculated for $\mathrm{C}_{29} \mathrm{H}_{23} \mathrm{O}_{4} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+} 467.1312$, found: 467.1320.

## (+)-3-Acetyl-2-phenyl-3-(4-phenylbuta-2,3-dien-1-yl)thiochroman-4-one (3ba):

The reaction was conducted at $30^{\circ} \mathrm{C}$ for 48 hours with commercially available ( $1 R, 1$ ' $R, 2 S, 2^{\prime} S$ )DuanPhos as the chiral ligand. $49.8 \mathrm{mg}, 61 \%$ yield, pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}$
 $=0.35$ (hexanes/ethyl acetate 20/1), 24.0:1 dr, $74 \%$ ee (major isomer), $[\alpha]^{20}{ }_{\mathrm{D}}=+0.69\left(c \quad 0.58, \mathrm{CHCl}_{3}\right)$. The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.18(\mathrm{dd}, J=8.0,1.2 \mathrm{~Hz}, 1 \mathrm{H}$ ), 7.46-7.41 $(\mathrm{m}, 1 \mathrm{H}), 7.30-7.23(\mathrm{~m}, 9 \mathrm{H}), 7.21-7.14(\mathrm{~m}, 3 \mathrm{H}), 6.18-6.03(\mathrm{~m}, 1 \mathrm{H})$, 5.48-5.37 (m, 1H), $4.86(\mathrm{~s}, 1 \mathrm{H}), 3.24-3.13(\mathrm{~m}, 1 \mathrm{H}), 2.80-2.70(\mathrm{~m}$, 1H), 2.11 ( $\mathrm{s}, 3 \mathrm{H}$ ). ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 207.4,205.2,194.4,140.8,137.1,133.9,133.8$, 130.9, 130.2, 128.8, 128.7, 128.6, 128.5, 127.4, 127.1, 126.8, 125.7, 95.5, 89.6, 67.1, 51.2, 33.7, 31.5. HPLC: Chiralcel OD-H column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}$, $n$-Hexane $/ i-\mathrm{PrOH}=95 / 5$, flow $=1.0 \mathrm{~mL} /$ min , retention time 9.4 min and 11.5 min (major). HRMS Calculated for $\mathrm{C}_{27} \mathrm{H}_{23} \mathrm{O}_{2} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+}$ 411.1413, found: 411.1415. Notably, the absolute and relative configurations of this allenylic alkylation product were not further assigned.

## 2-Phenyl-3-(4-phenylbuta-2,3-dien-1-yl)-3-(piperidine-1-carbonyl)thiochroman-4-one (3da):

The reaction was conducted at $-20^{\circ} \mathrm{C}$ for 168 h and the rac-3da was prepared with rac-BINAP at $-20^{\circ} \mathrm{C} .32 .3 \mathrm{mg}, 34 \%$ yield, pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.52$ (hexanes/ethyl
 acetate $5 / 1$ ), $24.0: 1 \mathrm{dr},>99 \%$ ee (major diastereoisomer), $[\alpha]^{20}{ }_{\mathrm{D}}=$ -49.90 (c 1.08, $\mathrm{CHCl}_{3}$ ). The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.09(\mathrm{dd}, J=7.9,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.51-7.43(\mathrm{~m}, 1 \mathrm{H})$, 7.37-7.33 (m, 1H), 7.33-7.28 (m, 3H), 7.27-7.21 (m, 7H), 7.19-7.14 $(\mathrm{m}, 1 \mathrm{H}), 6.22-6.02(\mathrm{~m}, 1 \mathrm{H}), 5.71-5.55(\mathrm{~m}, 1 \mathrm{H}), 4.87(\mathrm{~s}, 1 \mathrm{H}), 4.04-$ $3.14(\mathrm{~m}, 2 \mathrm{H}), 3.14-2.13(\mathrm{~m}, 4 \mathrm{H}), 1.50-1.37(\mathrm{~m}, 4 \mathrm{H}), 1.37-1.10(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 100 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 207.7,192.6,167.3,140.5,137.9,134.3,133.7,131.8,130.1,129.1,128.6,128.5,128.3$, $127.8,126.9,126.9,126.1,94.6,91.0,63.0,52.1,38.5,24.9,24.3$. HPLC: Chiralpak IB column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}, n$-Hexane $/ i-\mathrm{PrOH}=94 / 6$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 13.1 min and 20.6 min (major). HRMS Calculated for $\mathrm{C}_{31} \mathrm{H}_{30} \mathrm{NO}_{2} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+} 480.1992$, found: 480.2000.
(-)-Methyl (2R,3S)-3-((R)-4-(naphthalen-2-yl)buta-2,3-dien-1-yl)-6-nitro-4-oxo-2-phenylthio-chromane-3-carboxylate ( 3 mk ): The reaction was conducted at $-20^{\circ} \mathrm{C}$ for $168 \mathrm{~h} .91 .3 \mathrm{mg}, 88 \%$ yield, pale yellow solid, $\mathrm{mp} 197-198^{\circ} \mathrm{C}$, new compound, $\mathrm{R}_{\mathrm{f}}=0.12$ (hexanes/ethyl acetate 20/1),
 $32.3: 1 \mathrm{dr},>99 \%$ ee (major diastereoisomer), $[\alpha]^{20}{ }_{\mathrm{D}}=$ -223.76 (c 1.14, $\mathrm{CHCl}_{3}$ ). The major diaste- reoisomer: ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.92(\mathrm{~d}, J=2.5 \mathrm{~Hz}, 1 \mathrm{H}), 8.03$ $(\mathrm{dd}, J=8.7,2.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.75-7.65(\mathrm{~m}, 3 \mathrm{H}), 7.47(\mathrm{~s}, 1 \mathrm{H})$, $7.45-7.35$ (m, 7H), 7.31 (dd, $J=8.5,1.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.24-7.21$ $(\mathrm{m}, 1 \mathrm{H}), 6.33-6.18(\mathrm{~m}, 1 \mathrm{H}), 5.70-5.55(\mathrm{~m}, 1 \mathrm{H}), 5.11(\mathrm{~s}, 1 \mathrm{H}), 3.65(\mathrm{~s}, 3 \mathrm{H}), 3.28-3.11(\mathrm{~m}, 1 \mathrm{H})$, 2.66-2.50 (m, 1H). ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 208.1,190.5,168.9,149.6,145.5,134.2,133.5$, $132.6,131.1,130.8,129.5,129.2$, 128.8, 128.3, 128.1, 127.7, 127.7, 126.5, 126.4, 125.9, 125.7, $125.6,124.5,96.6,89.6,62.2,52.7,51.0,32.0$. HPLC: Chiralpak IB column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}$,
$n$-Hexane $/ i-\mathrm{PrOH}=80 / 20$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 12.7 min (minor) and 22.5 min (major). HRMS Calculated for $\mathrm{C}_{31} \mathrm{H}_{24} \mathrm{NO}_{5} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+} 522.1370$, found: 522.1377.

