Supporting Information

Chemical Fixation of CO₂/CS₂ to Access Iodoallenyl Oxazolidinones and Allenyl Thiazolidine-Thiones

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1 General Remarks

Unless otherwise noted, all commercially available reagents and solvents were used without further additional purification. Thin layer chromatography was performed using precoated silica gel plates and visualized with UV light at 254 nm. Flash column chromatography was performed with silica gel (40-60 μm). $^1$H and $^{13}$C nuclear magnetic resonance spectra (NMR) were obtained on a Bruker Avance II 400 MHz, Bruker Avance III 500 MHz or Bruker Avance NEO 600MHz recorded in ppm ($\delta$) downfield of TMS ($\delta = 0$) in CDCl$_3$ unless noted otherwise. Signal splitting patterns were described as singlet (s), doublet (d), triplet(t), quartet (q), quintet (quint), or multiplet (m), with coupling constants ($J$) in hertz (Hz). High resolution mass spectra (HRMS) were performed by an Agilent apparatus (TOF mass analyzer type) on an Electron Spray Injection (ESI) mass spectrometer. Melting points were determined by an XP-4 melting point apparatus.
2 Optimization Studies

Table S1. Optimization of reaction conditions for iodoallenyl oxazolidinone

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Solvent</th>
<th>Yield$^b$ (%)</th>
<th>d.r.</th>
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<tr>
<td>1</td>
<td>DBU</td>
<td>CHCl$_3$</td>
<td>28</td>
<td>1:1</td>
</tr>
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<td>2</td>
<td>TBD</td>
<td>CHCl$_3$</td>
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<td>DCE</td>
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<td>17</td>
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<td>Tol/1,4-Dioxane (4:1)</td>
<td>70</td>
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</table>

$^a$ Reaction conditions: 1a (0.1 mmol), base (0.2 mmol) and solvent (2 mL) were stirred for 10 min under CO$_2$ atmosphere (1 atm), and then NIS (0.12 mmol) was added and the mixture was stirred for 24 h at room temperature with CO$_2$ balloon. $^b$ Yield was determined by $^1$H NMR spectroscopy with dimethyl terephthalate as the internal standard. $^c$ Isolated yield. $^d$I$_2$ instead of NIS. $^e$ DIH instead of NIS.
Table S2. Optimization of reaction conditions for allenyl thiazolidine-2-thione

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Solvent</th>
<th>Yield(^b) (%)</th>
</tr>
</thead>
<tbody>
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<td>1</td>
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<td>CHCl(_3)</td>
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<tr>
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<td>DBU</td>
<td>CHCl(_3)</td>
<td>90</td>
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<tr>
<td>3</td>
<td>TBD</td>
<td>CHCl(_3)</td>
<td>96(^e) (93(^c))</td>
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<tr>
<td>4</td>
<td>DABCO</td>
<td>CHCl(_3)</td>
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<tr>
<td>5</td>
<td>Cs(_2)CO(_3)</td>
<td>CHCl(_3)</td>
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<tr>
<td>6</td>
<td>TBD</td>
<td>DCM</td>
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<td>DCE</td>
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<td>TBD</td>
<td>THF</td>
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<td>1,4-Dioxane</td>
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<td>EtOH</td>
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<td>DMF</td>
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<td>16</td>
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<td>CHCl(_3)</td>
<td>68</td>
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</table>

\(^a\) Reaction conditions: \(1a\) (0.1 mmol), base (0.15 mmol), CS\(_2\) (0.3 mmol) and solvent (1 mL) were stirred for 4 h at room temperature, \(^b\) Yield was determined by \(^1\)H NMR spectroscopy with dimethyl terephthalate as the internal standard, \(^c\) 1.0 eq. TBD was used, \(^d\) 0.2 eq. TBD was used, \(^e\) Isolated yield.

3 General procedure for the preparation of substrates

3.1 General procedure A \([1]\)
The amine (20 mmol, 2.0 eq.), K$_2$CO$_3$ (10 mmol, 1.0 eq.) and (n-Bu)$_3$NI (1 mmol, 0.1 eq.) was added to MeCN (25 mL), and the solution was cooled to 0 °C. 1,3-Dichloropropene (10 mmol, 1.0 eq.) was added dropwise over 10 minutes at the same temperature. The reaction mixture was allowed to warm to room temperature and stirred for 24 h. The mixture was filtered and concentrated in vacuo. The crude material was then purified by column chromatography on silica gel with petroleum ether/ethyl acetate to afford the expected product S1.

To a suspension of S1 (3 mmol, 1.0 eq.) Pd(PPh$_3$)$_4$ (0.15 mmol, 0.05 eq.), CuI (0.3 mmol, 0.1 eq.) in piperidine (6 mL) was added alkyne (3.3 mmol, 1.1 eq.) and the mixture was stirred for 20 h at room temperature. Saturated NH$_4$Cl aqueous solution (50 mL) was added and the aqueous phase was extracted with EtOAc (3 x 30 mL). The combined organic phases were washed with brine, dried over Na$_2$SO$_4$ and concentrated under reduced pressure. Purification by silica gel column chromatography with petroleum ether/ethyl acetate afforded S2.

S2 (1 mmol, 1.0 eq.) was dissolved in MeOH and K$_2$CO$_3$ was added (1 mmol, 1.0 eq.). The reaction mixture was stirred for 2 h at room temperature, quenched with NH$_4$Cl and the layers were separated. The aqueous phase was extracted with EtOAc (3 x 15 mL) and the combined organic phases were washed with water, brine and dried with Na$_2$SO$_4$. The solvent was removed under reduced pressure. Purification by silica gel column chromatography with petroleum ether/ethyl acetate afforded the corresponding product.

3.2 General procedure B

S3 (5 mmol, 1.0 eq.) and PPh$_3$ (7.5 mmol, 1.5 eq.) were dissolved in DCM (20 mL), and NBS (7.5 mmol, 1.5 eq.) was added and stirred at room temperature for 2 h. After filtration through a short pad of silica the solvent was removed in vacuo and the residue was purified by column chromatography with petroleum ether/ethyl acetate afforded S4. The amine (4 mmol, 2.0 eq.) and K$_2$CO$_3$ (2 mmol, 1.0 eq.) were added to MeCN (20 mL), and the solution was cooled to 0 °C. S4 (2 mmol, 1.0 eq.) was added dropwise over 10 min at the same temperature. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. The mixture was filtered and concentrated in vacuo. The crude material was then purified by column chromatography on silica gel with petroleum ether/ethyl acetate to afford the expected product S2.

S2 (1 mmol, 1.0 eq.) was dissolved in MeOH and K$_2$CO$_3$ was added (1 mmol, 1.0 eq.). The reaction mixture was stirred for 2 h at room temperature, quenched with saturated NH$_4$Cl aqueous and the layers were separated. The aqueous phase was extracted with...
EtOAc (3 x 15 mL) and the combined organic phases were washed with water, brine and dried with Na₂SO₄. The solvent was removed under reduced pressure. Purification by silica gel column chromatography with petroleum ether/ethyl acetate afforded the corresponding product.

### 3.3 General procedure C

**S1** (10 mmol, 1.0 eq.) was dissolved in 1,4-dioxane (30 mL) and K₂CO₃ (20 mL, 1 M aq.) was added. The solution was cooled to 0 °C, (Boc)₂O (15 mmol, 1.5 eq.) was added dropwise over 10 min at the same temperature. The reaction mixture was allowed to warm to room temperature and stirred for 4 h. Evaporate the solvent and add 30 mL of water to the reaction mixture. The aqueous phase was extracted with EtOAc (3 x 30 mL) and the combined organic phases were washed with brine and dried with Na₂SO₄. The solvent was removed under reduced pressure. Purification by silica gel column chromatography with petroleum ether/ethyl acetate afforded **S5**.

To a suspension of **S5** (3 mmol, 1 eq.) Pd(PPh₃)₄ (0.15 mmol, 0.05 eq.), CuI (0.3 mmol, 0.1 eq.) and n-BuNH₂ (6 mL) in THF (12 mL) was added propargyl alcohol (6 mmol, 2.0 eq.) and the mixture was stirred for 18 h at room temperature. Saturated NH₄Cl aqueous solution (40 mL) was added and the aqueous phase was extracted with EtOAc (3 x 30 mL). The combined organic phases were washed with H₂O, brine, dried over Na₂SO₄ and concentrated under reduced pressure. Purification by silica gel column chromatography with petroleum ether/ethyl acetate afforded the **S6**.

**S6** (2 mmol, 1.0 eq.) was dissolved in THF (10 mL) and the solution was cooled to 0 °C. Sodium hydride was added in portions and stirred for 30 min. CH₃I (2.4 mmol, 1.2 eq.) was added dropwise over 10 min at the same temperature and the reaction mixture was allowed to warm to room temperature and stirred for 12 h. Quenched with saturated NH₄Cl aqueous and the layers were separated. The aqueous phase was extracted with EtOAc (3 x 20 mL) and the combined organic phases were washed with brine and dried with Na₂SO₄. The solvent was removed under reduced pressure. Purification by silica gel column chromatography with petroleum ether/ethyl acetate afforded **S7**.

**S7** (1 mmol, 1.0 eq.) was dissolved in DCM (8 mL) and the solution was cooled to 0 °C. TFA (2 mL) was added and stirred for 2 h at the same temperature. Evaporate the solvent and add 15 mL of water to the reaction mixture and increase pH to 10 with saturated sodium carbonate aqueous. The aqueous phase was extracted with DCM (3 x 15 mL) and the combined organic phases were washed with brine and dried with
Na$_2$SO$_4$. The solvent was removed under reduced pressure. Purification by silica gel column chromatography with petroleum ether/ethyl acetate afforded the corresponding product.

