Supporting Information

Iridium and Brønsted Acid Cooperatively Catalyzed Chemodivergent and Stereoselective Reactions of Vinyl Benzoxazinones with Azlactones

Meng Sun, Xiao Wan, Si-Jia Zhou, Guang-Jian Mei and Feng Shi*

School of Chemistry and Materials Science, Jiangsu Normal University, Xuzhou 221116, China

E-mail: fshi@jsnu.edu.cn

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1. General information

$^1$H and $^{13}$C NMR spectra were measured at 400 and 100 MHz, respectively. The solvent used for NMR spectroscopy was CDCl$_3$, using tetramethylsilane as the internal reference. HRMS (ESI) was determined by a HRMS/MS instrument. Enantiomeric ratios ($er$) were determined by chiral high-performance liquid chromatography (chiral HPLC). The chiral columns used for the determination of Enantiomeric ratios by chiral HPLC were Chiralpak columns. Optical rotation values were measured with instruments operating at $\lambda = 589$ nm, corresponding to the sodium D line at the temperatures indicated. The X-ray source used for the single crystal X-ray diffraction analysis of compounds 3aa and chiral 3aa was a MoK$_\alpha$ ($\lambda = 0.71073$), and the thermal ellipsoid was drawn at the 30% probability level. Analytical grade solvents for the column chromatography were distilled before use. All starting materials commercially available were used directly. Substrates 1 were synthesized according to the literature method.$^1$

2. Screening of catalysts and condition optimization

Table S1. Condition optimization for $[4+2]$ cycloaddition$^a$

<table>
<thead>
<tr>
<th>entry</th>
<th>metal</th>
<th>B-H</th>
<th>solvent</th>
<th>$1a:2a$</th>
<th>$\text{dr}^b$</th>
<th>yield (%)$^c$</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>[Ir(cod)Cl]$_2$</td>
<td>-</td>
<td>toluene (0.1 M)</td>
<td>1:1</td>
<td>64:36</td>
<td>84</td>
</tr>
<tr>
<td>2</td>
<td>Pd(PPh$_3$)$_4$</td>
<td>-</td>
<td>toluene (0.1 M)</td>
<td>1:1</td>
<td>&gt;95:5</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>[Ir(cod)Cl]$_2$</td>
<td>-</td>
<td>THF (0.1 M)</td>
<td>1:1</td>
<td>72:28</td>
<td>85</td>
</tr>
<tr>
<td>4</td>
<td>[Ir(cod)Cl]$_2$</td>
<td>-</td>
<td>acetone (0.1 M)</td>
<td>1:1</td>
<td>75:25</td>
<td>92</td>
</tr>
<tr>
<td>5</td>
<td>[Ir(cod)Cl]$_2$</td>
<td>-</td>
<td>EtOAc (0.1 M)</td>
<td>1:1</td>
<td>72:28</td>
<td>89</td>
</tr>
<tr>
<td>6</td>
<td>[Ir(cod)Cl]$_2$</td>
<td>-</td>
<td>CH$_2$Cl$_2$ (0.1 M)</td>
<td>1:1</td>
<td>60:40</td>
<td>60</td>
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<td>7</td>
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<td>-</td>
<td>MeCN (0.1 M)</td>
<td>1:1</td>
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<td>9</td>
<td>[Ir(cod)Cl]$_2$</td>
<td></td>
<td>acetone (0.1 M)</td>
<td>1:1</td>
<td>75:25</td>
<td>30</td>
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<td>10</td>
<td>[Ir(cod)Cl]$_2$</td>
<td>AcOH</td>
<td>acetone (0.1 M)</td>
<td>1:1</td>
<td>72:28</td>
<td>80</td>
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<td>11</td>
<td>[Ir(cod)Cl]$_2$</td>
<td>PhCO$_2$H</td>
<td>acetone (0.1 M)</td>
<td>1:1</td>
<td>80:20</td>
<td>75</td>
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<td>12</td>
<td>[Ir(cod)Cl]$_2$</td>
<td>TsOH·H$_2$O</td>
<td>acetone (0.1 M)</td>
<td>1:1</td>
<td>94:6</td>
<td>67</td>
</tr>
<tr>
<td>13</td>
<td>[Ir(cod)Cl]$_2$</td>
<td>TsOH·H$_2$O</td>
<td>acetone (0.05 M)</td>
<td>1:1</td>
<td>94:6</td>
<td>67</td>
</tr>
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<td>14</td>
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<td>acetone (0.025 M)</td>
<td>1:1</td>
<td>94:6</td>
<td>80</td>
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<tr>
<td>15</td>
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<td>acetone (0.013 M)</td>
<td>1:1</td>
<td>94:6</td>
<td>70</td>
</tr>
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</table>

The reaction was conducted at the 0.05 mmol scale in a solvent at 25 °C for 1.5 h. The dr value was determined by 1H NMR spectroscopy. Isolated yield.