## Methyl 4-oxo-2-phenyl-3-(4-(o-tolyl)buta-2,3-dien-1-yl)thiochromane-3-carboxylate (3cb):

The reaction was conducted at $-20^{\circ} \mathrm{C}$ for $72 \mathrm{~h} .81 .7 \mathrm{mg}, 93 \%$ yield, pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.43$ (hexanes/ethyl acetate $20 / 1$ ), $32.3: 1 \mathrm{dr}, 99 \%$ ee (major diastereoisomer),
 $[\alpha]^{20}{ }_{\mathrm{D}}=-193.32$ (c 0.96, $\mathrm{CHCl}_{3}$ ). The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.17(\mathrm{dd}, J=8.2,1.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.48-7.21$ $(\mathrm{m}, 9 \mathrm{H}), 7.20-7.03(\mathrm{~m}, 3 \mathrm{H}), 6.47-6.18(\mathrm{~m}, 1 \mathrm{H}), 5.61-5.38(\mathrm{~m}, 1 \mathrm{H})$, $4.99(\mathrm{~s}, 1 \mathrm{H}), 3.64(\mathrm{~s}, 3 \mathrm{H}), 3.23-3.01(\mathrm{~m}, 1 \mathrm{H}), 2.68-2.53(\mathrm{~m}, 1 \mathrm{H})$, $2.24(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 208.0,192.4,169.7,141.6,135.6,135.0,133.3,132.2$, $130.8,130.5,130.4,129.2,128.9,128.5,127.5,127.3,127.0,126.1,125.6,92.8,88.9,62.7,52.4$, 51.2, 32.5, 19.8. HPLC: Chiralcel OD-H column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}$, $n$-Hexane $/ i-\mathrm{PrOH}=95 / 5$, flow $=$ $1.0 \mathrm{~mL} / \mathrm{min}$, retention time 10.1 min and 25.1 min (major). HRMS Calculated for $\mathrm{C}_{28} \mathrm{H}_{24} \mathrm{NaO}_{3} \mathrm{~S}$ $[\mathrm{M}+\mathrm{Na}]^{+} 463.1338$, found: 463.1342 .
(-)-Methyl -oxo-2-phenyl-3-(4-(m-tolyl)buta-2,3-dien-1-yl)thiochromane-3-carboxylate(3cc):
The reaction was conducted at $-20{ }^{\circ} \mathrm{C}$ for $72 \mathrm{~h} .86 .1 \mathrm{mg}, 98 \%$ yield, pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.43$ (hexanes/ethyl acetate 20/1), 49.0:1 dr, $99 \%$ ee (major diastereoisomer),
 $[\alpha]^{20}{ }_{\mathrm{D}}=-213.13\left(c \quad 0.70, \mathrm{CHCl}_{3}\right)$. The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.23-8.11(\mathrm{~m}, 1 \mathrm{H}), 7.44-7.31(\mathrm{~m}, 6 \mathrm{H})$, 7.26-7.22 (m, 2H), 7.16-7.10 (m, 1H), 7.01-6.95 (m, 3H), 6.16-5.97 (m, 1H), 5.59-5.42 (m, 1H), 4.99 (s, 1H), 3.65 (s, 3H), 3.19-3.07 (m, $1 \mathrm{H}), 2.65-2.55(\mathrm{~m}, 1 \mathrm{H}), 2.28(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ $207.4,192.4,169.7,141.5,138.1,135.6,133.8,133.2,130.9,130.5,129.1,128.9,128.5,128.5$, 127.9, 127.5, 127.3, 125.5, 124.0, 95.6, 89.7, 62.7, 52.3, 51.1, 32.5, 21.3. HPLC: Chiralcel OD-H column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}, n$-Hexane $/ i-\mathrm{PrOH}=95 / 5$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 9.7 min and 21.8 min (major). HRMS Calculated for $\mathrm{C}_{28} \mathrm{H}_{24} \mathrm{NaO}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{Na}]^{+} 463.1338$, found: 463.1341
(-)-Methyl 4-oxo-2-phenyl-3-(4-(p-tolyl)buta-2,3-dien-1-yl)thiochromane-3-carboxylate (3cd): The reaction was conducted at $-20^{\circ} \mathrm{C}$ for $72 \mathrm{~h} .84 .5 \mathrm{mg}, 96 \%$ yield, pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.43$ (hexanes/ethyl acetate $20 / 1$ ), $32.3: 1 \mathrm{dr}, 99 \%$ ee (major diastereoisomer),
 $[\alpha]^{20}{ }_{\mathrm{D}}=-193.85\left(c 0.57, \mathrm{CHCl}_{3}\right)$. The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.22-8.11(\mathrm{~m}, 1 \mathrm{H}), 7.43-7.31(\mathrm{~m}, 6 \mathrm{H})$, 7.26-7.22 (m, 2H), 7.12-7.01 (m, 4H), 6.19-5.94 (m, 1H), 5.59$5.40(\mathrm{~m}, 1 \mathrm{H}), 4.99(\mathrm{~s}, 1 \mathrm{H}), 3.65(\mathrm{~s}, 3 \mathrm{H}), 3.19-3.04(\mathrm{~m}, 1 \mathrm{H}), 2.66-$ $2.54(\mathrm{~m}, 1 \mathrm{H}), 2.30(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 207.2$, $192.5,169.7,141.5,136.8,135.6,133.2,130.9,130.9,130.5,129.3,129.1,128.9,128.5,127.3$, 126.7, 125.5, 95.4, 89.7, 62.7, 52.3, 51.1, 32.6, 21.2. HPLC: Chiralcel OD-H column, $254 \mathrm{~nm}, 30$ ${ }^{\circ} \mathrm{C}, n$-Hexane $/ i-\mathrm{PrOH}=95 / 5$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 9.6 min and 18.8 min (major). HRMS Calculated for $\mathrm{C}_{28} \mathrm{H}_{24} \mathrm{NaO}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{Na}]^{+} 463.1338$, found: 463.1342.
(-)-Methyl 3-(4-(3-fluorophenyl)buta-2,3-dien-1-yl)-4-oxo-2-phenylthiochromane-3-carboxylate (3ce): The reaction was conducted at $-20^{\circ} \mathrm{C}$ for 120 hours. $83.7 \mathrm{mg}, 94 \%$ yield, pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.38$ (hexanes/ethyl acetate 20/1), 32.3:1 dr, $99 \%$ ee (major
 diastereoisomer), $[\alpha]^{20}{ }_{\mathrm{D}}=-179.28\left(c 0.85, \mathrm{CHCl}_{3}\right)$. The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.20-8.13$ (m, $1 \mathrm{H}), 7.43-7.32(\mathrm{~m}, 6 \mathrm{H}), 7.27-7.17(\mathrm{~m}, 3 \mathrm{H}), 6.98-6.92(\mathrm{~m}, 1 \mathrm{H})$, 6.91-6.80 (m, 2H), 6.16-5.95 (m, 1H), 5.69-5.48 (m, 1H), $4.94(\mathrm{~s}$, $1 \mathrm{H}), 3.65(\mathrm{~s}, 3 \mathrm{H}), 3.20-3.02(\mathrm{~m}, 1 \mathrm{H}), 2.69-2.47(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 207.6$, 192.3, 169.6, $163.1\left(\mathrm{~d},{ }^{1} J_{\mathrm{F}-\mathrm{C}}=245.2 \mathrm{~Hz}\right), 141.5,136.5\left(\mathrm{~d},{ }^{3} J_{\mathrm{F}-\mathrm{C}}=7.7 \mathrm{~Hz}\right), 135.5,133.3,130.8$, $130.5,129.9\left(\mathrm{~d},{ }^{3} J_{\mathrm{F}-\mathrm{C}}=8.3 \mathrm{~Hz}\right), 129.2,128.9,128.5,127.2,125.6,122.6\left(\mathrm{~d},{ }^{4} J_{\mathrm{F}-\mathrm{C}}=2.7 \mathrm{~Hz}\right), 113.9$ $\left(\mathrm{d},{ }^{2} J_{\mathrm{F}-\mathrm{C}}=21.3 \mathrm{~Hz}\right), 113.4\left(\mathrm{~d},{ }^{2} J_{\mathrm{F}-\mathrm{C}}=22.4 \mathrm{~Hz}\right), 94.8\left(\mathrm{~d},{ }^{4} J_{\mathrm{F}-\mathrm{C}}=2.5 \mathrm{~Hz}\right), 90.4,62.6,52.4,51.3,32.4$. ${ }^{19} \mathrm{~F}$ NMR ( $376 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$-113.49. HPLC: Chiralcel OD-3 column, $254 \mathrm{~nm}, 30{ }^{\circ} \mathrm{C}$, $n$-Hexane $/ i-\mathrm{PrOH}=95 / 5$, flow $=0.8 \mathrm{~mL} / \mathrm{min}$, retention time 12.3 min and 35.0 min (major). HRMS Calculated for $\mathrm{C}_{27} \mathrm{H}_{21} \mathrm{FNaO}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{Na}]^{+} 467.1088$, found: 467.1084 .