### 3.4 General procedure D

S6 (2 mmol, 1.0 eq.), pyridine (6 mmol, 3.0 eq.) and DMAP (0.4 mmol, 0.2 eq.) was dissolved in DCM (5 mL) and the solution was cooled to 0 °C. Then Ac$_2$O (4 mmol, 2.0 eq.) was added, the reaction mixture was allowed to warm to room temperature and stirred for 12 h. Quenched with saturated NH$_4$Cl aqueous and the layers were separated. The aqueous phase was extracted with DCM (3 x 20 mL) and the combined organic phases were washed with brine and dried with Na$_2$SO$_4$. The solvent was removed under reduced pressure. Purification by silica gel column chromatography with petroleum ether/ethyl acetate afforded S8.

S8 (1 mmol, 1.0 eq.) was dissolved in DCM (8 mL) and the solution was cooled to 0 °C. TFA (2 mL) was added and stirred for 2 h at the same temperature. Evaporate the solvent and add 15 mL of water to the reaction mixture and increase pH to 10 with saturated sodium carbonate aqueous. The aqueous phase was extracted with DCM (3 x 15 mL) and the combined organic phases were washed with brine and dried with Na$_2$SO$_4$. The solvent was removed under reduced pressure. Purification by silica gel column chromatography with petroleum ether/ethyl acetate afforded the corresponding product.

### 3.5 General procedure E

Synthesis of S10 follows general procedure A.

S10 (1 mmol, 1.0 eq.) and AgNO$_3$ (0.1 mmol, 0.1 eq.) was dissolved in acetone and NBS was added (1.1 mmol, 1.1 eq.). The reaction mixture was stirred for 2 h at room temperature, quenched with saturated NH$_4$Cl aqueous and the layers were separated. The aqueous phase was extracted with EtOAc (3 x 15 mL) and the combined organic phases were washed with brine and dried with Na$_2$SO$_4$. The solvent was removed
under reduced pressure. Purification by silica gel column chromatography with petroleum ether/ethyl acetate afforded the corresponding product.

4 Confirmation of the relative stereochemistry of 2a

To assign the relative stereochemistry of the products and hence the mode of 1,4-addition (i.e., syn- versus anti-), the syn-2a was synthesized based on slightly modified methods from the literature.\[3-5\] By comparing the results we concluded that (E)-enynes underwent highly selective syn-1,4-addition to give products.

\[
\text{S2} \quad (2 \text{ mmol, } 1.0 \text{ eq.}) \quad \text{dissolved in 1,4-dioxane (10 mL) and K}_2\text{CO}_3 \quad (5 \text{ mL, } 1 \text{ M aq.}) \quad \text{was added. The solution was cooled to } 0 \degree \text{C, FmocCl (3 mmol, 1.5 eq.) was added over 10 min at the same temperature. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. Evaporate the solvent and add 20 mL of water to the reaction mixture. The aqueous phase was extracted with EtOAc (3 x 20 mL) and the combined organic phases were washed with brine and dried with Na}_2\text{SO}_4. \text{ The solvent was removed under reduced pressure. Purification by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 20: 1) afforded I (865 mg, 93%) as a yellow oil.}
\]

\[
\text{To a DCM solution (10 ml) of fmoc-protected substrate I (1.83 mmol, 1.0 eq.) was added } \text{m-} \text{chloroperbenzoic acid (2.74 mmol, 1.5 eq., 85% purity) at 0 \degree \text{C and the mixtures were stirred at room temperature for 12 h. The resulting solution was quenched with NaHCO}_3 \text{ solution, extracted with EtOAc (3 x 20 mL) and the combined organic phases were washed with brine and dried with Na}_2\text{SO}_4. \text{ The solvent was removed under reduced pressure. Purification by Et}_3\text{N-pretreated silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 20: 1) afforded trans-epoxyamine II (554 mg, 63%) as a yellow oil.}
\]

\[
\text{II} \quad (1.1 \text{ mmol, 1 eq.}) \quad \text{dissolved in MeOH and K}_2\text{CO}_3 \quad (3.85 \text{ mmol, 3.5 eq.}) \quad \text{was added. The reaction mixture was stirred for 8 h at room temperature, quenched with saturated NH}_4\text{Cl aqueous and the layers were separated. The aqueous phase was extracted with EtOAc (3 x 20 mL) and the combined organic phases were washed with water, brine and dried with Na}_2\text{SO}_4. \text{ The solvent was removed under reduced}
\]

S8
pressure. Purification by silica gel column chromatography (eluent: dichloromethane/ethyl acetate = 4: 1) afforded III (153 mg, 74%) as a yellow oil. To a solution of trans-epoxyamine III (0.8 mmol, 1.0 eq.) in THF/water (4:1, 20 mL) was added (NH₄)₂CO₃ (6.4 mmol, 8.0 eq.), and the heterogeneous mixture was vigorously stirred at room temperature for 18 h. The THF was then evaporated under reduced pressure and the resulting aqueous phase extracted with EtOAc (3 x 30 mL) and the combined organic phases were washed with brine and dried with Na₂SO₄. The solvent was removed under reduced pressure. Purification by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 1: 1) afforded anti-IV (126 mg, 68%, dr 15:1) as a colorless oil.

IV (0.5 mmol, 1.0 eq.), Et₃N (1 mmol, 2.0 eq.) and DMAP (0.025 mmol, 0.05 eq.) was dissolved in DCM (3 mL) and the solution was cooled to 0 °C. Then TsCl (0.6 mmol, 1.2 eq.) was added, the reaction mixture was allowed to warm to room temperature and stirred for 12 h. Quenched with saturated NH₄Cl aqueous and the layers were separated. The aqueous phase was extracted with DCM (3 x 15 mL) and the combined organic phases were washed with brine and dried with Na₂SO₄. The solvent was removed under reduced pressure. Purification by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 1: 1) afforded anti-V (181 mg, 94%) as a white solid.

In a glovebox, to a Schlenk flask equipped with a stir bar and charged with CuI (1.8 mmol, 4 eq.) was added THF (1 M). LiI (0.9 mmol, 2 eq.) and THF (0.6 M) were added to a separate vial. The Schlenk flask and vial were sealed, removed from the glovebox, and placed under an N₂ atmosphere. The CuI suspension was cooled to -78 °C. The LiI solution was transferred into the Schlenk flask. The mixture was stirred at -78 °C for 30 min and then stirred at room temperature for 30 min. The resulting cuprate solution was cooled to 0 °C. A solution of anti-V (0.45 mmol, 1.0 eq.) in THF (0.3 M) was added dropwise via syringe to the cuprate solution. The reaction proceeded with stirring at reflux for 1.5 h. After cooling the resulting mixture to room temperature, quenched with saturated NH₄Cl aqueous/NH₃·H₂O (1: 1) and the layers were separated. The aqueous phase was extracted with EtOAc (3 x 15 mL) and the combined organic phases were washed with brine and dried with Na₂SO₄. The solvent was removed under reduced pressure. Purification by silica gel column chromatography (eluent: dichloromethane/ethyl acetate = 20: 1) afforded syn-2a (70 mg, 46%) as a yellow oil.
5 Representative procedures for the synthesis of iodoallenyl oxazolidinone

To an oven dried vial was added 1a (17.1 mg, 0.1 mmol, 1.0 eq.uiv) and TBD (27.9 mg, 0.2 mmol, 2.0 eq.) in toluene:1,4-dioxane (2 mL, 4:1). The mixture was then stirred under CO\textsubscript{2} atmosphere (1 atm) at room temperature for 10 min. Then NIS (27 mg, 0.12 mmol, 1.2 eq.) was added and the mixture was stirred for 24 h with CO\textsubscript{2} ballon. The reaction was then quenched with saturated Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} (10 mL). The mixture was then extracted with EtOAc (3 × 10mL) and the combined organic phases were washed with brine and dried with Na\textsubscript{2}SO\textsubscript{4}. The solvent was removed under reduced pressure and the residue was then purified by column chromatography (eluent: petroleum ether/ethyl acetate = 3:1) to afford the pure product 2a (24.9 mg, 73%) as a yellow sticky oil.

6 Representative procedures for the synthesis of allenyl thiazolidine-2-thione

To an oven dried vial containing 1a (17.1 mg, 0.1 mmol, 1.0 eq.uiv) and TBD (21.0 mg, 0.15 mmol, 1.5 eq.) in CHCl\textsubscript{3} (1 mL) was added CS\textsubscript{2} (22.8 mg, 0.3 mmol, 3.0 eq.). The mixture was stirred for 4 h at room temperature. The solvent was removed under reduced pressure and the residue was then purified by column chromatography (eluent: petroleum ether/ethyl acetate = 5:1) to afford the pure product 3a (23.0 mg, 93%) as a light yellow solid.
7 Examples of failed conversions

8 Procedures for the post-modification of products

8.1 Preparation of dimethyl 2-(4-(3-benzyl-2-thioxothiazolidin-5-yl)-buta-2,3-dien-1-yl) malonate (4)[6]

To an oven dried Schlenk flask were added Pd(PPh₃)₄ (8.7 mg, 0.0075 mmol, 0.05 eq.uiv), 3o (47.9 mg, 0.15 mmol, 1.0 eq.uiv), dimethyl malonate (59.4 mg, 0.45
mmol, 3.0 eq.uiv), DCE (2 mL), and NaH (60% dispersion in mineral oil, 9 mg, 0.225 mmol, 1.5 eq.uiv) sequentially under N₂. After 12 h, the reaction was complete as monitored by TLC and quenched subseq. uently by 10 mL of water, and the resulting mixture was extracted with EtOAc (10 mL × 3). The combined organic layer was washed with brine (10 mL), dried with NaSO₄, filtered, and concentrated under vacuum. The mixture was purified with chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3: 1) to give the pure product 4 (41.6 mg, 71%) as a colorless oil.