**Table S2.** Condition optimization for catalytic asymmetric [4+2] cycloaddition

<table>
<thead>
<tr>
<th>entry</th>
<th>chiral catalyst</th>
<th>solvent</th>
<th>T (°C)</th>
<th>1a:2a</th>
<th>yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>dr&lt;sup&gt;c&lt;/sup&gt;</th>
<th>er&lt;sup&gt;d&lt;/sup&gt;</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>L1</td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>78</td>
<td>67:33</td>
<td>54:46</td>
</tr>
<tr>
<td>2</td>
<td>L2</td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>83</td>
<td>85:15</td>
<td>51:49</td>
</tr>
<tr>
<td>3</td>
<td>L3</td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>74</td>
<td>50:50</td>
<td>50:50</td>
</tr>
<tr>
<td>4</td>
<td>L4</td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>89</td>
<td>70:30</td>
<td>51:49</td>
</tr>
<tr>
<td>5</td>
<td>L5</td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>86</td>
<td>86:14</td>
<td>52:48</td>
</tr>
<tr>
<td>6</td>
<td>L6</td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>75</td>
<td>84:16</td>
<td>50:50</td>
</tr>
<tr>
<td>7</td>
<td>L7</td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>87</td>
<td>85:15</td>
<td>51:49</td>
</tr>
<tr>
<td>8</td>
<td>L8</td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>83</td>
<td>81:19</td>
<td>51:49</td>
</tr>
<tr>
<td>9</td>
<td>L9</td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>85</td>
<td>82:18</td>
<td>50:50</td>
</tr>
<tr>
<td>10</td>
<td>L10</td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>82</td>
<td>84:16</td>
<td>50:50</td>
</tr>
<tr>
<td>11</td>
<td>L11</td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>86</td>
<td>81:19</td>
<td>50:50</td>
</tr>
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<td>12</td>
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<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>89</td>
<td>83:17</td>
<td>50:50</td>
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<tr>
<td>13</td>
<td><strong>L13</strong></td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>60</td>
<td>79:21</td>
<td>75:25</td>
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<tr>
<td>14</td>
<td><strong>L14</strong></td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>75</td>
<td>80:20</td>
<td>54:46</td>
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<tr>
<td>15</td>
<td><strong>L15</strong></td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>63</td>
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<td>53:47</td>
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<tr>
<td>16</td>
<td><strong>L16</strong></td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>69</td>
<td>75:25</td>
<td>54:46</td>
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<tr>
<td>17</td>
<td><strong>L17</strong></td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>83</td>
<td>77:23</td>
<td>57:43</td>
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<tr>
<td>18</td>
<td><strong>L18</strong></td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>63</td>
<td>79:21</td>
<td>53:47</td>
</tr>
<tr>
<td>19</td>
<td><strong>L19</strong></td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>69</td>
<td>75:25</td>
<td>54:46</td>
</tr>
<tr>
<td>20</td>
<td><strong>L20</strong></td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>83</td>
<td>77:23</td>
<td>57:43</td>
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<tr>
<td>21</td>
<td><strong>L20</strong></td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>86</td>
<td>75:25</td>
<td>54:46</td>
</tr>
<tr>
<td>22</td>
<td><strong>L20</strong></td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>85</td>
<td>75:25</td>
<td>54:46</td>
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<tr>
<td>23</td>
<td><strong>L20</strong></td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>80</td>
<td>75:25</td>
<td>54:46</td>
</tr>
<tr>
<td>24</td>
<td><strong>L20</strong></td>
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<td>25</td>
<td>1:1.5</td>
<td>83</td>
<td>77:23</td>
<td>57:43</td>
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<tr>
<td>25</td>
<td><strong>L20</strong></td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>86</td>
<td>79:21</td>
<td>57:43</td>
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<td>26</td>
<td><strong>L20</strong></td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>86</td>
<td>79:21</td>
<td>57:43</td>
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<tr>
<td>27</td>
<td><strong>L20</strong></td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>85</td>
<td>75:25</td>
<td>54:46</td>
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<tr>
<td>28</td>
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<td>25</td>
<td>1:1.5</td>
<td>83</td>
<td>77:23</td>
<td>57:43</td>
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<tr>
<td>29</td>
<td><strong>L20</strong></td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>83</td>
<td>77:23</td>
<td>57:43</td>
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<td>30</td>
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<td>79:21</td>
<td>57:43</td>
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<td>31</td>
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<td>88</td>
<td>79:21</td>
<td>57:43</td>
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<td>32</td>
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<td>1:1.5</td>
<td>86</td>
<td>79:21</td>
<td>57:43</td>
</tr>
<tr>
<td>33</td>
<td><strong>L20</strong></td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>84</td>
<td>81:19</td>
<td>64:36</td>
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<tr>
<td>34</td>
<td><strong>L20</strong></td>
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<td>25</td>
<td>1:1.5</td>
<td>83</td>
<td>81:19</td>
<td>64:36</td>
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<tr>
<td>35</td>
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<td>1:1.5</td>
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<td>81:19</td>
<td>64:36</td>
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<tr>
<td>36</td>
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<td>PhMe (0.5 mL)</td>
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<td>1:1.5</td>
<td>83</td>
<td>81:19</td>
<td>64:36</td>
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<td>37</td>
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<td>81:19</td>
<td>64:36</td>
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<tr>
<td>38</td>
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<td>83</td>
<td>81:19</td>
<td>64:36</td>
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<tr>
<td>39</td>
<td><strong>L20</strong></td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>83</td>
<td>81:19</td>
<td>64:36</td>
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<tr>
<td>40</td>
<td><strong>L20</strong></td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>83</td>
<td>81:19</td>
<td>64:36</td>
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<tr>
<td>41</td>
<td><strong>L20</strong></td>
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<td>25</td>
<td>1:1.5</td>
<td>83</td>
<td>81:19</td>
<td>64:36</td>
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<tr>
<td>42</td>
<td><strong>L20</strong></td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>83</td>
<td>81:19</td>
<td>64:36</td>
</tr>
<tr>
<td>43</td>
<td><strong>L20</strong></td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>83</td>
<td>81:19</td>
<td>64:36</td>
</tr>
<tr>
<td>44</td>
<td><strong>L20</strong></td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>83</td>
<td>81:19</td>
<td>64:36</td>
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<tr>
<td>45</td>
<td><strong>L20</strong></td>
<td>PhMe (0.5 mL)</td>
<td>25</td>
<td>1:1.5</td>
<td>83</td>
<td>81:19</td>
<td>64:36</td>
</tr>
</tbody>
</table>

*The reaction was carried out at the 0.05 mmol scale in a solvent at T °C for 1.5 h. Isolated yield. The dr value was determined by ^1H NMR spectroscopy. The er value was determined by HPLC and referred to that of the major diastereomer.