(-)-Methyl 3-(4-(3-chlorophenyl)buta-2,3-dien-1-yl)-4-oxo-2-phenylthiochromane-3-carboxylate (3cf): The reaction was conducted at $-20^{\circ} \mathrm{C}$ for 120 hours. $83.1 \mathrm{mg}, 90 \%$ yield, pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.38$ (hexanes/ethyl acetate $20 / 1$ ), 32.3:1 dr, $99 \%$ ee (major diastereoisomer), $[\alpha]^{20}{ }_{\mathrm{D}}=-188.92\left(c\right.$ 0.84, $\left.\mathrm{CHCl}_{3}\right)$. The major
 diastereoisomer: ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.21-8.14$ (m, $1 \mathrm{H}), 7.44-7.32(\mathrm{~m}, 6 \mathrm{H}), 7.27-7.23(\mathrm{~m}, 2 \mathrm{H}), 7.20-7.10(\mathrm{~m}, 3 \mathrm{H})$, 7.08-7.01 (m, 1H), 6.16-5.92 (m, 1H), 5.67-5.51 (m, 1H), $4.93(\mathrm{~s}$, $1 \mathrm{H}), 3.65(\mathrm{~s}, 3 \mathrm{H}), 3.17-3.06(\mathrm{~m}, 1 \mathrm{H}), 2.65-2.55(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (100 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 207.6,192.3,169.6,141.5,136.1,135.5,134.5,133.3,130.8,130.5$, 129.7, 129.2, 129.0, 128.5, 127.2, 127.0, 126.7, 125.6, 125.0, 94.6, 90.4, 62.6, 52.4, 51.3, 32.4. HPLC: Chiralcel OD-3 column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}, n$-Hexane $/ i-\mathrm{PrOH}=95 / 5$, flow $=0.8 \mathrm{~mL} / \mathrm{min}$, retention time 12.7 min (minor) and 37.3 min (major). HRMS Calculated for $\mathrm{C}_{27} \mathrm{H}_{22} \mathrm{ClO}_{3} \mathrm{~S}$ $[\mathrm{M}+\mathrm{H}]^{+} 461.0973\left({ }^{35} \mathrm{Cl}\right)$ and $463.0953\left({ }^{37} \mathrm{Cl}\right)$, found: $461.0969\left({ }^{35} \mathrm{Cl}\right)$ and $463.0938\left({ }^{37} \mathrm{Cl}\right)$.
(-)-Methyl 3-(4-(3-bromophenyl)buta-2,3-dien-1-yl)-4-oxo-2-phenylthiochromane-3-carboxylate (3cg): The reaction was conducted at $-20^{\circ} \mathrm{C}$ for 120 hours. $94.4 \mathrm{mg}, 93 \%$ yield, pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.38$ (hexanes/ethyl acetate 20/1), 32.3:1 dr, $98 \%$ ee (major
 diastereoisomer), $[\alpha]^{20}{ }_{\mathrm{D}}=-173.55\left(c \quad 0.87, \mathrm{CHCl}_{3}\right)$. The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.18$ (dd, $J=7.8$, $1.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.43-7.23(\mathrm{~m}, 10 \mathrm{H}), 7.15-7.05(\mathrm{~m}, 2 \mathrm{H}), 6.15-5.93$ $(\mathrm{m}, 1 \mathrm{H}), 5.73-5.50(\mathrm{~m}, 1 \mathrm{H}), 4.93(\mathrm{~s}, 1 \mathrm{H}), 3.65(\mathrm{~s}, 3 \mathrm{H}), 3.23-3.01$ (m, 1H), 2.72-2.48 (m, 1H). ${ }^{13} \mathrm{C}$ NMR (100 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 207.6,192.3,169.6,141.5,136.3$, $135.5,133.3,130.8,130.5,130.0,129.9,129.6,129.2,129.0,128.6,127.3,125.6,125.4,122.8$, 94.5, $90.5,62.6,52.4,51.3,32.4$. HPLC: Chiralcel OD-3 column, $254 \mathrm{~nm}, 30{ }^{\circ} \mathrm{C}, n$-Hexane $/ i-\mathrm{Pr}-$ $\mathrm{OH}=95 / 5$, flow $=0.8 \mathrm{~mL} / \mathrm{min}$, retention time 13.1 min and 39.9 min (major). HRMS Calculated for $\mathrm{C}_{27} \mathrm{H}_{22} \mathrm{BrO}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+} 505.0468\left({ }^{79} \mathrm{Br}\right)$ and $507.0450\left({ }^{81} \mathrm{Br}\right)$, found: $505.0471\left({ }^{79} \mathrm{Br}\right)$ and $507.0454\left({ }^{81} \mathrm{Br}\right)$.
(-)-Methyl 3-(4-(3-methoxyphenyl)buta-2,3-dien-1-yl)-4-oxo-2-phenylthiochromane-3-carboxylate (3ch): The reaction was conducted at $-20^{\circ} \mathrm{C}$ for 72 hours. $84.6 \mathrm{mg}, 93 \%$ yield, pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.20$ (hexanes/ethyl acetate 20/1), 32.3:1 dr, $99 \%$ ee (major diastereoisomer), $[\alpha]^{20}{ }_{\mathrm{D}}=-192.34$ (c 1.02, $\mathrm{CHCl}_{3}$ ). The major
 diastereoisomer: ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 8.27-8.04 (m, $1 \mathrm{H}), 7.42-7.29(\mathrm{~m}, 6 \mathrm{H}), 7.25-7.21(\mathrm{~m}, 2 \mathrm{H}), 7.17-7.12(\mathrm{~m}, 1 \mathrm{H})$, 6.80-6.67 (m, 3H), 6.11-5.99 (m, 1H), 5.61-5.42 (m, 1H), 4.98 $(\mathrm{s}, 1 \mathrm{H}), 3.76(\mathrm{~s}, 3 \mathrm{H}), 3.64(\mathrm{~s}, 3 \mathrm{H}), 3.17-3.05(\mathrm{~m}, 1 \mathrm{H})$, $2.65-2.54(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (100 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 207.4,192.4,169.7,159.9,141.5,135.6,135.4$, $133.2,130.8,130.5,129.5,129.2,128.9,128.5,127.3,125.5,119.5,113.1,111.9,95.6,90.0,62.7$, 55.2, 52.3, 51.2, 32.4. HPLC: Chiralcel OD-3 column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}, n-\mathrm{Hexane} / i-\mathrm{PrOH}=94 / 6$, flow $=0.8 \mathrm{~mL} / \mathrm{min}$, retention time 14.7 min and 32.0 min (major). HRMS Calculated for $\mathrm{C}_{28} \mathrm{H}_{25} \mathrm{O}_{4} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+} 457.1468$, found: 457.1473.
(-)-Methyl 3-(4-(3,5-dimethylphenyl)buta-2,3-dien-1-yl)-4-oxo-2-phenylthiochromane-3-carboxylate (3ci): The reaction was conducted at $-20^{\circ} \mathrm{C}$ for $120 \mathrm{~h} .89 .1 \mathrm{mg}, 98 \%$ yield, pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.33$ (hexanes/ethyl acetate 20/1), 49.0:1 dr, $99 \%$ ee (major