8.2 Preparation of (E)-3-benzyl-5-(2-methylbuta-1,3-dien-1-yl)thiazolidine-2-thione (5)\[7\]

\[
\begin{align*}
\text{Bn} & \quad \text{OAc} \\
\text{NH} & \quad \text{Me} \\
\text{S} & \quad \text{S} \\
3o & \quad \text{5}
\end{align*}
\]

To an oven dried Schlenk flask were added FeCl₃ (1.2 mg, 0.0075 mmol, 0.05 eq.uiv), 3o (47.9 mg, 0.15 mmol, 1.0 eq.uiv), and toluene (2 mL) sequentially under a N₂ atmosphere at room temperature. A solution of methyl magnesium bromide (1.0 M in THF, 0.45 mL, 3.0 eq.uiv) was then added with a syringe to the reaction mixture within 5 min at -78 °C. After 4 h, the reaction was complete as monitored by TLC and quenched subseq. uently by dropwise addition of saturated NH₄Cl aqueous (1 mL) at -78 °C. After warming up to room temperature and extraction with EtOAc (3 × 15 mL), the organic layer was washed sequ. uentially with diluted HCl (5%, aq.), a saturated aqueous solution of water, NaHCO₃, and brine. After being dried over anhydrous Na₂SO₄, filtered, and concentrated under vacuum. The mixture was purified with chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5: 1) to give the pure product 5 (26.8 mg, 65%) as a light yellow solid.

8.3 Preparation of 3-(4-methylbenzyl)-5-(3-phenylpropa-1,2-dien-1-yl)oxa-zolidin-2-one (6)\[8\]

\[
\begin{align*}
\text{Me} & \quad \text{O} \\
\text{N} & \quad \text{I} \\
2d & \quad \text{6}
\end{align*}
\]

To an oven dried vial were added Ag₂O (88 mg, 0.41 mmol), PhB(OH)₂ (25.6 mg, 0.21 mmol) and 2d (49.6 mg, 0.14 mmol) in THF (3.0 mL). Degassed DI H₂O (0.3 mL) was added and the solution was stirred at room temperature for 2 h. Quenched
with saturated NH$_4$Cl aqueous and the layers were separated. The aqueous phase was extracted with EtOAc (3 x 20 mL) and the combined organic phases were washed with brine and dried with Na$_2$SO$_4$. The solvent was removed under reduced pressure. Purification by silica gel column chromatography with petroleum ether/ethyl acetate = 5: 1 afforded 6 (28.6 mg, 67%) as a yellow sticky oil.

9 Characterization data of products

**syn-3-Benzyl-5-(3-iodopropa-1,2-dien-1-yl)oxazolidin-2-one (2a)**
25.1 mg, 73% yield, d.r. 16:1, yellow sticky oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39 – 7.31 (m, 3H), 7.30 – 7.27 (m, 2H), 5.89 (dd, $J = 5.8$, 1.8 Hz, 1H), 5.22 (t, $J = 5.8$ Hz, 1H), 5.09 – 4.99 (m, 1H), 4.46 (d, $J = 15.0$ Hz, 1H), 4.40 (d, $J = 15.0$ Hz, 1H), 3.58 (t, $J = 8.7$ Hz, 1H), 3.27 (dd, $J = 8.9$, 5.6 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) (two aromatic carbon missing) δ 204.5, 157.2, 135.5, 128.9, 128.2, 128.1, 93.9, 68.9, 48.4, 48.3, 38.7. HRMS (ESI-TOF) m/z calcd for C$_{13}$H$_{12}$INaO$_2$ $^+$ (M+Na)$^+$ 363.9805, found 363.9806.

**syn-5-(3-Iodopropa-1,2-dien-1-yl)-3-(2-methylbenzyl)oxazolidin-2-one (2b)**
29.8 mg, 84% yield, d.r. >20:1, yellow sticky oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.25 – 7.17 (m, 4H), 5.88 (dd, $J = 5.8$, 1.8 Hz, 1H), 5.22 (t, $J = 5.8$ Hz, 1H), 5.08 – 4.98 (m, 1H), 4.48 (d, $J = 14.9$ Hz, 1H), 4.42 (d, $J = 14.9$ Hz, 1H), 3.53 (t, $J = 8.7$ Hz, 1H), 3.22 (dd, $J = 9.0$, 5.6 Hz, 1H), 2.33 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 204.4, 156.8, 136.9, 133.3, 130.8, 129.0, 128.3, 126.3, 94.0, 68.9, 48.5, 46.4, 38.6, 19.1. HRMS (ESI-TOF) m/z calcd for C$_{14}$H$_{14}$INaO$_2$ $^+$ (M+Na)$^+$ 377.9967, found 377.9973.

**syn-5-(3-Iodopropa-1,2-dien-1-yl)-3-(3-methylbenzyl)oxazolidin-2-one (2c)**
31.1 mg, 87% yield, d.r. 18:1, yellow sticky oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.25 (t, $J = 7.5$ Hz, 1H), 7.15 – 7.05 (m, 3H), 5.89 (dd, $J = 5.8$, 1.8 Hz, 1H), 5.23 (t, $J = 5.8$ Hz, 1H), 5.01 – 5.06 (m, 1H), 4.41 (d, $J = 14.8$, 1H), 4.37 (d, $J = 14.8$, 1H), 3.58 (t, $J = 8.7$ Hz, 1H), 3.27 (dd, $J = 8.9$, 5.6 Hz, 1H), 2.36 (s, 3H). $^{13}$C NMR (101 MHz,
CDCl3) δ 204.5, 157.1, 138.7, 135.5, 128.9, 128.8(3), 128.7(8), 125.2, 94.0, 68.9, 48.4, 48.3, 38.6, 21.4. HRMS (ESI-TOF) m/z calcd for C14H14INaO2+ (M+Na)+ 377.9967, found 377.9973.

**syn-5-(3-Iodopropa-1,2-dien-1-yl)-3-(4-methylbenzyl)oxazolidin-2-one (2d)**

28.1 mg, 79% yield, d.r. >20:1, yellow sticky oil. 1H NMR (500 MHz, CDCl3) δ 7.17 (s, 4H), 5.89 (dd, J = 5.8, 1.8 Hz, 1H), 5.22 (t, J = 5.8 Hz, 1H), 5.02 (ddt, J = 7.8, 5.7, 1.8 Hz, 1H), 4.41 (d, J = 14.8 Hz, 1H), 4.37 (d, J = 14.8 Hz, 1H), 3.56 (t, J = 8.7 Hz, 1H), 3.26 (dd, J = 9.0, 5.6 Hz, 1H). 13C NMR (126 MHz, CDCl3) δ 204.5, 157.1, 137.8, 132.5, 129.6, 128.2, 94.0, 68.9, 48.3, 48.0, 38.6, 21.1. HRMS (ESI-TOF) m/z calcd for C14H14INaO2+ (M+Na)+ 377.9967, found 377.9973.

**syn-5-(3-Iodopropa-1,2-dien-1-yl)-3-(4-methoxybenzyl)oxazolidin-2-one (2e)**

25.1 mg, 67% yield, d.r. >20:1, yellow sticky oil. 1H NMR (500 MHz, CDCl3) δ 7.21 (d, J = 8.6 Hz, 2H), 6.89 (d, J = 8.6 Hz, 2H), 5.90 (dd, J = 5.8, 1.8 Hz, 1H), 5.22 (t, J = 5.8 Hz, 1H), 5.06 – 4.98 (m, 1H), 4.39 (d, J = 14.7 Hz, 1H), 4.35 (d, J = 14.7 Hz, 1H), 3.81 (s, 3H), 3.56 (t, J = 8.7 Hz, 1H), 3.25 (dd, J = 9.0, 5.6 Hz, 1H). 13C NMR (126 MHz, CDCl3) δ 204.5, 157.1, 137.8, 132.5, 129.6, 128.2, 94.0, 68.8, 55.3, 48.3, 47.7, 38.6. HRMS (ESI-TOF) m/z calcd for C14H14INaO3+ (M+Na)+ 393.9916, found 393.9920.