We performed a preliminary investigation on the catalytic asymmetric version of the formal [4+2] cycloaddition (Scheme S1). After condition optimization (Table S2), we found that the cooperative catalytic system of iridium and chiral thiourea-tertiary amine **L20** could promote the...
reaction to provide a chiral 3aa in a high yield (80%), a considerable diastereoselectivity of 84:16 dr and a high enantioselectivity of 93:7 er. Under the optimal conditions, several chiral products of 3 were synthesized in moderate to good diastereo- and enantioselectivities. A possible activation mode of the cooperative catalysis was suggested to explain the generation of chiral 3aa with the observed (3R,4S)-configuration. The iridium catalyst and chiral thiourea-tertiary amine catalyst simultaneously activated the two reaction partners, and the enantioselectivity was achieved by the stereocontrol of the chiral thiourea-tertiary amine on the azlactones via hydrogen-bonding interactions. Therefore, the catalytic asymmetric version also provided a cooperative catalysis-enabled reaction for vinyl benzoxazinanones. Notably, this reaction has established a scarcely reported cooperative catalysis of iridium and chiral H-bonding catalyst.

Scheme S1. Investigation on the catalytic asymmetric version.
3. Effect of the C4-substituent of azlactones on the chemoselectivity and the generality of the substitution reactions

As suggested in Scheme S2, when azlactone 4a attacked the π-allyl-Ir intermediate, the branch-selective allylic alkylation was unfavored due to the existence of the bulky C4-phenyl group. In contrast, the linear-selective allylic alkylation was favored because there was less steric hindrance when azlactone 4a attacked the π-allyl-Ir intermediate from the terminal position. Thus, the favored linear-selective allylic alkylation resulted in the formation of 5aa. However, apart from steric effect, the softness/hardness of azlactones 4 bearing different C4-substituents should also account for the observed chemoselectivity.

Scheme S2. Effect of the C4-substituent of azlactones on the chemoselectivity.

Table S3. Generality of the substitution reactions

<table>
<thead>
<tr>
<th>entry</th>
<th>5</th>
<th>R¹(1)</th>
<th>R/Ar (4)</th>
<th>E/Z⁶</th>
<th>yield (%) ⁷</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5aa</td>
<td>H (1a)</td>
<td>Ph/Ph (4a)</td>
<td>83:17</td>
<td>92</td>
</tr>
<tr>
<td>2</td>
<td>5ab</td>
<td>H (1a)</td>
<td>o-ClC₆H₄/Ph (4b)</td>
<td>95:5</td>
<td>95</td>
</tr>
<tr>
<td>3</td>
<td>5ac</td>
<td>H (1a)</td>
<td>m-ClC₆H₄/Ph (4c)</td>
<td>91:9</td>
<td>51</td>
</tr>
<tr>
<td>4</td>
<td>5ad</td>
<td>H (1a)</td>
<td>p-MeC₆H₄/Ph (4d)</td>
<td>91:9</td>
<td>87</td>
</tr>
<tr>
<td>5</td>
<td>5ae</td>
<td>H (1a)</td>
<td>Ph/m-ClC₆H₄ (4e)</td>
<td>83:17</td>
<td>95</td>
</tr>
<tr>
<td>6</td>
<td>5af</td>
<td>H (1a)</td>
<td>Ph/p-FC₆H₄ (4f)</td>
<td>83:17</td>
<td>83</td>
</tr>
<tr>
<td>7</td>
<td>5da</td>
<td>6-Me (1d)</td>
<td>Ph/Ph (4a)</td>
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<td>Ph/Ph (4a)</td>
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<td>5fa</td>
<td>6-F (1f)</td>
<td>Ph/Ph (4a)</td>
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<td>Ph/Ph (4a)</td>
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<td>5ha</td>
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<td>Ph/Ph (4a)</td>
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<td>12</td>
<td>5ia</td>
<td>7-F (1i)</td>
<td>Ph/Ph (4a)</td>
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<td>93</td>
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</table>

⁶The reaction was carried out at the 0.1 mmol scale in acetone (0.025 M) at 25 °C for 1.5 h, and the molar ratio of 1:4 was 1:1.5. ⁷The E/Z value was determined by ¹H NMR spectroscopy. ⁸Isolated yield.
4. Procedure for the synthesis of products 3 and characterization data

Under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1 (0.1 mmol), azlactone 2 (0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography to afford pure product 3.

**ethyl 3-benzamido-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3aa):**

Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1a (32.9 mg, 0.1 mmol), azlactone 2a (35 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 3aa (48.7 mg) in 94% yield as light yellow solid. m.p. 78-79 °C; inseparable diastereomers (dr= 94:6); ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 8.3 Hz, 2H), 7.74 (d, J = 8.1 Hz, 1H), 7.60 (d, J = 7.4 Hz, 2H), 7.51 – 7.46 (m, 1H), 7.40 – 7.34 (m, 5H), 7.20 (d, J = 7.5 Hz, 1H), 7.14 (d, J = 7.6 Hz, 1H), 7.03 (s, 1H), 5.82 – 5.69 (m, 1H), 5.47 (d, J = 10.1 Hz, 1H), 5.33 (d, J = 16.9 Hz, 1H), 4.97 (d, J = 9.5 Hz, 1H), 4.01 – 3.91 (m, 1H), 3.86 – 3.76 (m, 1H), 2.47 (s, 3H), 0.71 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.1, 165.9, 165.4, 145.1, 135.6, 135.1, 133.4, 131.9, 130.9, 129.7, 129.3, 128.5, 128.3, 127.6, 126.9, 126.2, 126.1, 123.7, 122.2, 68.3, 62.9, 45.5, 21.8, 13.2; IR (KBr): 2986, 1733, 1669, 1506, 1265, 1159, 933, 740 cm⁻¹; HRMS (ESI-TOF) m/z: [M - H]⁺ Calcd for C₂₈H₂₅N₂O₆S 517.1434, found 517.1422.