 diastereoisomer), $[\alpha]^{20}{ }_{\mathrm{D}}=-195.93$ (c 0.74, $\mathrm{CHCl}_{3}$ ). The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.25-8.08(\mathrm{~m}$, $1 \mathrm{H}), 7.43-7.29(\mathrm{~m}, 6 \mathrm{H}), 7.26-7.22(\mathrm{~m}, 2 \mathrm{H}), 6.87-6.72(\mathrm{~m}, 3 \mathrm{H})$, 6.13-5.92 (m, 1H), 5.57-5.39 (m, 1H), 5.00 ( $\mathrm{s}, 1 \mathrm{H}), 3.65(\mathrm{~s}, 3 \mathrm{H})$, 3.25-3.06 (m, 1H), 2.66-2.53 (m, 1H), $2.24(\mathrm{~s}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 207.5,192.4,169.8,141.5,138.0,135.6,133.7,133.2,130.9,130.5,129.1$, $128.8,128.5,127.3,125.5,124.7,95.7,89.5,62.7,52.3,51.0,32.5,21.2$. HPLC: Chiralcel OD-H column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}, n$-Hexane $/ i-\mathrm{PrOH}=96 / 4$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 9.3 min and 20.1 min (major). HRMS Calculated for $\mathrm{C}_{29} \mathrm{H}_{27} \mathrm{O}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+} 455.1675$, found: 455.1682.
(-)-Methyl 3-(4-([1,1'-biphenyl]-4-yl)buta-2,3-dien-1-yl)-4-oxo-2-phenylthiochromane-3-carboxylate (3cj): The reaction was conducted at $-20^{\circ} \mathrm{C}$ for $120 \mathrm{~h} .96 .2 \mathrm{mg}, 96 \%$ yield, pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.31$ (hexanes/ethyl acetate 20/1), 49.0:1 dr, $99 \%$ ee (major diastereoisomer), $[\alpha]^{20}{ }_{\mathrm{D}}=-186.99\left(c\right.$ 1.10, $\left.\mathrm{CHCl}_{3}\right)$. The major
 diastereoisomer: ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.22-8.12$ (m, $1 \mathrm{H}), 7.58-7.53(\mathrm{~m}, 2 \mathrm{H}), 7.50-7.45(\mathrm{~m}, 2 \mathrm{H}), 7.43-7.30(\mathrm{~m}, 9 \mathrm{H})$, 7.26-7.22 (m, 4H), 6.22-6.04 (m, 1H), 5.66-5.48 (m, 1H), $5.00(\mathrm{~s}$, $1 \mathrm{H}), 3.65(\mathrm{~s}, 3 \mathrm{H}), 3.21-3.03(\mathrm{~m}, 1 \mathrm{H}), 2.69-2.56(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (100 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 207.6,192.4,169.7,141.5,140.8,139.9,135.6,133.3,133.0,130.8$, $130.5,129.2,128.9,128.8,128.5,127.3,126.9,125.6,95.2,90.0,62.7,52.4,51.2,32.5$. HPLC: Chiralpak ID + IC column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}, n-\mathrm{Hexane} / i-\mathrm{PrOH}=94 / 6$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 43.1 min (major) and 47.4 min (minor). HRMS Calculated for $\mathrm{C}_{33} \mathrm{H}_{27} \mathrm{O}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+} 503.1675$, found: 503.1673.
(-)-Methyl 3-(4-(naphthalen-2-yl)buta-2,3-dien-1-yl)-4-oxo-2-phenylthiochromane-3-carboxylate (3ck): The reaction was conducted at $-20^{\circ} \mathrm{C}$ for $120 \mathrm{~h} .90 .4 \mathrm{mg}, 95 \%$ yield, pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.30$ (hexanes/ethyl acetate 20/1), 24.0:1 dr, $99 \%$ ee (major diastereoisomer), $[\alpha]^{20}{ }_{\mathrm{D}}=-160.81$ (c 1.10, $\mathrm{CHCl}_{3}$ ). The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.18$ (dd, $J=$ $7.9,1.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.76-7.67(\mathrm{~m}, 3 \mathrm{H}), 7.55-7.52(\mathrm{~m}, 1 \mathrm{H}), 7.45-$ $7.31(\mathrm{~m}, 9 \mathrm{H}), 7.24-7.19(\mathrm{~m}, 2 \mathrm{H}), 6.35-6.16(\mathrm{~m}, 1 \mathrm{H}), 5.69-5.50$ $(\mathrm{m}, 1 \mathrm{H}), 5.01(\mathrm{~s}, 1 \mathrm{H}), 3.64(\mathrm{~s}, 3 \mathrm{H}), 3.23-3.07(\mathrm{~m}, 1 \mathrm{H}), 2.70-$ $2.59(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 208.0,192.4,169.7,141.5,135.6,133.6,133.2$, $132.7,131.5,130.8,130.5,129.2,128.9,128.5,128.2,127.7,127.7,127.3,126.2,125.7,125.6$, 124.8, 95.9, 90.2, 62.8, 52.4, 51.2, 32.6. HPLC: Chiralpak IC column, $254 \mathrm{~nm}, 3{ }^{\circ} \mathrm{C}$, $n$-Hexane/ $i-\mathrm{PrOH}=94 / 6$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 20.5 min (minor) and 22.8 min (major). HRMS Calculated for $\mathrm{C}_{31} \mathrm{H}_{28} \mathrm{NO}_{3} \mathrm{~S}\left[\mathrm{M}+\mathrm{NH}_{4}\right]^{+}$494.1784, found: 494.1777.
(-)-Methyl 4-oxo-2-phenyl-3-(4-(thiophen-3-yl)buta-2,3-dien-1-yl)thiochromane-3-carboxylate (3cl): The reaction was conducted at $-20^{\circ} \mathrm{C}$ for $120 \mathrm{~h} .78 .2 \mathrm{mg}, 90 \%$ yield, pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.32$ (hexanes/ethyl acetate $20 / 1$ ), $32.3: 1 \mathrm{dr}, 98 \%$ ee (major diastereoisomer $),[\alpha]^{20}{ }_{\mathrm{D}}=-187.60\left(c \quad 0.92, \mathrm{CHCl}_{3}\right)$. The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.22-8.13(\mathrm{~m}, 1 \mathrm{H}), 7.42-7.32$ $(\mathrm{m}, 6 \mathrm{H}), 7.25-7.18(\mathrm{~m}, 3 \mathrm{H}), 6.99-6.91(\mathrm{~m}, 2 \mathrm{H}), 6.31-5.97(\mathrm{~m}, 1 \mathrm{H})$, $5.52-5.41(\mathrm{~m}, 1 \mathrm{H}), 4.97(\mathrm{~s}, 1 \mathrm{H}), 3.64(\mathrm{~s}, 3 \mathrm{H}), 3.15-3.05(\mathrm{~m}, 1 \mathrm{H})$, 2.63-2.54 (m, 1H). ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 207.6, 192.4, $169.7,141.5,135.6,135.1,133.2,130.8,130.5,129.2,128.9,128.5,127.3,126.3,125.9,125.5$, 121.0, $90.1,89.1,62.7,52.3,51.1,32.6$. HPLC: Chiralcel OD-3 column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}, n$-Hexane $/ i-\mathrm{PrOH}=93 / 7$, flow $=0.8 \mathrm{~mL} / \mathrm{min}$, retention time 11.9 min (minor) and 25.4 min (major). HRMS Calculated for $\mathrm{C}_{25} \mathrm{H}_{24} \mathrm{NO}_{3} \mathrm{~S}_{2}\left[\mathrm{M}+\mathrm{NH}_{4}\right]^{+} 450.1192$, found: 450.1182.