**syn-3-(4-Fluorobenzyl)-5-(3-iodopropa-1,2-dien-1-yl)oxazolidin-2-one (2f)**

31.9 mg, 89% yield, d.r. >20:1, yellow sticky oil. 1H NMR (500 MHz, CDCl3) δ 7.29 – 7.25 (m, 2H), 7.05 (t, J = 8.6 Hz, 2H), 5.93 (dd, J = 5.8, 1.8 Hz, 1H), 5.23 (t, J = 5.8 Hz, 1H), 5.09 – 5.00 (m, 1H), 4.43 (d, J = 14.9 Hz, 1H), 4.38 (d, J = 14.9 Hz, 1H), 3.58 (t, J = 8.7 Hz, 1H), 3.27 (dd, J = 8.9, 5.6 Hz, 1H). 13C NMR (101 MHz, CDCl3) (two aromatic carbon missing) δ 204.5, 162.5 (d, J = 246.8 Hz), 157.1, 131.4 (d, J = 3.3 Hz), 129.9 (d, J = 8.1 Hz), 115.8 (d, J = 21.6 Hz), 93.9, 68.9, 48.4, 47.6, 38.7. HRMS (ESI-TOF) m/z calcd for C13H11IFNNaO2+ (M+Na)+ 381.9716, found 381.9720.
**syn-3-(4-Chlorobenzyl)-5-(3-iodopropa-1,2-dien-1-yl)oxazolidin-2-one (2g)**

33.7 mg, 90% yield, d.r. 15:1, yellow sticky oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37 – 7.32 (m, 2H), 7.23 (d, $J = 8.5$ Hz, 2H), 5.94 (dd, $J = 5.8$, 1.8 Hz, 1H), 5.23 (t, $J = 5.8$ Hz, 1H), 5.09 – 4.99 (m, 1H), 4.43 (d, $J = 15.0$ Hz, 1H), 4.37 (d, $J = 15.0$ Hz, 1H), 3.58 (t, $J = 8.6$ Hz, 1H), 3.26 (dd, $J = 8.9$, 5.7 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) (two aromatic carbon missing) δ 204.5, 157.1, 134.1, 134.0, 129.5, 129.1, 93.9, 68.9, 48.5, 47.7, 38.8. HRMS (ESI-TOF) m/z calcd for C$_{13}$H$_{11}$IClNNaO$_2$ $^+$ (M+Na)$^+$ 397.9421, found 397.9424.

**syn-3-(4-Bromobenzyl)-5-(3-iodopropa-1,2-dien-1-yl)oxazolidin-2-one (2h)**

35.4 mg 90% yield, d.r. 13:1, yellow sticky oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.50 (d, $J = 8.4$ Hz, 2H), 7.17 (d, $J = 8.4$ Hz, 2H), 5.94 (dd, $J = 5.8$, 1.8 Hz, 1H), 5.23 (t, $J = 5.8$ Hz, 1H), 5.08 – 5.01 (m, 1H), 4.41 (d, $J = 15.0$ Hz, 1H), 4.36 (d, $J = 15.0$ Hz, 1H), 3.58 (t, $J = 8.7$ Hz, 1H), 3.26 (dd, $J = 8.9$, 5.6 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) (two aromatic carbon missing) δ 204.5, 157.1, 134.6, 132.1, 129.9, 122.1, 93.8, 68.9, 48.5, 47.7, 38.8. HRMS (ESI-TOF) m/z calcd for C$_{13}$H$_{11}$IBrNNaO$_2$ $^+$ (M+Na)$^+$ 441.8916, found 441.8921.

**syn-Methyl 4-((5-(3-iodopropa-1,2-dien-1-yl)-2-oxooxazolidin-3-yl)methyl)benzoate (2i)**

25.6 mg, 64% yield, d.r. 15:1, yellow sticky oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.04 (d, $J = 8.2$ Hz, 2H), 7.36 (d, $J = 8.2$ Hz, 2H), 5.94 (dd, $J = 5.8$, 1.7 Hz, 1H), 5.24 (t, $J = 5.8$ Hz, 1H), 5.10 – 5.03 (m, 1H), 4.52 (d, $J = 15.3$ Hz, 1H), 4.45 (d, $J = 15.3$ Hz, 1H), 3.92 (s, 3H), 3.60 (t, $J = 8.6$ Hz, 1H), 3.28 (dd, $J = 8.8$, 5.6 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) (two aromatic carbon missing) δ 204.5, 166.6, 157.2, 140.6, 130.2, 130.0, 128.0, 93.8, 68.9, 52.2, 48.6, 48.0, 38.8. HRMS (ESI-TOF) m/z calcd for C$_{13}$H$_{14}$INNaO$_4$ $^+$ (M+Na)$^+$ 421.9865, found 421.9870.
**syn-5-(3-Iodoprop-1,2-dien-1-yl)-3-(naphthalen-1-ylmethyl)oxazolidin-2-one (2j)**

35.6 mg, 90% yield, d.r. >20:1, yellow sticky oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.10 (d, $J = 8.7$ Hz, 1H), 7.93 – 7.84 (m, 2H), 7.61 – 7.50 (m, 2H), 7.48 – 7.39 (m, 2H), 5.36 (dd, $J = 5.8$, 1.7 Hz, 1H), 5.12 (t, $J = 5.8$ Hz, 1H), 4.98 (d, $J = 14.6$ Hz, 1H), 4.79 (d, $J = 14.6$ Hz, 1H), 3.48 (t, $J = 8.7$ Hz, 1H), 3.13 (dd, $J = 9.1$, 5.2 Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 204.4, 156.7, 133.9, 131.5, 131.1, 129.4, 128.8, 127.7, 127.0, 126.3, 125.2, 123.7, 93.6, 69.0, 48.0, 46.7, 38.4. HRMS (ESI-TOF) m/z calcd for C$_{17}$H$_{14}$INaO$_2$ $^+$ (M+Na)$^+$ 413.9967, found 413.9971.

**syn-3-(Furan-2-ylmethyl)-5-(3-iodoprop-1,2-dien-1-yl)oxazolidin-2-one (2k)**

26.2 mg, 79% yield, d.r. 10:1, yellow solid, mp = 73.1 – 74.1 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44 – 7.34 (m, 1H), 6.38 – 6.24 (m, 2H), 5.96 (dd, $J = 5.9$, 1.8 Hz, 1H), 5.24 (t, $J = 5.9$ Hz, 1H), 5.11 – 4.97 (m, 1H), 4.43 (s, 2H), 3.68 (t, $J = 8.7$ Hz, 1H), 3.39 (dd, $J = 7.1$, 3.4 Hz, 2H), 1.59 (d, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) (two aromatic carbon missing) $\delta$ 204.7, 156.8, 149.3, 142.9, 110.6, 109.0, 93.8, 69.0, 48.8, 40.9, 38.6. HRMS (ESI-TOF) m/z calcd for C$_{11}$H$_{10}$INaO$_3$ $^+$ (M+Na)$^+$ 353.9598, found 353.9596.

**syn-5-(3-Iodoprop-1,2-dien-1-yl)-3-((S)-1-phenylethyl)oxazolidin-2-one (2l)**

25.6 mg, 72% yield, d.r. 1.3:1, yellow sticky oil.

**Major isomer:** $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 – 7.30 (m, 5H), 6.03 (dd, $J = 5.8$, 1.8 Hz, 1H), 5.29 – 5.19 (m, 2H), 4.99 – 4.92 (m, 1H), 3.32 (dd, $J = 7.1$, 3.4 Hz, 2H), 1.59 (d, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) (two aromatic carbon missing) $\delta$ 204.6, 156.5, 139.3, 128.8, 128.0, 127.0, 94.1, 68.9, 51.6, 44.9, 38.4, 16.3. HRMS (ESI-TOF) m/z calcd for C$_{14}$H$_{14}$INaO$_2$ $^+$ (M+Na)$^+$ 377.9967, found 377.9959.

**Minor isomer:** $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 – 7.31 (m, 5H), 5.66 (dd, $J = 5.8$, 1.8 Hz, 1H), 5.23 (q, $J = 7.1$ Hz, 1H), 5.12 (t, $J = 5.6$ Hz, 1H), 5.07 – 5.00 (m, 1H), 3.65 (t, $J = 8.6$ Hz, 1H), 3.04 (dd, $J = 8.9$, 4.9 Hz, 1H), 1.59 (d, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) (two aromatic carbon missing) $\delta$ 204.2, 156.6, 139.4, 128.8, 127.9, 127.1, 93.9, 68.9, 51.4, 44.3, 38.6, 16.2. HRMS (ESI-TOF) m/z calcd for C$_{14}$H$_{14}$INaO$_2$ $^+$ (M+Na)$^+$ 377.9967, found 377.9959.
syn-5-(3-Iodopropa-1,2-dien-1-yl)-3-phenethoxazolidin-2-one (2m)
27.7 mg, 78% yield, d.r. 12:1, yellow sticky oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35 – 7.29 (m, 2H), 7.26 – 7.19 (m, 3H), 5.95 (dd, $J$ = 5.9, 1.7 Hz, 1H), 5.18 (t, $J$ = 5.9 Hz, 1H), 5.02 – 4.92 (m, 1H), 3.58 – 3.50 (m, 3H), 3.25 (dd, $J$ = 8.8, 5.8 Hz, 1H), 2.90 (t, $J$ = 7.2 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) (two aromatic carbon missing) $\delta$ 204.6, 157.0, 138.2, 128.7, 128.7, 126.7, 94.0, 68.8, 49.7, 45.4, 38.6, 34.0. HRMS (ESI-TOF) m/z calcd for C$_{14}$H$_{14}$INNaO$_2$ $^+$ (M+Na)$^+$ 377.9967, found 377.9971.

syn-3-Butyl-5-(3-iodopropa-1,2-dien-1-yl)oxazolidin-2-one (2n)
22.4 mg, 73% yield, d.r. >20:1, yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.03 (dd, $J$ = 5.8, 1.8 Hz, 1H), 5.28 (t, $J$ = 5.8 Hz, 1H), 5.11 – 5.00 (m, 1H), 3.70 (t, $J$ = 8.7 Hz, 1H), 3.40 (dd, $J$ = 8.9, 5.8 Hz, 1H), 3.26 (td, $J$ = 7.1, 1.9 Hz, 2H), 1.59 – 1.49 (m, 2H), 1.40 – 1.30 (m, 2H), 0.94 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 204.6, 157.1, 94.1, 68.7, 49.0, 43.9, 38.6, 29.4, 19.8, 13.7. HRMS (ESI-TOF) m/z calcd for C$_{10}$H$_{14}$INNaO$_2$ $^+$ (M+Na)$^+$ 329.9969, found 329.9969.