**ethyl 3-benzamido-5-methyl-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ba):** Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to
the mixture of vinyl benzoxazinanone 1b (34.3 mg, 0.1 mmol), azlactone 2a (35 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 3ba (45.8 mg) in 86% yield as light yellow solid.

m.p. 85-86 °C; inseparable diastereomers (dr > 95:5); ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 8.2 Hz, 1H), 7.49 – 7.26 (m, 7H), 7.22 (t, J = 8.0 Hz, 1H), 7.02 (d, J = 7.6 Hz, 1H), 6.68 (s, 1H), 6.11 – 5.98 (m, 1H), 5.12 – 4.94 (m, 2H), 4.43 (d, J = 7.5 Hz, 1H), 4.32 – 4.13 (m, 2H), 2.45 (s, 3H), 2.25 (s, 3H), 1.21 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 162.7, 161.7, 160.4, 140.5, 131.6, 131.3, 130.6, 128.6, 128.5, 127.2, 124.7, 124.6, 123.8, 122.7, 122.5, 122.1, 116.0, 113.7, 100.0, 63.0, 57.9, 43.2, 17.0, 14.3, 9.1; IR (KBr): 2962, 1735, 1654, 1473, 1260, 1085, 798, 668 cm⁻¹; HRMS (ESI-TOF) m/z: [M - H]⁻ Calcd for C₂₉H₂₇N₂O₆S 531.1590, found 531.1598.

ethyl 3-benzamido-5-chloro-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ca): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1c (36.3 mg, 0.1 mmol), azlactone 2a (35 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 3ca (44.2 mg) in 80% yield as light yellow solid.

m.p. 74-75 °C; inseparable diastereomers (dr > 95:5); ¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, J = 8.1 Hz, 2H), 7.55 – 7.41 (m, 4H), 7.41 – 7.30 (m, 4H), 7.25 – 7.15 (m, 2H), 6.99 (s, 1H), 6.07 – 5.92 (m, 1H), 5.21 (d, J = 16.9 Hz, 1H), 5.11 (d, J = 10.1 Hz, 1H), 4.40 (d, J = 8.8 Hz, 1H), 4.32 – 4.14 (m, 2H), 2.46 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.0, 161.3, 160.6, 140.5, 132.6, 131.6, 128.3, 128.1, 127.7, 127.3, 124.9, 124.2, 123.8, 122.3, 116.1, 114.0, 62.9, 58.4, 46.1, 17.0, 9.0; IR (KBr): 2917, 1738, 1650, 1454, 1259, 1169, 992, 749 cm⁻¹; HRMS (ESI-TOF) m/z: [M - H]⁻ Calcd for C₂₉H₂₇ClN₂O₆S 551.1044, found 551.1041.
ethyl 3-benzamido-6-methyl-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3da): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1d (34.3 mg, 0.1 mmol), azlactone 2a (35 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 3da (44.2 mg) in 83% yield as light yellow solid.

m.p. 80–81 °C; inseparable diastereomers (dr > 95:5); ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, J = 8.3 Hz, 2H), 7.65 – 7.57 (m, 3H), 7.51 – 7.46 (m, 1H), 7.42 – 7.33 (m, 4H), 7.17 (d, J = 8.3 Hz, 1H), 7.00 (s, 1H), 6.94 (s, 1H), 5.84 – 5.70 (m, 1H), 5.47 (d, J = 10.1 Hz, 1H), 5.32 (d, J = 16.8 Hz, 1H), 4.90 (d, J = 9.4 Hz, 1H), 4.04 – 3.91 (m, 1H), 3.84 – 3.74 (m, 1H), 2.47 (s, 3H), 2.34 (s, 3H), 0.73 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.2, 165.9, 165.4, 145.0, 135.9, 135.7, 133.4, 132.6, 131.9, 131.1, 129.6, 129.2, 128.5, 128.1, 128.0, 127.0, 126.7, 123.5, 122.1, 68.3, 62.9, 45.6, 21.7, 21.0, 13.2; IR (KBr): 3126, 1733, 1669, 1399, 1172, 1086, 811, 668 cm⁻¹; HRMS (ESI-TOF) m/z: [M - H] Calcd for C₂₉H₂₇N₂O₆S 531.1590, found 531.1600.

ethyl 3-benzamido-6-methoxy-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ea): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1e (35.9 mg, 0.1 mmol), azlactone 2a (35 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 3ea (46.1 mg) in 84% yield as light yellow solid.

m.p. 78–79 °C; inseparable diastereomers (dr > 95:5); ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, J = 8.3 Hz, 2H), 7.65 (d, J = 8.9 Hz, 1H), 7.60 (d, J = 7.3 Hz, 2H), 7.51 – 7.46 (m, 1H), 7.42 – 7.33 (m, 4H), 7.01 (s, 1H), 6.92 – 6.85 (m, 1H), 6.69 (d, J = 1.9 Hz, 1H), 5.82 – 5.68 (m, 1H), 5.46 (d,
J = 10.1 Hz, 1H), 5.31 (d, J = 16.8 Hz, 1H), 4.89 (d, J = 8.9 Hz, 1H), 4.04 – 3.93 (m, 1H), 3.90 – 3.81 (m, 1H), 3.80 (s, 3H), 2.47 (s, 3H), 0.78 (t, J = 7.1 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 166.1, 165.9, 165.3, 157.7, 145.0, 135.6, 133.4, 131.9, 130.8, 130.0, 129.6, 129.2, 128.5, 128.1, 127.0, 123.8, 123.5, 112.5, 111.8, 68.3, 62.9, 55.6, 45.7, 21.7, 13.3; IR (KBr): 2982, 1733, 1670, 1489, 1219, 1152, 936, 710 cm
-1; HRMS (ESI-TOF) m/z: [M - H] Calcd for C29H27N2O7S 547.1539, found 547.1536;

ethyl 3-benzamido-6-fluoro-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3fa):
Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1f (34.7 mg, 0.1 mmol), azlactone 2a (35 mg, 0.15 mmol), [Ir(COD)Cl]2 (3.4 mg, 0.005 mmol) and TsOH·H2O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 3fa (49.8 mg) in 93% yield as light yellow solid.
m.p. 83-84 °C; inseparable diastereomers (dr =95:5); 1H NMR (400 MHz, CDCl3) δ 8.05 (d, J = 8.3 Hz, 2H), 7.75 – 7.69 (m, 1H), 7.58 (d, J = 7.4 Hz, 2H), 7.52 – 7.46 (t, J = 7.3 Hz, 1H), 7.42 – 7.35 (m, 4H), 7.12 – 7.03 (m, 2H), 6.93 – 6.85 (m, 1H), 5.75 – 5.59 (m, 1H), 5.48 (d, J = 10.1 Hz, 1H), 5.33 (d, J = 16.8 Hz, 1H), 4.98 (d, J = 9.5 Hz, 1H), 4.08 – 3.95 (m, 1H), 3.91 – 3.81 (m, 1H), 2.48 (s, 3H), 0.79 (t, J = 7.1 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 165.9, 165.0, 160.6 (J = 250 Hz), 145.3, 135.3, 133.2, 132.0, 131.0, 130.2 129.8, 129.3, 128.5, 127.0, 124.3, 123.9 (J = 10 Hz), 114.2, 114.0, 113.5 (J = 20 Hz), 68.2, 63.2, 45.3, 21.8, 13.3; IR (KBr): 2978, 1744, 1671, 1487, 1367, 1173, 931, 708 cm
-1; HRMS (ESI-TOF) m/z: [M - H] Calcd for C28H24FN2O6S 535.1339, found 535.1330;