## (-)-Methyl 4-oxo-3-(penta-2,3-dien-1-yl)-2-phenylthiochromane-3-carboxylate (3cm):

The reaction was conducted at $-20^{\circ} \mathrm{C}$ for $120 \mathrm{~h} .39 .3 \mathrm{mg}, 54 \%$ yield, pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.39$ (hexanes/ethyl acetate $20 / 1$ ), $7.3: 1 \mathrm{dr}, 97 \%$ ee (major diastereoisomer), $[\alpha]^{20}{ }_{\mathrm{D}}=-173.75\left(c 0.85, \mathrm{CHCl}_{3}\right)$. The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR
 ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.29-8.02(\mathrm{~m}, 1 \mathrm{H}), 7.44-7.31(\mathrm{~m}, 6 \mathrm{H}), 7.28-7.22$ $(\mathrm{m}, 2 \mathrm{H}), 5.08-4.92(\mathrm{~m}, 3 \mathrm{H}), 3.66(\mathrm{~s}, 3 \mathrm{H}), 3.06-2.95(\mathrm{~m}, 1 \mathrm{H}), 2.52-2.40$ $(\mathrm{m}, 1 \mathrm{H}), 1.55-1.48(\mathrm{~m}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 207.0$, 192.6, 169.8, 141.4, 135.7, 133.1, 131.0, 130.4, 129.1, 128.8, 128.4, 127.3, 125.5, 86.8, 85.2, 63.0, 52.3, 50.7, 32.6, 14.1. HPLC: Chiralpak AD-3 column, $254 \mathrm{~nm}, 30$ ${ }^{\circ} \mathrm{C}, n$-Hexane $/ i-\mathrm{PrOH}=97 / 3$, flow $=0.8 \mathrm{~mL} / \mathrm{min}$, retention time 18.8 min and 19.8 min (major). HRMS Calculated for $\mathrm{C}_{22} \mathrm{H}_{21} \mathrm{O}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+} 365.1206$, found: 365.1208.
(-)-Methyl 4-oxo-2-phenyl-3-(4-phenylpenta-2,3-dien-1-yl)thiochromane-3-carboxylate (3cn): The reaction was conducted at $30{ }^{\circ} \mathrm{C}$ for $120 \mathrm{~h} .63 .7 \mathrm{mg}, 72 \%$ yield, pale yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.41$ (hexanes/ethyl acetate $20 / 1$ ), $6.7: 1 \mathrm{dr}, 90 \%$ ee (major diastereoisomer),
$[\alpha]^{20}{ }_{\mathrm{D}}=-109.42\left(c 0.88, \mathrm{CHCl}_{3}\right)$. The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.17$ (dd, $J=7.9,1.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.41-7.37(\mathrm{~m}, 1 \mathrm{H}), 7.36-7.29(\mathrm{~m}, 5 \mathrm{H}), 7.28-7.12(\mathrm{~m}, 7 \mathrm{H}), 5.45-5.32(\mathrm{~m}$, $1 \mathrm{H}), 5.01(\mathrm{~s}, 1 \mathrm{H}), 3.62(\mathrm{~s}, 3 \mathrm{H}), 3.22-3.10(\mathrm{~m}, 1 \mathrm{H}), 2.65-2.50(\mathrm{~m}$,
 $1 \mathrm{H}), 1.99(\mathrm{~d}, J=2.9 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 206.8$, $192.3,169.8,141.4,136.7,135.9,133.2,130.7,130.4,128.9,128.8$, $128.5,128.3,127.3,126.9,125.8,125.4,101.9,87.7,62.7,52.3$, 50.4, 32.7, 16.9. HPLC: Chiralpak AD-H column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}$, $n$-Hexane $/ i-\mathrm{Pr}-\mathrm{OH}=96 / 4$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 14.0 min and 17.1 min (major). HRMS Calculated for $\mathrm{C}_{28} \mathrm{H}_{24} \mathrm{NaO}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{Na}]^{+} 463.1338$, found: 463.1346.

## The Chemo- or Regioselective Isomers with the Different EWG

2-Benzylidene-1-(2-((1-phenylbuta-1,3-dien-2-yl)thio)phenyl)-3-(piperidin-1-yl)propane-1,3dione (4'da): $46.1 \mathrm{mg}, 48 \%$ yield, yellow viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.18$ (hexanes/ethyl acetate $5 / 1$ ), 16.7/1 ( $Z / E$ or $E / Z$ ). The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3} \delta 7.56-$
 $7.42(\mathrm{~m}, 4 \mathrm{H}), 7.41-7.26(\mathrm{~m}, 10 \mathrm{H}), 7.09(\mathrm{~s}, 1 \mathrm{H}), 7.00(\mathrm{~s}, 1 \mathrm{H}), 6.83(\mathrm{dd}, J=$ $16.8,10.5 \mathrm{~Hz}, 1 \mathrm{H}), 5.74(\mathrm{~d}, J=16.8 \mathrm{~Hz}, 1 \mathrm{H}), 5.28(\mathrm{~d}, J=10.6 \mathrm{~Hz}, 1 \mathrm{H})$, 3.89-3.62 (m, 2H), 3.57-3.26 (m, 2H), 1.77-1.45 (m, 5H), 1.20-0.96 (m, 1H).
${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 194.7,165.5,143.8,139.2,137.2,136.1$, $134.4,133.4,133.2,131.7,131.2,130.8,130.6,130.0,129.4,129.0,128.9,128.4,127.9,126.3$, 120.1, 47.8, 42.4, 26.1, 25.3, 24.6. HRMS Calculated for $\mathrm{C}_{31} \mathrm{H}_{30} \mathrm{NO}_{2} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+} 480.1992$, found: 480.2001. (The Z/E configuration of carbon-carbon double bond is not further assigned)

## (-)-2-Nitro-3-phenyl-1-(2-((4-phenylbuta-2,3-dien-1-yl)thio)phenyl)prop-2-en-1-one (4aa):

The reaction was conducted at $30^{\circ} \mathrm{C}$ for 24 h with $\mathbf{L} 1.59 .3 \mathrm{mg}, 72 \%$ yield, pale yellow viscous
 liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.26$ (hexanes/ethyl acetate 20/1), $84 \%$ ee, single isomer, $[\alpha]^{20}{ }_{\mathrm{D}}=-178.56\left(c 0.63, \mathrm{CHCl}_{3}\right) .{ }^{1} \mathrm{H} \mathrm{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 8.67-8.48 (m, 1H), 7.61-7.50 (m, 3H), 7.48-7.18 (m, 10H), 7.18-7.12 (m, 1H), 6.15-6.01 (m, 1H), 5.90-5.75 (m, 1H), 3.47-3.32 (m, 2H). ${ }^{13} \mathrm{C}$ NMR ( 100 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 205.8,179.7,149.9,137.5,136.3,134.6,132.8,131.3,130.5,129.5$, 129.2, 128.7, 128.6, 128.5, 127.4, 126.8, 126.7, 125.6, 95.6, 93.5, 28.6. HPLC: Chiralpak IA column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}$, $n$-Hexane $/ i-\mathrm{PrOH}=94 / 6$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 15.2 min and 16.2 min (major). HRMS Calculated for $\mathrm{C}_{25} \mathrm{H}_{19} \mathrm{KNO}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{K}]^{+} 452.0717$, found: 452.0731. (The absolute configuration of allene moiety is not further assigned)

## 4. Scale-up Synthesis



The metal precursor $\operatorname{Pd}(\mathrm{dba})_{2}(0.26 \mathrm{mmol}, 0.150 \mathrm{~g})$, the chiral ligand $(R)$-DTB-BIPHEP (L4) $(0.286 \mathrm{mmol}, 0.295 \mathrm{~g})$ and tetrahydrofuran $(23 \mathrm{~mL})$ were placed in a dried Schlenk tube under nitrogen atmosphere. The mixture was stirred at $30^{\circ} \mathrm{C}$ for 30 min . Then, the mixture was cooled to $-20^{\circ} \mathrm{C}$. Then, the substrate thiochromanone $1 \mathrm{c}(2.6 \mathrm{mmol}, 0.776 \mathrm{~g}), 5 \AA \mathrm{MS}(0.650 \mathrm{~g})$ and 1,8 -dia-zabicyclo[5,4,0]undec-7-ene (DBU, $3.12 \mathrm{mmol}, 0.47 \mathrm{~mL}$ ) were added, and the reaction was stirred at $-20^{\circ} \mathrm{C}$ for 10 minutes. Sequentially, allenylic carbonate $\mathbf{2 a}(3.9 \mathrm{mmol}, 0.851 \mathrm{~g})$ and tetrahydrofuran ( 3.0 mL ) were added slowly. The mixture was stirred at $-20^{\circ} \mathrm{C}$ for 168 hours. After the completion of the reaction, the volatiles were directly removed under the reduced pressure. The crude residue was quickly purified by column chromatography on silica gel (hexanes/ethyl acetate /dichloromethane 100/1/2-100/3/6) to give the chiral allenylic alkylation product 3ca $0.987 \mathrm{~g}, 89 \%$ isolated yield, 24.0:1 dr and $99 \%$ ee for the major diastereoisomer.