syn-3-(3-Chloropropyl)-5-(3-iodopropa-1,2-dien-1-yl)oxazolidin-2-one (2o)
17.0 mg, 52% yield, d.r. >20:1, yellow stick oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.07 (dd, $J$ = 5.8, 1.9 Hz, 1H), 5.28 (t, $J$ = 5.8 Hz, 1H), 5.13 – 5.03 (m, 1H), 3.76 (t, $J$ = 8.6 Hz, 1H), 3.48 – 3.39 (m, 3H), 2.11 – 2.02 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 204.6, 157.1, 93.9, 68.8, 49.7, 42.0, 41.9, 38.8, 30.3. HRMS (ESI-TOF) m/z calcd for C$_9$H$_{11}$ClINaO$_2$ $^+$ (M+Na)$^+$ 349.9412, found 349.9416.

syn-3-Benzyl-5-(3-iodopropa-1,2-dien-1-yl)-5-methyloxazolidin-2-one (2p)
34.0 mg, 95% yield, d.r. >20:1, yellow solid, mp = 96.5-97.5 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.39 – 7.31 (m, 3H), 7.28 (d, $J$ = 6.7 Hz, 2H), 5.84 (d, $J$ = 5.8 Hz, 1H), 5.21 (d, $J$ = 5.8 Hz, 1H), 4.49 (d, $J$ = 14.9 Hz, 1H), 4.37 (d, $J$ = 14.9 Hz, 1H), 3.40 (d, $J$ = 8.9 Hz, 1H), 3.22 (d, $J$ = 8.9 Hz, 1H), 1.54 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) (two aromatic carbon missing) $\delta$ 203.1, 156.8, 135.7, 128.9, 128.2, 128.0, 98.9, 76.1, 54.5, 48.2, 39.0, 25.7. HRMS (ESI-TOF) m/z calcd for C$_{15}$H$_{14}$INNaO$_2$ $^+$ (M+Na)$^+$ 377.9967,
found 377.9972.

**syn-3-Benzyl-5-ethyl-5-(3-iodopropa-1,2-dien-1-yl)oxazolidin-2-one (2q)**
32.8 mg, 89% yield, d.r. 18:1, yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.40 – 7.27 (m, 5H), 5.80 (d, $J = 5.8$ Hz, 1H), 5.17 (d, $J = 5.8$ Hz, 1H), 4.50 (d, $J = 14.9$ Hz, 1H), 4.35 (d, $J = 14.9$ Hz, 1H), 3.36 (d, $J = 9.0$ Hz, 1H), 3.23 (d, $J = 9.0$ Hz, 1H), 1.89 – 1.77 (m, 2H), 0.94 (t, $J = 7.5$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) (two aromatic carbon missing) $\delta$ 203.2, 156.9, 135.7, 128.9, 128.2, 128.0, 98.0, 79.1, 52.2, 48.2, 39.0, 32.2, 7.4. HRMS (ESI-TOF) m/z calcd for C$_{15}$H$_{16}$INNaO$_2^+$ (M+Na)$^+$ 392.0118, found 392.0114.

**syn-3-Benzyl-5-(4-iodobuta-2,3-dien-2-yl)oxazolidin-2-one (2r)**
27.2 mg, 77% yield, d.r. 11:1, yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.41 – 7.27 (m, 5H), 5.79 – 5.67 (m, 1H), 4.90 (t, $J = 7.9$ Hz, 1H), 4.47 (d, $J = 14.8$ Hz, 1H), 4.39 (d, $J = 14.8$ Hz, 1H), 3.55 (t, $J = 9.0$ Hz, 1H), 3.31 (dd, $J = 9.0$, 5.7 Hz, 1H), 1.86 (d, $J = 2.4$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) (two aromatic carbon missing) $\delta$ 202.5, 157.2, 135.5, 128.9, 128.2, 128.1, 103.6, 72.0, 48.3, 47.4, 38.1, 14.3. HRMS (ESI-TOF) m/z calcd for C$_{14}$H$_{14}$INNaO$_2^+$ (M+Na)$^+$ 377.9967, found 377.9973.

**3-Benzyl-5-(propa-1,2-dien-1-yl)thiazolidine-2-thione (3a)**
23.0 mg, 93% yield, light yellow solid, mp = 71.6–72.4 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 – 7.28 (m, 5H), 5.22 (q, $J = 6.8$ Hz, 1H), 5.02 (d, $J = 14.5$ Hz, 1H), 4.93 (d, $J = 14.5$ Hz, 1H), 4.90 – 4.82 (m, 1H), 4.80 – 4.71 (m, 1H), 4.24 – 4.15 (m, 1H), 4.02 (dd, $J = 11.6$, 7.6 Hz, 1H), 3.82 (dd, $J = 11.6$, 5.5 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) (two aromatic carbon missing) $\delta$ 208.0, 196.1, 135.1, 128.9, 128.3, 128.2, 90.0, 79.0, 60.4, 52.6, 41.8. HRMS (ESI-TOF) m/z calcd for C$_{13}$H$_{14}$NS$_2^+$ (M+H)$^+$ 248.0563, found 248.0566.
3-(2-Methylbenzyl)-5-(propa-1,2-dien-1-yl)thiazolidine-2-thione (3b)
25.0 mg, 96% yield, white solid, mp = 65.5-66.5 °C. 
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$
7.41 – 7.09 (m, 4H), 5.22 (q, $J$ = 6.8 Hz, 1H), 5.01 (d, $J$ = 14.8 Hz, 1H), 4.91 (d, $J$ = 14.8 Hz, 1H), 4.88 – 4.72 (m, 2H), 4.24 – 4.13 (m, 1H), 3.92 (dd, $J$ = 11.6, 7.6 Hz, 1H), 3.73 (dd, $J$ = 11.6, 5.5 Hz, 1H), 2.33 (s, 3H).
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$
208.0, 195.6, 137.0, 133.0, 130.9, 129.2, 128.5, 126.4, 90.1, 79.1, 60.2, 51.0, 41.7, 19.5. HRMS (ESI-TOF) m/z calcd for C$_{14}$H$_{16}$NS$_2$ $^+$ (M+H)$^+$ 262.0724, found 262.0728.

3-(3-Methylbenzyl)-5-(propa-1,2-dien-1-yl)thiazolidine-2-thione (3c)
25.6 mg, 98% yield, white solid, mp = 76.8-77.4 °C. 
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$
7.24 (t, $J$ = 7.6 Hz, 1H), 7.14 (s, 1H) 7.13 (d, $J$ = 7.6 Hz, 2H), 5.23 (q, $J$ = 6.8 Hz, 1H), 4.96 (d, $J$ = 14.5 Hz, 2H), 4.91 (d, $J$ = 14.3 Hz, 2H), 4.90 – 4.82 (m, 1H), 4.82 – 4.73 (m, 1H), 4.28 – 4.14 (m, 1H), 4.01 (dd, $J$ = 11.6, 7.7 Hz, 1H), 4.82 – 4.74 (m, 1H), 2.35 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$
208.1, 195.9, 138.7, 134.9, 129.0, 129.0, 128.8, 125.4, 90.0, 78.9, 60.4, 52.6, 41.8, 21.4. HRMS (ESI-TOF) m/z calcd for C$_{14}$H$_{16}$NS$_2$ $^+$ (M+H)$^+$ 262.0724, found 262.0728.

3-(4-Methylbenzyl)-5-(propa-1,2-dien-1-yl)thiazolidine-2-thione (3d)
23.7 mg, 91% yield, white solid, mp = 111.6-112.5 °C. 
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$
7.23 (d, $J$ = 7.9 Hz, 2H), 7.16 (d, $J$ = 7.9 Hz, 2H), 5.22 (q, $J$ = 6.8 Hz, 1H), 4.95 (d, $J$ = 14.5 Hz, 1H), 4.91 (d, $J$ = 14.5 Hz, 1H), 4.91 – 4.82 (m, 1H), 4.82 – 4.74 (m, 1H), 4.23 – 4.12 (m, 1H), 4.01 (dd, $J$ = 11.6, 7.7 Hz, 1H), 3.80 (dd, $J$ = 11.6, 5.6 Hz, 1H), 2.35 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) (two aromatic carbon missing) $\delta$
208.1, 195.8, 138.1, 132.0, 129.6, 128.3, 90.0, 78.9, 60.4, 52.4, 41.8, 21.2. HRMS (ESI-TOF) m/z calcd for C$_{14}$H$_{16}$NS$_2$ $^+$ (M+H)$^+$ 262.0724, found 262.0728.

3-(4-Methoxybenzyl)-5-(propa-1,2-dien-1-yl)thiazolidine-2-thione (3e)
24.8 mg, 90% yield, light yellow solid, mp = 101.2-102.2 °C. 
$^1$H NMR (400 MHz,
CDCl$_3$ δ 7.28 (d, $J$ = 8.6 Hz, 2H), 6.87 (d, $J$ = 8.6 Hz, 2H), 5.21 (q, $J$ = 6.8 Hz, 1H), 4.93 (d, $J$ = 14.4 Hz, 1H), 4.86 (d, $J$ = 14.4 Hz, 1H), 4.87 – 4.83 (m, 1H), 4.82 – 4.74 (m, 1H), 4.21 – 4.14 (m, 1H), 4.00 (dd, $J$ = 11.6, 7.7 Hz, 1H), 3.81 (s, 3H), 3.80 (dd, $J$ = 11.6, 5.6 Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) (two aromatic carbon missing) δ 208.1, 195.6, 159.6, 129.8, 127.1, 114.3, 90.0, 78.9, 60.3, 55.3, 52.0, 41.8. HRMS (ESI-TOF) m/z calcd for C$_{14}$H$_{15}$NNaOS$_2$ $^{+}$ (M+Na)$^+$ 300.0493, found 300.0500.