ethyl 3-benzamido-6-chloro-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ga):
Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1g (36.3 mg, 0.1 mmol), azlactone 2a (35 mg, 0.15 mmol), [Ir(COD)Cl]2 (3.4 mg, 0.005 mmol) and TsOH·H2O (4.0 mg, 0.02 mmol). Then, the reaction
mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 3ga (45.8 mg) in 83% yield as light yellow solid.

m.p.74-75 °C; inseparable diastereomers (dr > 95:5); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, $J$ = 8.3 Hz, 2H), 7.70 (d, $J$ = 8.7 Hz, 1H), 7.57 (d, $J$ = 7.3 Hz, 2H), 7.52 – 7.47 (m, 1H), 7.43 – 7.31 (m, 5H), 7.13 (s, 1H), 7.09 (s, 1H), 5.73 – 5.59 (m, 1H), 5.49 (d, $J$ = 10.0 Hz, 1H), 5.33 (d, $J$ = 16.7 Hz, 1H), 4.99 (d, $J$ = 9.6 Hz, 1H), 4.09 – 3.98 (m, 1H), 3.91 – 3.80 (m, 1H), 2.48 (s, 3H), 0.79 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.9, 165.8, 164.9, 145.4, 135.1 133.6, 133.2, 132.0, 131.7, 130.5, 130.1, 129.9, 129.3, 128.5, 127.4, 126.9, 126.3, 124.5, 123.4, 68.1, 63.3, 45.2, 21.8, 13.3; IR (KBr): 3124, 1734, 1670, 1479, 1399, 1154, 935, 810 cm$^{-1}$; HRMS (ESI-TOF) m/z: [M - H] Calcd for C$_{28}$H$_{24}$ClN$_2$O$_6$S 551.1044, found 551.1040.

ethyl 3-benzamido-6-bromo-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ha): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoazinanone 1h (40.6 mg, 0.1 mmol), azlactone 2a (35 mg, 0.15 mmol), [Ir(COD)Cl]$_2$ (3.4 mg, 0.005 mmol) and TsOH.H$_2$O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 3ha (54.8 mg) in 92% yield as light yellow solid.

m.p. 80-81 °C; inseparable diastereomers (dr > 95:5); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, $J$ = 8.3 Hz, 2H), 7.64 (d, $J$ = 8.7 Hz, 1H), 7.57 (d, $J$ = 7.3 Hz, 2H), 7.52 – 7.47 (m, 2H), 7.42 – 7.36 (m, 4H), 7.27 (s, 1H), 7.09 (s, 1H), 5.73 – 5.58 (m, 1H), 5.49 (d, $J$ = 10.0 Hz, 1H), 5.33 (d, $J$ = 16.7 Hz, 1H), 4.99 (d, $J$ = 9.5 Hz, 1H), 4.10 – 3.99 (m, 1H), 3.91 – 3.80 (m, 1H), 2.48 (s, 3H), 0.79 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.8, 164.8, 145.4, 135.1, 134.1, 133.2, 132.0, 130.7, 130.4, 130.0, 129.9, 129.3, 129.2, 128.5, 126.9, 124.5, 123.7, 119.5, 68.2, 63.3, 45.1, 21.8, 13.3; IR (KBr): 2983, 1734, 1670, 1476, 1362, 1155, 1085, 933, 749 cm$^{-1}$; HRMS (ESI-TOF) m/z: [M - H] Calcd for C$_{28}$H$_{24}$BrN$_2$O$_6$S 595.0539, found 595.0544.
ethyl 3-benzamido-7-fluoro-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ia): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1i (34.7 mg, 0.1 mmol), azlactone 2a (35 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 3ia (48.2 mg) in 90% yield as light yellow solid.

m.p. 129-130 °C; inseparable diastereomers (dr = 92:8); ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 8.3 Hz, 2H), 7.60 (d, J = 7.5 Hz, 2H), 7.57 – 7.52 (m, 1H), 7.52 – 7.47 (m, 1H), 7.42 – 7.36 (m, 4H), 7.13 – 7.07 (m, 1H), 7.05 (s, 1H), 6.97 – 6.90 (m, 1H), 5.78 – 5.63 (m, 1H), 5.47 (d, J = 10.0 Hz, 1H), 5.32 (d, J = 16.8 Hz, 1H), 4.92 (d, J = 9.5 Hz, 1H), 4.07 – 3.96 (m, 1H), 3.89 – 3.80 (m, 1H), 2.48 (s, 3H), 0.79 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.0, 165.9, 165.1, 161.7 (J = 240 Hz), 145.4, 145.3, 135.3, 133.2, 132.0, 130.6 (J = 10 Hz), 129.7, 129.4, 128.5, 127.3 (J = 10 Hz), 126.7, 124.1, 124.0, 112.6 (J = 20 Hz), 110.2 (J = 30 Hz), 68.2, 63.1, 45.0, 21.8, 13.3; IR (KBr): 2988, 1748, 1670, 1507, 1275, 1177, 847, 750 cm⁻¹; HRMS (ESI-TOF) m/z: [M-H]- Calcd for C₂₈H₂₄FN₂O₆S 535.1339, found 535.1351.

ethyl 3-benzamido-7-chloro-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ja): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1j (36.3 mg, 0.1 mmol), azlactone 2a (35 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 3ja (44.7 mg) in 81% yield as light yellow solid.