The racemate was prepared by running reaction with an achiral 1,3-bis(diphenylphosphino)propane ligand at $30{ }^{\circ} \mathrm{C}$. Notably, the product 3ca was a little sensitive to water or alcohol, which would lead to slight decrease of dr value.

## 5. Product Elaborations

### 5.1. The Oxidation of Sulfide



At $-78^{\circ} \mathrm{C}$, to a solution of (-)-3ca ( $85.3 \mathrm{mg}, 0.2 \mathrm{mmol}, 99 \% \mathrm{ee}$ ) in dichloromethane ( 3.0 mL ) was added 3-chloroperoxybenzoic acid ( $m$-CPBA) ( $60.9 \mathrm{mg}, 0.3 \mathrm{mmol}, 85 \%$ ) in dichloromethane $(2.0 \mathrm{~mL})$. The mixture was stirred at $-78^{\circ} \mathrm{C}$ for 48 hours. Then, to the reaction mixture was added a solution of $m$-CPBA ( $60.9 \mathrm{mg}, 0.3 \mathrm{mmol}, 85 \%$ ) in dichloromethane ( 10 mL ). The mixture was stirred at $-78^{\circ} \mathrm{C}$ for another 48 hours. After that, it was quenched with aqueous sodium bicarbonate and warmed to room temperature. The aqueous layer was extracted with dichloromethane. The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under the reduced pressure. The residue was purified by flash chromatography on silica gel using hexanes/ethyl acetate (5/1-3/1) as eluent to give the oxidative product sulfoxide 5

Methyl 4-oxo-2-phenyl-3-(4-phenylbuta-2,3-dien-1-yl)thiochromane-3-carboxylate 1-oxide (5): $71.7 \mathrm{mg}, 81 \%$ yield, colorless viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.23$ (hexanes/ethyl acetate $3 / 1), 19.0: 1 \mathrm{dr}, 99 \%$ ee (major diastereoisomer), $[\alpha]^{20}{ }_{\mathrm{D}}=-357.57\left(c 1.00, \mathrm{CHCl}_{3}\right)$. The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.10(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 8.03(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H})$, $7.81(\mathrm{t}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.62(\mathrm{t}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.45-7.34(\mathrm{~m}, 5 \mathrm{H}), 7.25-7.06(\mathrm{~m}, 5 \mathrm{H}), 6.17-6.01$ $(\mathrm{m}, 1 \mathrm{H}), 5.38-5.26(\mathrm{~m}, 1 \mathrm{H}), 4.82(\mathrm{~s}, 1 \mathrm{H}), 3.76(\mathrm{~s}, 3 \mathrm{H}), 3.44-3.29(\mathrm{~m}, 1 \mathrm{H}), 2.51-2.37(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 207.5,190.8,169.0,147.6,135.0,133.3,131.2,129.9,129.6,129.6$, 129.4, 129.1, 128.6, 127.3, 126.9, 96.1, 88.4, 70.5, 63.6, 53.1, 32.5. HPLC: Chiralpak AD-3 column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}$, $n$-Hexane $/ i-\mathrm{PrOH}=70 / 30$, flow $=0.7 \mathrm{~mL} / \mathrm{min}$, retention time 27.6 min (major) and 32.7 min. HRMS Calculated for $\mathrm{C}_{27} \mathrm{H}_{22} \mathrm{NaO}_{4} \mathrm{~S}[\mathrm{M}+\mathrm{Na}]^{+} 465.1131$, found: 465.1139.

At room temperature, to a solution of (-)-3ca ( $85.3 \mathrm{mg}, 0.2 \mathrm{mmol}, 99 \% \mathrm{ee}$ ) in dichloromethane $(3.0 \mathrm{~mL})$ was added $m$ - $\mathrm{CPBA}(121.8 \mathrm{mg}, 0.6 \mathrm{mmol}, 85 \%)$ in dichloromethane $(2.0 \mathrm{~mL})$. The mixture was stirred for 24 hours. Then, the reaction mixture was quenched with saturated sodium bicarbonate aqueous solution, and the aqueous layer was extracted three times with dichloromethane. The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under the reduced pressure. The residue was purified by flash chromatography on silica gel using hexanes/ethyl acetate $(5 / 1)$ as eluent to give the oxidative product sulfone 6 .
(-)-Methyl 4-oxo-2-phenyl-3-(4-phenylbuta-2,3-dien-1-yl)thiochromane-3-carboxylate 1,1-dioxide (6): $60.9 \mathrm{mg}, 66 \%$ yield, colorless viscous liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.51$ (hexanes/ ethyl acetate $3 / 1$ ), 11.5:1 dr, $99 \%$ ee (major diastereoisomer), $[\alpha]^{20}{ }_{\mathrm{D}}=-135.23\left(c 1.05, \mathrm{CHCl}_{3}\right)$. The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.33-8.20(\mathrm{~m}, 1 \mathrm{H}), 8.03-7.96(\mathrm{~m}, 1 \mathrm{H})$, 7.84-7.72 (m, 2H), 7.64-7.53 (m, 2H), 7.49-7.38 (m, 3H), 7.25-7.10 (m, 3H), 7.12-7.05 (m, 2H), 6.08-5.93 (m, 1H), 5.49-5.38 (m, 1H), 5.11 ( $\mathrm{s}, 1 \mathrm{H}), 3.69(\mathrm{~s}, 3 \mathrm{H}), 3.31-3.17(\mathrm{~m}, 1 \mathrm{H}), 2.64-2.50(\mathrm{~m}$, 1H). ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 207.4,189.6,169.0,141.6,134.7,133.4,133.2,131.8,130.7$, $130.2,129.4,128.7,128.7,127.4,126.8,125.7,123.9,96.5,88.8,68.3,63.1,53.3,33.9$. HPLC: Chiralpak IC column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}, n$-Hexane $/ i-\mathrm{PrOH}=65 / 35$, flow $=0.8 \mathrm{~mL} / \mathrm{min}$, retention time 22.8 min and 40.9 min (major). HRMS Calculated for $\mathrm{C}_{27} \mathrm{H}_{22} \mathrm{NaO}_{5} \mathrm{~S}[\mathrm{M}+\mathrm{Na}]^{+}$481.1080, found: 481.1078 .

### 5.2. The Hydrogenation of Allenyl Functional Group



To a solution of the chiral allenylic alkylation product (-)-3ca ( $42.7 \mathrm{mg}, 0.1 \mathrm{mmol}, 99 \%$ ee) in ethyl acetate $(1.0 \mathrm{~mL})$ was added $10 \% \mathrm{Pd} / \mathrm{C}(5.3 \mathrm{mg}, 0.005 \mathrm{mmol})$. The resulting mixture was degassed and stirred under hydrogen gas balloon pressure for about 13 hours at $25^{\circ} \mathrm{C}$. After the completion of hydrogenation, the volatiles were removed under the reduced pressure. The crude residue was purified by flash column chromatography on silica gel using hexanes/ethyl acetate $(30 / 1-20 / 1)$ as eluent to give the desirable allene hydrogenation product $(2 R, 3 S)-(+)-7$.
(2R,3S)-(+)-Methyl 4-oxo-2-phenyl-3-(4-phenylbutyl)thiochromane-3-carboxylate (7):
$40.8 \mathrm{mg}, 95 \%$ yield, colorless liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.28$ (hexanes/ethyl acetate 20/1), $97 \%$ ee, $[\alpha]^{20}{ }_{\mathrm{D}}=+14.31\left(c 1.02, \mathrm{CHCl}_{3}\right) .{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.16(\mathrm{dd}, J=8.2,1.3 \mathrm{~Hz}, 1 \mathrm{H})$, 7.43-7.37 (m, 1H), 7.33-7.22 (m, 9H), 7.18-7.09 (m, 3H), 4.68 (s, 1H), 3.61 ( $\mathrm{s}, 3 \mathrm{H}), 2.62-2.44(\mathrm{~m}$, $2 \mathrm{H}), 2.17-2.05(\mathrm{~m}, 1 \mathrm{H}), 1.93-1.80(\mathrm{~m}, 1 \mathrm{H}), 1.63-1.48(\mathrm{~m}, 3 \mathrm{H}), 1.27-1.17(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 100 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 192.7,170.4,142.4,141.3,136.1,133.1,130.9,130.4,129.0,128.7,128.5,128.4$, $128.3,127.2,125.7,125.5,62.6,52.2,51.9,35.5,32.8,31.8,24.2$. HPLC: Chiralpak AD-H column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}$, $n$-Hexane $/ i-\mathrm{PrOH}=95 / 5$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 11.7 min and 14.4 min (major). HRMS Calculated for $\mathrm{C}_{27} \mathrm{H}_{26} \mathrm{NaO}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{Na}]^{+} 453.1495$, found: 453.1503.