3-(4-Fluorobenzyl)-5-(propa-1,2-dien-1-yl)thiazolidine-2-thione (3f)
25.8 mg, 97% yield, white solid, mp = 112.5-113.5 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.34 (dd, $J$ = 8.6, 5.4 Hz, 2H), 7.04 (t, $J$ = 8.6 Hz, 2H), 5.22 (q, $J$ = 6.7 Hz, 1H), 4.99 (d, $J$ = 14.5 Hz, 1H), 4.89 (d, $J$ = 14.5 Hz, 1H), 4.90 – 4.83 (m, 1H), 4.83 – 4.73 (m, 1H), 4.24 – 4.15 (m, 1H), 4.02 (dd, $J$ = 11.5, 7.6 Hz, 1H), 3.82 (dd, $J$ = 11.5, 5.4 Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) (two aromatic carbon missing) δ 208.0, 196.1, 162.6 (d, $J$ = 247.1 Hz), 130.9 (d, $J$ = 8.2 Hz), 115.9 (d, $J$ = 21.5 Hz), 90.0, 79.1, 60.3, 51.8, 41.7. HRMS (ESI-TOF) m/z calcd for C$_{13}$H$_{13}$FNS$_2$ $^{+}$ (M+H)$^+$ 266.0473, found 262.0477.

3-(4-Chlorobenzyl)-5-(propa-1,2-dien-1-yl)thiazolidine-2-thione (3g)
26.9 mg, 96% yield, light yellow solid, mp = 129.5-130.5 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.34 – 7.28 (m, 4H), 5.23 (q, $J$ = 6.8 Hz, 1H), 4.99 (d, $J$ = 14.7 Hz, 1H), 4.89 (d, $J$ = 14.7 Hz, 1H), 4.91 – 4.83 (m, 1H), 4.83 – 4.73 (m, 1H), 4.25 – 4.16 (m, 1H), 4.02 (dd, $J$ = 11.5, 7.6 Hz, 1H), 3.81 (dd, $J$ = 11.5, 5.5 Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) (two aromatic carbon missing) δ 208.0, 196.3, 134.2, 133.5, 129.7, 129.1, 90.0, 79.1, 60.3, 51.8, 41.8. HRMS (ESI-TOF) m/z calcd for C$_{13}$H$_{13}$ClNS$_2$ $^{+}$ (M+H)$^+$ 283.0718, found 282.0180.

3-(4-Bromobenzyl)-5-(propa-1,2-dien-1-yl)thiazolidine-2-thione (3h)
30.8 mg, 94% yield, light yellow solid, mp = 132.7-133.5 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.48 (d, $J$ = 8.4 Hz, 2H), 7.23 (d, $J$ = 8.4 Hz, 2H), 5.23 (q, $J$ = 6.8 Hz, 1H), 4.97 (d, $J$ = 14.7 Hz, 1H), 4.88 (d, $J$ = 14.7 Hz, 1H), 4.90 – 4.86 (m, 1H), 4.82 – 4.75 (m, 1H), 4.25 – 4.15 (m, 1H), 4.02 (dd, $J$ = 11.5, 7.6 Hz, 1H), 3.81 (dd, $J$ = 11.5, 5.5 Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) (two aromatic carbon missing) δ 208.0, 196.4,
134.1, 132.1, 130.0, 122.3, 90.0, 79.1, 60.3, 51.9, 41.8. HRMS (ESI-TOF) m/z calcd for C$_{13}$H$_{13}$BrNS$_2$\(^+\) (M+H)$^+$ 325.9673, found 325.9670.

Methyl 4-((5-(propa-1,2-dien-1-yl)-2-thioxothiazolidin-3-yl)methyl)benzoate (3i)
19.1 mg, 63% yield, white solid, mp = 80.6-81.5 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.03 (d, $J$ = 8.2 Hz, 2H), 7.41 (d, $J$ = 8.2 Hz, 2H), 5.23 (q, $J$ = 6.8 Hz, 1H), 5.09 (d, $J$ = 14.9 Hz, 1H), 4.97 (d, $J$ = 14.9 Hz, 1H), 4.92 – 4.84 (m, 1H), 4.84 – 4.74 (m, 1H), 4.25 – 4.16 (m, 1H), 4.03 (dd, $J$ = 11.5, 7.6 Hz, 1H), 3.92 (s, 3H), 3.82 (dd, $J$ = 11.5, 7.6 Hz, 1H), 3.68 (dd, $J$ = 11.5, 7.6 Hz, 1H), 3.09 – 2.97 (m, 2H). 13C NMR (101 MHz, CDCl$_3$) δ 208.0, 196.6, 166.6, 140.1, 130.2, 128.1, 90.0, 79.2, 60.4, 52.2, 52.2, 41.7. HRMS (ESI-TOF) m/z calcd for C$_{115}$H$_{16}$NO$_2$S$_2$\(^+\) (M+H)$^+$ 306.0622, found 306.0628.

3-(Naphthalen-1-ylmethyl)-5-(propa-1,2-dien-1-yl)thiazolidine-2-thione (3j)
27.3 mg, 92% yield, white solid, mp = 113.4-114.3 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.10 (d, $J$ = 8.2 Hz, 1H), 7.95 – 7.82 (m, 2H), 7.65 – 7.50 (m, 2H), 7.46 (d, $J$ = 4.8 Hz, 2H), 5.50 (d, $J$ = 14.6 Hz, 1H), 5.24 (d, $J$ = 14.6 Hz, 1H), 4.68 – 4.59 (m, 1H), 4.44 – 4.32 (m, 1H), 4.11 – 4.02 (m, 1H), 3.85 (dd, $J$ = 11.6, 7.6 Hz, 1H), 3.68 (dd, $J$ = 11.7, 5.2 Hz, 1H), 3.09 – 2.97 (m, 2H). 13C NMR (101 MHz, CDCl$_3$) δ 207.7, 195.4, 133.9, 131.7, 131.1, 129.5, 128.8, 128.1, 127.2, 126.4, 125.3, 124.0, 89.9, 78.8, 59.8, 51.4, 41.6. HRMS (ESI-TOF) m/z calcd for C$_{17}$H$_{16}$NS$_2$\(^+\) (M+H)$^+$ 298.0724, found 298.0725.

3-Phenethyl-5-(propa-1,2-dien-1-yl)thiazolidine-2-thione (3k)
24.4 mg, 93% yield, yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38 – 7.24 (m, 5H), 5.20 (q, $J$ = 6.9 Hz, 1H), 4.99 – 4.86 (m, 2H), 4.16 (q, $J$ = 7.1 Hz, 1H), 4.05 – 3.91 (m, 3H), 3.79 (dd, $J$ = 11.5, 5.7 Hz, 1H), 3.09 – 2.97 (m, 2H). 13C NMR (101 MHz, CDCl$_3$) δ 208.2, 195.2, 138.0, 128.9, 128.8, 126.9, 90.0, 78.9, 62.3, 50.9, 42.2, 32.8. HRMS (ESI-TOF) m/z calcd for C$_{14}$H$_{16}$NS$_2$\(^+\) (M+H)$^+$ 262.0724, found 262.0729.
3-Butyl-5-(propa-1,2-dien-1-yl)thiazolidine-2-thione (3l)
19.6 mg, 92% yield, yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 5.30 (q, $J = 6.8$ Hz, 1H), 5.05 – 4.85 (m, 2H), 4.29 – 4.18 (m, 1H), 4.14 (dd, $J = 11.4$, 7.5 Hz, 1H), 3.95 (dd, $J = 11.4$, 5.3 Hz, 1H), 3.85 – 3.65 (m, 2H), 1.64 (p, $J = 7.5$ Hz, 2H), 1.37 (h, $J = 7.3$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 208.1, 195.0, 90.2, 79.0, 61.2, 49.0, 41.9, 28.9, 20.0, 13.8. HRMS (ESI-TOF) m/z calcld for C$_{10}$H$_{16}$NS$_2$ + (M+H)$^+$ 214.0724, found 214.0728.