m.p. 72-73 °C; inseparable diastereomers (dr = 91:9); ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 1.6 Hz, 1H), 7.59 (d, J = 7.5 Hz, 2H), 7.52 – 7.47 (m, 1H), 7.42 – 7.36 (m, 4H), 7.23 – 7.18 (m, 1H), 7.13 – 7.01 (m, 2H), 5.76 – 5.62 (m, 1H), 5.47 (d, J = 10.0 Hz, 1H), 5.32 (d, J = 16.8 Hz, 1H), 4.95 (d, J = 9.6 Hz, 1H), 4.06 – 3.95 (m, 1H), 3.90 – 3.81 (m, 1H), 2.49
ethyl 3-benzamido-8-methyl-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ka): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoazinanone 1k (34.3 mg, 0.1 mmol), azlactone 2a (35 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 3ka (46.8 mg) in 88% yield as light yellow solid.

m.p. 79-80 °C; inseparable diastereomers (dr = 95:5); ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, J = 8.2 Hz, 2H), 7.57 (d, J = 7.4 Hz, 2H), 7.50 – 7.44 (m, 1H), 7.43 – 7.32 (m, 4H), 7.30 (d, J = 7.6 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.01 (d, J = 7.4 Hz, 1H), 6.57 (s, 1H), 6.08 – 5.91 (m, 1H), 5.48 (d, J = 10.1 Hz, 1H), 5.30 (d, J = 16.9 Hz, 1H), 4.41 (s, 1H), 3.88 – 3.73 (m, 2H), 2.61 (s, 3H), 2.50 (s, 3H), 0.79 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.9, 166.0, 165.9, 145.3, 135.8, 135.4, 134.7, 133.6, 131.9, 131.4, 131.1, 130.6, 130.1, 129.3, 128.5, 128.3, 128.2, 127.3, 126.6, 123.6, 123.2, 68.4, 62.6, 47.0, 21.8, 20.9, 13.1; IR (KBr): 2987, 1733, 1670, 1507, 1275, 1158, 936, 749 cm⁻¹; HRMS (ESI-TOF) m/z: [M - H]⁻ Calcd for C₂₉H₂₅ClN₂O₆S 551.1044, found 551.1062.

ethyl 3-benzamido-2-oxo-1-tosyl-6-(trifluoromethyl)-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3la): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoazinanone 1l (39.7 mg, 0.1 mmol), azlactone 2a (35 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol) Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 3la (46.8 mg) in 88% yield as light yellow solid.

m.p. 79-80 °C; inseparable diastereomers (dr = 95:5); ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, J = 8.2 Hz, 2H), 7.57 (d, J = 7.4 Hz, 2H), 7.50 – 7.44 (m, 1H), 7.43 – 7.32 (m, 4H), 7.30 (d, J = 7.6 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.01 (d, J = 7.4 Hz, 1H), 6.57 (s, 1H), 6.08 – 5.91 (m, 1H), 5.48 (d, J = 10.1 Hz, 1H), 5.30 (d, J = 16.9 Hz, 1H), 4.41 (s, 1H), 3.88 – 3.73 (m, 2H), 2.61 (s, 3H), 2.50 (s, 3H), 0.79 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.9, 166.0, 165.9, 145.3, 135.8, 135.4, 134.7, 133.6, 131.9, 131.4, 131.1, 130.6, 130.1, 129.3, 128.5, 128.3, 128.2, 127.3, 126.6, 123.6, 123.2, 68.4, 62.6, 47.0, 21.8, 20.9, 13.1; IR (KBr): 2987, 1733, 1670, 1507, 1275, 1158, 936, 749 cm⁻¹; HRMS (ESI-TOF) m/z: [M - H]⁻ Calcd for C₂₉H₂₅ClN₂O₆S 551.1590, found 551.1589.
chromatography (toluene/ethyl acetate = 20:1) to afford pure product \(3\text{la}\) (49.8 mg) in 85% yield as light yellow solid.

m.p. 89-90 °C; inseparable diastereomers (dr = 95:5); \(^1\)H NMR (400 MHz, CDCl \(_3\)) \(\delta\) 8.07 (d, \(J = 8.4\) Hz, 2H), 7.90 (d, \(J = 8.5\) Hz, 1H), 7.66 (d, \(J = 8.4\) Hz, 1H), 7.61 – 7.54 (m, 2H), 7.53 – 7.46 (m, 1H), 7.44 – 7.34 (m, 5H), 7.14 (s, 1H), 5.74 – 5.60 (m, 1H), 5.53 (dd, \(J = 10.0, 1.3\) Hz, 1H), 5.42 – 5.31 (m, 1H), 5.09 (d, \(J = 9.6\) Hz, 1H), 4.11 – 3.99 (m, 1H), 3.88 – 3.75 (m, 1H), 2.50 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl \(_3\)) \(\delta\) 165.9, 165.8, 164.9, 145.7, 138.0, 135.0, 133.2, 132.2, 130.2, 129.8, 129.6, 129.4, 128.7, 128.2 (\(J = 33\) Hz), 127.0, 125.0, 124.7 (\(J = 4\) Hz), 123.7 (\(J = 265\) Hz), 123.4 (\(J = 4\) Hz), 122.4, 68.2, 63.4, 45.2, 21.9, 13.2; IR (KBr): 2959, 1748, 1671, 1546, 1335, 1154, 935, 662 cm \(^{-1}\); HRMS (ESI-TOF) m/z: [M - H] \(^{-}\) Calcd for C\(_{29}\)H\(_{24}\)F\(_3\)N\(_2\)O\(_6\)S 585.1307, found 585.1321.