### 5.3. The Reduction of Carbonyl Functional Group



To a solution of lithium aluminium tetrahydride ( $15.2 \mathrm{mg}, 0.4 \mathrm{mmol}$ ) in diethyl ether $(7.0 \mathrm{~mL})$ at $-78^{\circ} \mathrm{C}$, the chiral compound (-)-3ca ( $85.3 \mathrm{mg}, 0.2 \mathrm{mmol}, 99 \%$ ee) and diethyl ether ( 1.0 mL ) were added. The mixture was stirred at $-78^{\circ} \mathrm{C}$ for 5 hours. The reaction was quenched with 0.5 M potassium sodium tartrate aqueous solution $(1.0 \mathrm{~mL})$ and warmed to room temperature. After filtration through the celite, the combined organic layer was dried over sodium sulfate, filtered and concentrated under the reduced pressure. The residue was purified by column chromatography on silica gel using hexanes/ethyl acetate (20/1-10/1) as eluent to afford the desirable ketone carbonyl reductive product (-)-8.

The relative configuration of the hydroxyl group of the reductive product $\mathbf{8}$ was assigned as $S$ by NOE.
(-)-Methyl 4-hydroxy-2-phenyl-3-(4-phenylbuta-2,3-dien-1-yl)thiochromane-3-carboxylate 8: $58.8 \mathrm{mg}, 69 \%$ yield, colorless liquid, new compound, $\mathrm{R}_{\mathrm{f}}=0.48$ (hexanes/ethyl acetate $5 / 1$ ), 13.3:1 $\mathrm{dr}, 99 \%$ ee (major diastereoisomer), $[\alpha]^{20}{ }_{\mathrm{D}}=-33.73\left(c 0.83, \mathrm{CHCl}_{3}\right)$. The major diastereoisomer: ${ }^{1} \mathrm{H}$ NMR $\left(700 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.52(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.49-7.42(\mathrm{~m}, 2 \mathrm{H}), 7.29-7.17(\mathrm{~m}, 11 \mathrm{H})$, 6.15-6.08 (m, 1H), 5.56-5.53 (m, 1H), $5.17(\mathrm{~d}, J=6.3 \mathrm{~Hz}, 1 \mathrm{H}), 4.58(\mathrm{~s}, 1 \mathrm{H}), 3.55(\mathrm{~s}, 3 \mathrm{H}), 3.43(\mathrm{~d}$, $J=6.4 \mathrm{~Hz}, 1 \mathrm{H}), 2.87-2.82(\mathrm{~m}, 1 \mathrm{H}), 2.52-2.48(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $175 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 207.0$, 173.6, 138.6, 133.9, 133.9, 132.7, 130.4, 130.2, 128.6, 128.3, 127.9, 127.7, 127.1, 126.9, 125.8, 125.2, 94.8, 89.4, 72.3, 55.4, 52.0, 50.1, 36.4. HPLC: Chiralpak IA + AS-H column, $254 \mathrm{~nm}, 30$ ${ }^{\circ} \mathrm{C}, n$-Hexane $/ i-\mathrm{PrOH}=95 / 5$, flow $=0.8 \mathrm{~mL} / \mathrm{min}$, retention time 62.0 min and 72.2 min (major). HRMS Calculated for $\mathrm{C}_{27} \mathrm{H}_{24} \mathrm{NaO}_{3} \mathrm{~S}[\mathrm{M}+\mathrm{Na}]^{+} 451.1338$, found: 451.1335.

## The NOE Result of Carbonyl Reduction (-)-8



Figure S1. NOE spectrum of (-)-8

## 6. Determination of Absolute Configuration

To determine the absolute configuration of (-)-methyl 3-(4-(naphthalen-2-yl)buta-2,3 -dien-1-yl) -6-nitro-4-oxo-2-phenylthiochromane-3-carboxylate ( $\mathbf{3 m k}, 32.3: 1 \mathrm{dr},>99 \%$ ee): (-)-3mk was completely dissolved in dichloromethane ( 2.0 mL ), and $n$-hexane $(2.0 \mathrm{~mL})$ was added slowly at room temperature. The solvent diffused slowly, and the single crystal was obtained after about 36 hours. The structure in Figure $\mathbf{S} 2$ showed the absolute configuration is $\left(2 R, 3 S, R_{\mathrm{a}}\right)$. The CCDC number is 2214958. These details can be obtained free of charge via www.ccdc.com.ac.uk/ data_request/cif from the Cambridge Crystallographic Data Centre.


Figure S2. X-Ray Structure of $(-)-\left(2 R, 3 S, R_{\mathrm{a}}\right)-\mathbf{3 m k}$

| Identification code | mo_d8v22443_0m |
| :---: | :---: |
| Empirical formula | $\mathrm{C}_{31} \mathrm{H}_{23} \mathrm{NO}_{5} \mathrm{~S}$ |
| Formula weight | 521.56 |
| Temperature | 213(2) K |
| Wavelength | 0.71073 A |
| Crystal system | Orthorhombic |
| Space group | P 212121 |
| Unit cell dimensions | $\mathrm{a}=6.8379(3) \AA \quad \alpha=90^{\circ}$ |
|  | $\mathrm{b}=16.3952(5) \AA \quad \beta=90^{\circ}$ |
|  | $\mathrm{c}=22.7541(8) \AA \quad \gamma=90^{\circ}$ |
| Volume | 2550.93(16) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.358 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.170 \mathrm{~mm}^{-1}$ |
| F(000) | 1088 |
| Crystal size | $0.200 \times 0.150 \times 0.120 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 2.641 to $25.997^{\circ}$. |
| Index ranges | $-8<=\mathrm{h}<=8,-20<=\mathrm{k}<=18,-28<=\mathrm{l}<=28$ |
| Reflections collected | 22409 |
| Independent reflections | $5005[\mathrm{R}(\mathrm{int})=0.0593]$ |
| Completeness to theta $=25.242^{\circ}$ | 99.4\% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7456 and 0.5174 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 5005 / 0 / 344 |
| Goodness-of-fit on F2 | 1.025 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0366, \mathrm{wR} 2=0.0887$ |
| R indices (all data) | $\mathrm{R} 1=0.0415, \mathrm{wR} 2=0.0925$ |
| Absolute structure parameter | 0.02(4) |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.187 and -0.168 e. $\AA^{-3}$ |

## 7. References

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## 8. Copy of NMR and HPLC Spectra
















