3-Cyclohexyl-5-(propa-1,2-dien-1-yl)thiazolidine-2-thione (3m)
23.6 mg, 99% yield, light yellow solid, mp = 117.8-118.6 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 5.27 (q, $J = 6.8$ Hz, 1H), 5.05 – 4.87 (m, 2H), 4.78 – 4.67 (m, 1H), 4.25 – 4.13 (m, 1H), 4.04 (dd, $J = 11.5$, 7.3 Hz, 1H), 3.90 (dd, $J = 11.5$, 5.2 Hz, 1H), 1.92 – 1.79 (m, 4H), 1.70 (d, $J = 13.6$ Hz, 1H), 1.49 – 1.28 (m, 4H), 1.18 – 1.05 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 208.0, 194.0, 90.2, 79.1, 57.6, 56.7, 42.1, 30.1, 29.9, 25.4(4), 25.4, 25.3(6). HRMS (ESI-TOF) m/z calcld for C$_{12}$H$_{18}$NS$_2$ + (M+H)$^+$ 240.0881, found 240.0883.

syn-3-Benzyl-5-(4-methoxybuta-1,2-dien-1-yl)thiazolidine-2-thione (3n)
25.7 mg, 88% yield, d.r. 7:1, yellow oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.40 – 7.30 (m, 5H), 5.52 – 5.35 (m, 1H), 5.36 – 5.25 (m, 1H), 5.08 (d, $J = 14.6$ Hz, 1H), 4.87 (d, $J = 14.6$ Hz, 1H), 4.26 – 4.16 (m, 1H), 4.02 (dd, $J = 11.6$, 7.6 Hz, 1H), 3.90 (dd, $J = 11.5$, 5.2 Hz, 1H), 2.38 (dd, $J = 6.5$, 2.4 Hz, 2H), 3.79 (dd, $J = 11.6$, 5.8 Hz, 1H), 1.99 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) (two aromatic carbon missing) δ 204.4, 196.0, 134.9, 129.0, 128.3, 128.3, 92.7, 91.7, 69.7, 60.8, 58.1, 52.6, 42.1. HRMS (ESI-TOF) m/z calcld for C$_{13}$H$_{17}$NNaS$_2$ + (M+Na)$^+$ 314.0649, found 314.0655.

syn-4-(3-Benzyl-2-thioxothiazolidin-5-yl)buta-2,3-dien-1-yl acetate (3o)
24.2 mg, 76% yield, d.r. >20:1, light yellow solid, mp = 64.5-65.4 °C. $^1$H NMR (600
MHz, CDCl$_3$) $\delta$ 7.40 – 7.30 (m, 5H), 5.47 (q, $J$ = 6.4, 5.9 Hz, 1H), 5.43 – 5.36 (m, 1H), 5.08 (d, $J$ = 14.6 Hz, 1H), 4.88 (d, $J$ = 14.6 Hz, 1H), 4.54 – 4.45 (m, 2H), 4.24 – 4.17 (m, 1H), 4.03 (dd, $J$ = 11.7, 7.8 Hz, 1H), 3.80 (dd, $J$ = 11.7, 5.5 Hz, 1H), 2.04 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) (two aromatic carbon missing) $\delta$ 204.6, 195.8, 170.6, 134.9, 129.0, 128.3, 128.3, 93.0, 91.4, 61.3, 60.5, 52.6, 41.7, 20.9. HRMS (ESI-TOF) m/z calcd for C$_{16}$H$_{17}$NNaO$_2$S$_2$ $^+$(M+Na)$^+$ 342.0598, found 342.0592.

\[ \text{syn-4-(3-Benzyl-2-thioxothiazolidin-5-yl)buta-2,3-dien-1-yl methyl carbonate (3p)} \]
23.2 mg, 69% yield, d.r. >20:1, yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41 – 7.28 (m, 5H), 5.50 (q, $J$ = 6.4 Hz, 1H), 5.46 – 5.37 (m, 1H), 5.09 (d, $J$ = 14.6 Hz, 1H), 4.88 (d, $J$ = 14.6 Hz, 1H), 4.61 – 4.47 (m, 2H), 4.26 – 4.16 (m, 1H), 4.03 (dd, $J$ = 11.6, 7.7 Hz, 1H), 3.84 – 3.77 (m, 1H), 3.76 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) (two aromatic carbon missing) $\delta$ 205.1, 195.8, 155.4, 134.9, 129.0, 128.3, 128.3, 93.0, 90.7, 64.7, 60.6, 55.0, 52.6, 41.7. HRMS (ESI-TOF) m/z calcd for C$_{16}$H$_{17}$NNaO$_2$S$_2$ $^+$(M+Na)$^+$ 358.0538, found 358.0552.

\[ \text{syn-4-(3-Benzyl-2-thioxothiazolidin-5-yl)buta-2,3-dien-1-yl pivalate (3q)} \]
33.5 mg, 93% yield, d.r. 12:1, yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 – 7.29 (m, 5H), 5.45 (q, $J$ = 6.2 Hz, 1H), 5.41 – 5.34 (m, 1H), 5.09 (d, $J$ = 14.6 Hz, 1H), 4.91 (d, $J$ = 14.6 Hz, 1H), 4.53 – 4.44 (m, 2H), 4.26 – 4.16 (m, 1H), 4.03 (dd, $J$ = 11.6, 7.7 Hz, 1H), 3.79 (dd, $J$ = 11.6, 5.8 Hz, 1H), 1.17 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) (two aromatic carbon missing) $\delta$ 204.6, 196.0, 178.1, 134.9, 129.0, 128.3, 128.3, 93.0, 90.7, 91.5, 61.1, 60.7, 52.6, 42.0, 38.7, 27.2. HRMS (ESI-TOF) m/z calcd for C$_{19}$H$_{23}$NNaO$_2$S$_2$ $^+$(M+Na)$^+$ 384.1068, found 384.1071.

\[ \text{syn-4-(3-Benzyl-2-thioxothiazolidin-5-yl)buta-2,3-dien-1-yl benzoate (3r)} \]
32.3 mg, 85% yield, d.r. 14:1, light yellow solid, mp = 67.4-68.2 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.05 – 7.98 (m, 2H), 7.61 – 7.52 (m, 1H), 7.47 – 7.39 (m, 2H), 7.38 – 7.26 (m, 5H), 5.58 (qd, $J$ = 6.1, 1.8 Hz, 1H), 5.45 – 5.36 (m, 1H), 5.03 (d, $J$ = 14.5 Hz, 1H), 4.85 (d, $J$ = 14.5 Hz, 1H), 4.75 (dd, $J$ = 6.1, 2.6 Hz, 2H), 4.27 – 4.16 (m, 1H), 3.96 (dd, $J$ = 11.7, 7.8 Hz, 1H), 3.71 (dd, $J$ = 11.7, 5.8 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) (four aromatic carbon missing) $\delta$ 204.7, 195.9, 166.1, 134.9, 133.2, 129.8,
129.7, 129.0, 128.5, 128.3, 128.2, 93.1, 91.4, 61.7, 60.6, 52.6, 41.9. HRMS (ESI-TOF) m/z calcd for C_{21}H_{19}NNaO_{2}S_{2}^{+} (M+Na)^{+} 404.0755, found 404.0760.

**syn-3-Benzyl-5-(4-hydroxybuta-1,2-dien-1-yl)thiazolidine-2-thione (3s)**
18.6 mg, 67% yield, d.r. 4:1, yellow solid, mp = 103.2-104.2 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.47 – 7.27 (m, 5H), 5.54 (q, $J$ = 5.9, 1H), 5.46 – 5.34 (m, 1H), 5.06 (d, $J$ = 14.6 Hz, 1H), 4.90 (d, $J$ = 14.6 Hz, 1H), 4.22 – 4.14 (m, 1H), 4.12 – 4.02 (m, 3H), 3.86 – 3.79 (m, 1H), 1.59 (br s, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 203.2, 195.9, 134.9, 128.9(9), 128.9(7), 128.4, 128.3(3), 128.3(1), 96.1, 93.4, 60.8, 59.9, 52.6, 42.0. HRMS (ESI-TOF) m/z calcd for C$_{14}$H$_{15}$NNaOS$_2$^{+} (M+Na)$^+$ 300.0493, found 300.0500.

**syn-3-Benzyl-5-(3-bromopropa-1,2-dien-1-yl)thiazolidine-2-thione (3t)**
20.5 mg, 63% yield, d.r. 3:1, light yellow solid, mp = 129.5-130.7 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39 – 7.31 (m, 5H), 6.16 (dd, $J$ = 5.6, 1.5 Hz, 1H), 5.48 – 5.40 (m, 1H), 5.14 (d, $J$ = 14.6 Hz, 1H), 4.85 (d, $J$ = 14.6 Hz, 1H), 4.34 – 4.22 (m, 1H), 4.14 – 4.02 (m, 1H), 3.82 (dd, $J$ = 11.7, 4.8 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) (two aromatic carbon missing) δ 202.2, 195.2, 134.8, 129.0, 128.4, 128.3, 98.7, 75.2, 60.3, 52.8, 41.1. HRMS (ESI-TOF) m/z calcd for C$_{13}$H$_{13}$BrNS$_2$^{+} (M+H)$^+$ 325.9673, found 325.9672.

**syn-3-Benzyl-5-(3-phenylpropa-1,2-dien-1-yl)thiazolidine-2-thione (3u)**
17.3 mg, 54% yield, d.r. 13:1, yellow solid, mp = 91.3-92.5 °C. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.36 – 7.28 (m, 5H), 7.29 – 7.26 (m, 2H), 7.26 – 7.20 (m, 3H), 6.38 (dd, $J$ = 6.3, 2.2 Hz, 1H), 5.71 (t, $J$ = 6.5 Hz, 1H), 5.13 (d, $J$ = 14.7 Hz, 1H), 4.55 (d, $J$ = 14.7 Hz, 1H), 4.29 – 4.22 (m, 1H), 4.03 (dd, $J$ = 11.6, 7.4 Hz, 1H), 3.90 (dd, $J$ = 11.6, 4.8 Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) (two aromatic carbon missing) δ 204.7, 195.5, 134.8, 132.7, 128.9(1), 128.8(9), 128.3, 128.2, 127.9, 127.1, 98.7, 94.9, 60.3, 52.8, 42.1. HRMS (ESI-TOF) m/z calcd for C$_{19}$H$_{18}$NS$_2$^{+} (M+H)$^+$ 324.0881, found 324.0881.
**syn-3-Benzyl-5-(hepta-1,2-dien-1-yl)thiazolidine-2-thione (3v)**

12.1 mg, 40% yield, d.r. 9:1, yellow oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.40 – 7.30 (m, 5H), 5.35 – 5.31 (m, 1H), 5.23 – 5.16 (m, 1H), 5.10 (d, $J = 14.6$ Hz, 1H), 4.85 (d, $J = 14.6$ Hz, 1H), 4.25 – 4.13 (m, 1H), 4.00 (dd, $J = 11.5$, 7.8 Hz, 1H), 3.79 (dd, $J = 11.5$, 6.3 Hz, 1H), 2.03 – 1.87 (m, 2H), 1.35 – 1.28 (m, 4H), 0.88 (t, $J = 6.9$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) (two aromatic carbon missing) δ 203.9, 196.5, 135.1, 128.9, 128.2(2), 128.1(8), 95.4, 90.4, 60.8, 42.7, 30.9, 28.1, 22.1, 13.7. HRMS (ESI-TOF) m/z calcd for C$_{17}$H$_{22}$NS$_2$ (M+H)$^+$ 304.1194, found 304.1198.