\textbf{ethyl 3-benzamido-2-oxo-1-tosyl-7-(trifluoromethyl)-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ma):} Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone \(1\text{m}\) (39.7 mg, 0.1 mmol), azlactone \(2\text{a}\) (35 mg, 0.15 mmol), [Ir(COD)Cl] \(_2\) (3.4 mg, 0.005 mmol) and TsOH \(\cdot\) H\(_2\)O (4.0 mg, 0.01 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product \(3\text{ma}\) (55.7 mg) in 95% yield as light yellow solid.

m.p. 131-132 °C; inseparable diastereomers (dr = 93:7); \(^1\)H NMR (400 MHz, CDCl \(_3\)) \(\delta\) 8.07 (d, \(J = 8.4\) Hz, 2H), 8.02 (s, 1H), 7.62 – 7.56 (m, 2H), 7.53 – 7.46 (m, 2H), 7.43 – 7.35 (m, 4H), 7.29 (d, \(J = 7.9\) Hz, 1H), 7.12 (s, 1H), 5.75 – 5.61 (m, 1H), 5.50 (dd, \(J = 10.1, 1.3\) Hz, 1H), 5.40 – 5.30 (m, 1H), 5.08 (d, \(J = 9.4\) Hz, 1H), 4.05 – 3.93 (m, 1H), 3.88 – 3.77 (m, 1H), 2.49 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl \(_3\)) \(\delta\) 165.9, 165.8, 164.7, 145.6, 135.6, 135.0, 132.6 (\(J = 9\) Hz), 133.1, 130.3, 130.0, 129.9, 129.4, 128.7, 128.6, 127.2, 127.0, 125.7 (\(J = 222\) Hz), 122.6 (\(J = 37\) Hz), 119.2 (\(J = 39\) Hz), 68.2, 63.3, 45.3, 21.8, 13.0; IR (KBr): 2963, 1748, 1669, 1507, 1335, 1154, 935, 668 cm \(^{-1}\); HRMS (ESI-TOF) m/z: [M - H] \(^{-}\) Calcd for C\(_{29}\)H\(_{24}\)F\(_3\)N\(_2\)O\(_6\)S 585.1307, found 585.1313.
ethyl

3-(2-methylbenzamido)-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ab): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1a (32.9 mg, 0.1 mmol), azlactone 2b (37.1 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 3ab (50.5 mg) in 95% yield as light yellow solid.

m.p. 82-83 °C; inseparable diastereomers (dr > 95:5); ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.1 Hz, 1H), 7.46 – 7.26 (m, 5H), 7.24 – 7.09 (m, 4H), 6.71 (s, 1H), 5.85 – 5.69 (m, 1H), 5.57 (d, J = 9.9 Hz, 1H), 5.43 (d, J = 16.8 Hz, 1H), 5.08 (d, J = 8.6 Hz, 1H), 4.04 – 3.90 (m, 1H), 3.87 – 3.72 (m, 1H), 2.44 (s, 3H), 2.10 (s, 3H), 0.72 (d, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.7, 161.2, 160.3, 140.4, 132.2, 130.7, 130.3, 129.9, 126.4, 126.2, 125.5, 125.3, 124.3, 123.5, 122.8, 122.0, 121.3, 120.8, 118.8, 117.5, 63.4, 58.3, 40.5, 17.0, 14.7, 8.4; IR (KBr): 2978, 1742, 1671, 1476, 1363, 1159, 933, 749 cm⁻¹; HRMS (ESI-TOF) m/z: [M - H]⁻ Calcd for C₂₉H₂₇N₂O₆S 531.1590, found 531.1592.

ethyl 3-(2-fluorobenzamido)-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ac): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1a (37.7 mg, 0.1 mmol), azlactone 2c (37.7 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 3ac (48.2 mg) in 90% yield as light yellow solid.

m.p. 71-72 °C; inseparable diastereomers (dr = 95:5); ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 8.3 Hz, 2H), 7.82 – 7.76 (m, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.49 – 7.42 (m, 1H), 7.40 – 7.35 (m, 3H), 7.25 – 7.13 (m, 3H), 7.12 – 7.04 (m, 1H), 5.92 – 5.71 (m, 1H), 5.48 (d, J
ethyl 3-(2-chlorobenzamido)-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ad): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1a (32.9 mg, 0.1 mmol), azlactone 2d (40.1 mg, 0.15 mmol), \([\text{Ir(COD)Cl}]_2\) (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 3ad (45.3 mg) in 82% yield as light yellow solid.

m.p. 77-78 °C; inseparable diastereomers (dr = 88:12); \(^1\)H NMR (400 MHz, CDCl₃) δ 8.07 (d, \(J = 8.3\) Hz, 2H), 7.76 (d, \(J = 8.1\) Hz, 1H), 7.45 (d, \(J = 7.6\) Hz, 1H), 7.41 – 7.27 (m, 6H), 7.24 – 7.19 (m, 1H), 7.16 (d, \(J = 7.6\) Hz, 1H), 5.81 – 5.67 (m, 1H), 5.53 (d, \(J = 10.0\) Hz, 1H), 5.41 (d, \(J = 16.8\) Hz, 1H), 5.02 (d, \(J = 9.5\) Hz, 1H), 4.02 – 3.91 (m, 1H), 3.85 – 3.74 (m, 1H), 2.46 (s, 3H), 0.72 (t, \(J = 7.1\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl₃) δ 165.8, 165.0, 164.7, 145.2, 135.5, 135.0, 133.3, 131.8, 131.2, 130.6, 130.5, 130.4, 129.9, 129.2, 128.2, 127.6, 126.9, 126.2, 126.1, 123.9, 122.2, 68.9, 63.0, 45.4, 21.7, 13.1; IR (KBr): 2984, 1733, 1683, 1558, 1362, 1160, 933, 747 cm⁻¹; HRMS (ESI-TOF) m/z: [M - H] Calcd for C₂₈H₂₄FN₂O₆S 535.1339, found 535.1339.

ethyl 3-(2-bromobenzamido)-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ae): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1a (32.9 mg, 0.1 mmol), azlactone 2e (46.8 mg, 0.15 mmol), \([\text{Ir(COD)Cl}]_2\) (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 3ae (45.3 mg) in 82% yield as light yellow solid.