19F NMR LL-9-12A in CDCI3



































































































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$\begin{array}{lll}\text { Totals : } & 6554.37207 \quad 242.19690\end{array}$
$=====================================$

| Acq. Operator Acq. Instrument Injection Date Acq. Method Last chanced Analysis Method Last changed Sample Info | Instrument 1 <br> 12/28/2022 3:40:27 AM <br> Location : - <br> C: \CHEM32\1\METHODS\DEF_LC.M <br> 12/28/2022 3:38:28 AM <br> (modified after loading) <br> C: \CHEM32\1\METHOD S\DEF_LC.M <br> 12/28/2022 7:11:09 AM <br> IB, Hexane/i-ProH $=94 / 6,1.0 \mathrm{~mL} / \mathrm{min}, 30 \circ \mathrm{C}, 254 \mathrm{~nm}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |
| ${ }_{6} \times 1{ }_{10}{ }_{10}$ |  |  |  |  |


sorted By
lution: $\quad \vdots \quad \begin{aligned} & 1.0000 \\ & 1.0000\end{aligned}$
Si gmal 1: vid 1 A , wavelength $=254$ nii


-

$=================$
$* \star=\pi$

Instrument 1 12/28/2022 7:11:14 AM
page 1 of 1











ilution:
Si gmal 1: vid 1 A , wavelength=254 nim


Totals: $\quad 1.03000 e 4 \quad 164.48252$
$===================$
$\pi * \pi$
$\pi$ End of Report $\pi \pi$





$\begin{array}{lllll}\substack{\text { Sorted By } \\ \text { Hultiplier: }} & : & \text { Siomal } & \\ \vdots\end{array}$
Dilution:
Use Multiplier $\& ~ D i l u t i o n ~ F a c t o r ~ w i t h ~ I S T D s ~$
$\vdots$
Si gmal 1: vid 1 A , Wavelength=254 mil




Totals :
1.22881e4 264.48662
$==================$
**t End of Report
Instrument 1 7/21/2022 11:39:56 pM
page 1 of 1




Sorted by
Kultiplier: $\quad$ : Sicmal

Si gnal 1: YTWD 1 A , Wavelength $=254 \mathrm{~nm}$




Totals: $8972.11060 \quad 181.68064$







Signal 1: VID 1 A , wavelength $=254$ nia



Totals : $\quad 6504.08458 \quad 129.24908$

## ample Name: $\mathrm{LL}-10-48 \mathrm{D}+\mathrm{D}+\mathrm{-}$ - <br> 




Instrument 1 7/20/2022 3:16:46 uK
Page 1 of 1



[^0]
Instrument 1 7/20/2022 3:17:46
age 1 of 1



| Acq. Operator <br> Acq. Instrument | Instrument 1 | Location : |
| :---: | :---: | :---: |
|  |  |  |
|  |  |  |
| Last chanced | 9/29/2022 7:49:40 PM |  |
| ${ }_{\text {Analvsis }}$ Method | C:\CHEM32 $\ 1$ \METHODS\DEF_LC.M |  |
| st changed |  |  |
| e Info |  |  |


$==========================================================$
$\begin{aligned} & \text { Sorted By } \\ & \text { Hultiplier: }\end{aligned} \quad: \quad$ Siomal $^{\text {Simal }} \quad 1.0000$

Signal 1: vid 1 A , wavelength=254 niil



$\begin{array}{cccccc}15.539 \\ 20.120 & \text { BB } & 0.4939 & 0.47 .86770 & 1.43551 \\ 0.5762 & 7214.99951 & 194.17969 & 0.6524 \\ 98.329\end{array}$
Totals :

$$
7337.60013 \quad 200.50386
$$





Dilution:
Use Hultiplier \& Dilution Factor with 1.0000
ISTD
Si gmal 1: vid 1 A , Wavelength=254 nim





$$
\begin{array}{lll}
\text { Totals : } & 2.25106 e 4 & 671.40259
\end{array}
$$


Instrument 1 7/29/2022 4:35:55 AM


$====================================$
Area Percent Report
$\begin{aligned} & \text { Sorted By } \\ & \text { Multiplier: }\end{aligned} \quad: \quad \stackrel{\text { Simal }}{\vdots} \quad 1.0000$

Si gmal 1: YTDD 1 A , Wavelength $=254 \mathrm{~nm}$




Totals: $\quad 1.29734$ e4 $\quad 376.26203$

Instrument 1 7/29/2022 4:34:08 AM
Page 1 of 1



$\underset{\text { Dillution: }}{\text { Use Multiplier }}$ \& Dilution Factor with ISTDs
Si gmal 1: VTDP 1 A , wavelength=254 nim
Peak RetTime Type width Area Height area

 $\begin{array}{lll}\text { Totals : } & 1.23608 \mathrm{e} 4 & 658.76772\end{array}$

$(+/-)-3 \mathrm{cl}$

Instrument 17/29/2022 4:48:29 A"


$\begin{aligned} & \text { Sorted By } \\ & \text { Multiplier: }\end{aligned} \quad: \quad \stackrel{\text { Simal }}{\vdots} \quad 1.0000$
$\stackrel{\text { Use Multiplier }}{ }$ \& Dilution Factor with $\frac{1.0000}{\text { ISTDs }}$
Si gmal 1: vid 1 A , wavelength=254 nim

$$
7940.02232 \quad 262.33011
$$





$\begin{aligned} & \text { Sorted By } \\ & \text { Multipiplier: }\end{aligned} \quad: \quad$ Simal
$\underset{\text { ilution: }}{\text { Use Multiplier }}$ \& Dilution Factor with isTo
Si gmal 1: VID 1 A , Wavelength $=254$ nil


Totals: $\quad 2603.80988 \quad 135.48223$

Instrument 18/26/2022 9:31:10 pl
page 1 of 1



$\underset{\substack{\text { Dilution: } \\ \text { Use Multiplier }}}{\vdots} \begin{gathered}\text { Dilution Factor with } \\ 1.00000 \\ \text { ISTD }\end{gathered}$
Si gmal 1: VWD 1 A , Wavelength=254 nil




$(+/-)-3 \mathrm{cn}$

$$
\begin{array}{ll}
8771.34857 & 452.20248
\end{array}
$$

Instrument 14/7/2023 8:21:08



$\underbrace{\substack{4 / 7 / 20238: 22: 14 \mathrm{AM} \\ \text { (modified after } \\ \text { and }}}_{\text {Last changed }}$



$\begin{aligned} & \text { Sorted by } \\ & \text { Multiplier: }\end{aligned} \quad: \quad$ Simal

Si gmal 1: VTWD 1 A , Wavelength=254 nim




(-) -3 cn
Totals :
$1.06454 \mathrm{e}^{4} \quad 479.93896$
Instrument 14/7/2023 8:23:10 an
Page 1 of 1



$\qquad$
$===================$


Si gnal 1: YTWD 1 A , Wavelength $=254 \mathrm{~nm}$


Totals: $\quad 8158.50720 \quad 381.04285$
(-)-4aa



ample Name: LLi-11-16 $+/--$ Chill




Ignal 1: Vad 1 A , Wavelength $=254 \mathrm{nin}$

 $4238.17017 \quad 245.18861$
(+/-)-7
*** End of Report ***



sorted Bv

Si gmal 1: vid 1 A , Wavelength=254 mil

$\begin{array}{lllllll}1 & 11.703 \text { VB } & 0.2459 & 19.75402 & 1.21869 & 1.6311 \\ 2 & 14.428 & \mathrm{BB} & 0.3005 & 119.25352 & 61.03853 & 98.3689\end{array}$
Totals : $\quad 1211.10754 \quad 62.25722$


Page 1 of 1


##  <br>  <br> Acc. Operator Acq. $\operatorname{Instrument~}$ $\vdots$ Instrument 1 $\quad$ Location : <br>  <br>  <br>  <br>  <br>  <br>  <br> sorted By <br>  <br>  <br> Si gmal 1: पुD 1 A , wavelength=254 nim <br>  <br>  <br> | 3 | 63.978 |  |  |  |  |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 4 | VB | 1.1444 | 235.30170 |  |  |
| 42.164 | BB | 1.2935 | $1.45549 e 4$ | 172.422087 | 1.577 | <br> $$
\begin{array}{llll} \text { Totals : } & 1.49212 e 4 & 177.58876 \end{array}
$$ <br> nstrument 112/1/2022 2:28:56 A


[^0]:    