**3-Benzyl-5-methyl-5-(propa-1,2-dien-1-yl)thiazolidine-2-thione (3w)**

11.7 mg, 45% yield, yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.47 – 7.33 (m, 5H), 5.38 (t, $J = 6.6$ Hz, 1H), 5.12 (d, $J = 14.5$ Hz, 1H), 5.02 – 4.81 (m, 3H), 3.89 (d, $J = 11.4$ Hz, 1H), 3.64 (d, $J = 11.4$ Hz, 1H), 1.56 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) (two aromatic carbon missing) δ 207.1, 196.5, 135.1, 128.4, 128.3, 95.5, 79.9, 66.4, 52.6, 50.9, 25.9. HRMS (ESI-TOF) m/z calcd for C$_{14}$H$_{16}$NS$_2$ (M+H)$^+$ 262.0724, found 262.0728.

**3-Benzyl-5-(buta-2,3-dien-2-yl)thiazolidine-2-thione (3x)**

13.5 mg, 52% yield, yellow solid, mp = 86.6-87.5 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.50 – 7.28 (m, 5H), 4.99 (d, $J = 14.4$ Hz, 1H), 4.93 (d, $J = 14.4$ Hz, 1H), 4.75 – 4.68 (m, 1H), 4.66 – 4.57 (m, 1H), 4.10 – 4.05 (m, 1H), 4.01 (dd, $J = 11.5$, 7.8 Hz, 1H), 3.93 (dd, $J = 11.5$, 4.5 Hz, 1H), 1.69 (t, $J = 3.1$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) (two aromatic carbon missing) δ 205.4, 195.7, 134.9, 128.9, 128.5, 128.3, 97.7, 77.8, 59.4, 52.7, 45.6, 16.1. HRMS (ESI-TOF) m/z calcd for C$_{14}$H$_{16}$NS$_2$ (M+H)$^+$ 262.0724, found 262.0725.

**3-Benzyl-5-(3-(trimethylsilyl)prop-2-yn-1-yl)thiazolidine-2-thione (3y)**
28.4 mg, 89% yield, white solid, mp = 116.7-117.4 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.50 – 7.29 (m, 5H), 5.04 (d, $J$ = 14.6 Hz, 1H), 4.97 (d, $J$ = 14.6 Hz, 1H), 4.02 (dd, $J$ = 11.8, 3.9 Hz, 1H), 3.79 – 3.63 (m, 1H), 2.65 – 2.46 (m, 2H), 0.14 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) (two aromatic carbon missing) δ 195.9, 135.0, 129.0, 128.3, 128.2, 101.4, 88.1, 59.9, 52.6, 41.6, 26.4, 0.1. HRMS (ESI-TOF) m/z calcd for C$_{16}$H$_{22}$NSiS$_2$ $^{+}$ (M+H)$^+$ 320.0967, found 320.0963.

3-Benzy l-6-(prop-2-yn-1-yl)-1,3-thiazinane-2-thione (3z)
15.7 mg, 60% yield, light green solid, mp = 69.4-70.8 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.48 – 7.29 (m, 5H), 5.49 (t, $J$ = 14.6 Hz, 1H), 5.29 (t, $J$ = 15.1 Hz, 1H), 4.57 – 4.39 (m, 1H), 3.72 – 3.38 (m, 3H), 2.84 – 2.55 (m, 2H), 2.45 – 2.31 (m, 1H), 2.25 – 2.06 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) (two aromatic carbon missing) δ 192.2 (192.0), 135.04 (135.01), 128.91 (128.93), 128.1 (128.09), 81.2 (81.0), 76.0 (75.6), 64.5 (64.0), 57.7, 52.1 (51.2), 48.6 (48.4), 26.3 (25.2). HRMS (ESI-TOF) m/z calcd for C$_{14}$H$_{16}$NS $^+$ (M+H)$^+$ 262.0719, found 262.0724.

Dimethyl 2-(4-(3-benzyl-2-thioxothiazolidin-5-yl)buta-2,3-dien-1-yl)malonate (4)
41.6 mg, 71% yield, d.r. 1:2:1, colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39 – 7.31 (m, 5H), 5.39 – 5.15 (m, 2H), 5.09 – 4.97 (m, 1H), 4.90 (dd, $J$ = 14.5, 6.3 Hz, 1H), 4.19 – 4.08 (m, 1H), 4.06 – 3.95 (m, 1H), 3.82 – 3.74 (m, 1H), 3.71 (d, $J$ = 2.1 Hz, 6H), 3.45 – 3.37 (m, 1H), 2.58 – 2.51 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) (two aromatic carbon missing) δ 204.3 (203.6), 196.2 (195.8), 169.0 (168.9), 135.1 (135.0), 129.0 (128.9), 128.4, 128.3 (128.2), 92.4 (92.0), 91.6 (92.1), 60.8 (60.1), 52.71 (52.67), 52.6 (52.5), 50.8 (50.6), 42.6 (42.0), 27.5 (27.4). HRMS (ESI-TOF) m/z calcd for C$_{19}$H$_{22}$NO$_4$S$_2$ $^+$ (M+H)$^+$ 392.0985, found 392.0982.

3-Benzyl-5(2-methylbuta-1,3-dien-1-yl)thiazolidine-2-thione (5)
17.9 mg, 65% yield, d.r. 9:1, light yellow solid, mp = 83.8-84.6 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.42 – 7.29 (m, 5H), 6.57 (dd, $J$ = 17.1, 10.9 Hz, 1H), 5.41 – 5.27 (m, 2H), 5.27 – 5.18 (m, 1H), 5.02 (d, $J$ = 14.6 Hz, 2H), 4.96 (d, $J$ = 14.6 Hz, 2H), 4.86 – 4.74 (m, 1H), 3.98 (dd, $J$ = 11.5, 7.8 Hz, 1H), 3.66 (dd, $J$ = 11.4, 8.1 Hz, 1H), 1.81 (d,
$J = 1.4$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) (two aromatic carbon missing) $\delta$ 197.1, 137.4, 135.0, 132.0, 129.0, 128.2(9), 128.2(6), 124.9, 117.5, 61.3, 52.6, 40.7, 19.8. HRMS (ESI-TOF) m/z calcd for C$_{15}$H$_{18}$NS$_2$ $^+$ (M+H)$^+$ 276.0876, found 276.0870.

\[
\begin{align*}
\text{syn-3-(4-Methylbenzyl)-5-((S)-3-phenylpropa-1,2-dien-1-yl)oxazolidin-2-one (6)}
\end{align*}
\]
19.5 mg, 67% yield, d.r. 4.5:1, yellow sticky oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37 – 7.27 (m, 2H), 7.27 – 7.20 (m, 3H), 7.20 – 7.10 (m, 4H), 6.28 (dd, $J = 6.4$, 1.8 Hz, 1H), 5.93 – 5.72 (m, 1H), 5.10 – 5.00 (m, 1H), 4.39 (s, 2H), 3.61 – 3.50 (m, 1H), 3.35 – 3.22 (m, 1H), 2.35 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) (two aromatic carbon missing) $\delta$ 205.8, 157.5, 137.8, 132.6, 132.4, 129.6, 129.5, 128.8, 128.2, 127.8, 127.1, 98.4, 94.5, 71.1, 48.6, 48.0, 21.1. HRMS (ESI-TOF) m/z calcd for C$_{20}$H$_{20}$NO$_2$ $^+$ (M+H)$^+$ 306.1489, found 306.1485.

10 Single crystal X-ray diffraction data of 3o

\[\text{Figure S1. ORTEP diagram of 3o (CCDC: 2348815). Thermal ellipsoids are shown at the 30% probability level.}\]
### Table S3. Crystal data and structure refinement for 3o.

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<tr>
<th>Identification code</th>
<th>3o</th>
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<td>C(<em>{16})H(</em>{17})NO(_2)S(_2)</td>
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<td>Temperature [K]</td>
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<td>(a) [Å]</td>
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<tr>
<td>(b) [Å]</td>
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<td>(c) [Å]</td>
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<td>(\gamma) [°]</td>
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<td>(\mu) [mm(^{-1})]</td>
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<td>(F(000))</td>
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<td>Crystal colour</td>
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<td>Crystal shape</td>
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<td>Radiation</td>
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<td>Independent reflections</td>
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<td>Goodness-of-fit on (F^2)</td>
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<td>Final (R) indexes [(I \geq 2\sigma(I))]</td>
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<td>Final (R) indexes [all data]</td>
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11 Reference:


12 NMR Spectra
2b
dr > 20:1
Me

2c
dr > 20:1

S34
S36

2d

$\text{dr} > 20:1$
2g  
\text{dr 15:1}
S43
dr > 20:1
2I (major isomer)
21 (major isomer)
2m

dr 12:1
2n

dr > 20:1
Cl\text{-} \text{N}-\text{O} \quad 2\alpha
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2q
dr 18:1
$\text{2r}$

$\text{dr 11:1}$
3d
S113
S120
6

dr 4.5:1