m.p. 77-78 °C; inseparable diastereomers (dr = 88:12); \(^1\)H NMR (400 MHz, CDCl₃) δ 8.07 (d, \(J = 8.3\) Hz, 2H), 7.76 (d, \(J = 8.1\) Hz, 1H), 7.45 (d, \(J = 7.6\) Hz, 1H), 7.41 – 7.27 (m, 6H), 7.24 – 7.19 (m, 1H), 7.16 (d, \(J = 7.6\) Hz, 1H), 5.81 – 5.67 (m, 1H), 5.53 (d, \(J = 10.0\) Hz, 1H), 5.41 (d, \(J = 16.8\) Hz, 1H), 5.02 (d, \(J = 9.5\) Hz, 1H), 4.02 – 3.91 (m, 1H), 3.85 – 3.74 (m, 1H), 2.46 (s, 3H), 0.72 (t, \(J = 7.1\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl₃) δ 165.8, 165.0, 164.7, 145.2, 135.5, 135.0, 133.3, 131.8, 131.2, 130.6, 130.5, 130.4, 129.9, 129.2, 128.2, 127.6, 126.9, 126.2, 126.1, 123.9, 122.2, 68.9, 63.0, 45.4, 21.7, 13.1; IR (KBr): 2984, 1733, 1683, 1558, 1362, 1160, 933, 747 cm⁻¹; HRMS (ESI-TOF) m/z: [M - H] Calcd for C₂₈H₂₄ClN₂O₆S 551.1044, found 551.1035.
chromatography (toluene/ethyl acetate = 20:1) to afford pure product 3ae (56.6 mg) in 95% yield as light yellow solid.
m.p. 70-71 °C; inseparable diastereomers (dr = 95:5); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.06 (d, $J$ = 8.2 Hz, 2H), 7.77 (d, $J$ = 8.1 Hz, 1H), 7.53 (d, $J$ = 7.6 Hz, 1H), 7.40 – 7.34 (m, 4H), 7.32 – 7.27 (m, 1H), 7.25 – 7.19 (m, 2H), 7.16 (d, $J$ = 7.5 Hz, 1H), 7.05 (s, 1H), 5.83 – 5.67 (m, 1H), 5.55 (d, $J$ = 9.8 Hz, 1H), 5.45 (d, $J$ = 16.8 Hz, 1H), 5.03 (d, $J$ = 9.3 Hz, 1H), 4.01 – 3.89 (m, 1H), 3.85 – 3.74 (m, 1H), 2.44 (s, 3H), 0.72 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.8, 165.7, 164.9, 145.2, 135.9, 135.6, 135.0, 133.6, 131.7, 130.7, 130.0, 129.8, 129.2, 128.2, 127.6, 127.3, 126.2, 126.1, 124.0, 119.6, 68.7, 63.0, 45.4, 21.8, 13.2; IR (KBr): 2981, 1734, 1653, 1507, 1159, 933, 749 cm$^{-1}$; HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for C$_{28}$H$_{24}$BrN$_2$O$_6$S 595.0539, found 595.0540.

ethyl

3-(3-methylbenzamido)-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3af):

Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1a (32.9 mg, 0.1 mmol), azlactone 2f (37.1 mg, 0.15 mmol), [Ir(COD)Cl]$_2$ (3.4 mg, 0.005 mmol) and TsOH$\cdot$H$_2$O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 3af (44.1 mg) in 83% yield as light yellow solid.
m.p. 102-103 °C; inseparable diastereomers (dr > 95:5); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.08 (d, $J$ = 8.3 Hz, 2H), 7.75 (d, $J$ = 8.1 Hz, 1H), 7.45 – 7.33 (m, 5H), 7.31 – 7.27 (m, 2H), 7.24 – 7.19 (m, 1H), 7.15 (d, $J$ = 7.6 Hz, 1H), 7.02 (s, 1H), 5.81 – 5.67 (m, 1H), 5.46 (d, $J$ = 10.1 Hz, 1H), 5.32 (d, $J$ = 16.8 Hz, 1H), 4.98 (d, $J$ = 9.6 Hz, 1H), 4.02 – 3.90 (m, 1H), 3.87 – 3.74 (m, 1H), 2.49 (s, 3H), 2.36 (s, 3H), 0.71 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.2, 166.0, 165.4, 145.0, 138.3, 135.6, 135.1, 133.3, 132.7, 130.9, 129.8, 129.2, 128.4, 127.8, 127.5, 126.2, 126.0, 123.9, 123.6, 122.2, 68.4, 62.9, 45.5, 21.8, 21.3, 13.2; IR (KBr): 2984, 1771, 1698, 1576, 1175, 1086, 935, 740 cm$^{-1}$; HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for C$_{29}$H$_{25}$BrN$_2$O$_6$S 531.1590, found 531.1597.
ethyl 3-(3-chlorobenzamido)-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ag): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1a (32.9 mg, 0.1 mmol), azlactone 2g (40.1 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol) Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 3ag (52.4 mg) in 95% yield as light yellow solid.

m.p. 78-79 °C; inseparable diastereomers (dr = 95:5); ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, J = 8.3 Hz, 2H), 7.74 (d, J = 8.1 Hz, 1H), 7.52 (d, J = 7.4 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.37 (d, J = 8.1 Hz, 3H), 7.34 – 7.28 (m, 1H), 7.24 – 7.18 (m, 1H), 7.14 (d, J = 7.6 Hz, 1H), 7.03 (s, 1H), 5.81 – 5.66 (m, 1H), 5.47 (d, J = 10.4 Hz, 1H), 5.31 (d, J = 17.0 Hz, 1H), 4.95 (d, J = 9.6 Hz, 1H), 4.03 – 3.90 (m, 1H), 3.84 – 3.74 (m, 1H), 2.49 (s, 3H), 0.70 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.0, 165.2, 164.6, 145.2, 135.5, 135.1, 135.0, 134.8, 132.0, 130.8, 129.8, 129.2, 128.2, 127.6, 126.2, 126.1, 124.8, 123.7, 122.2, 68.5, 63.1, 45.4, 21.8, 13.1; IR (KBr): 2982, 1733, 1674, 1558, 1368, 1161, 933, 750 cm⁻¹; HRMS (ESI-TOF) m/z: [M - H] Calcd for C₂₈H₂₄ClN₂O₆S 551.1044, found 551.1041.

ethyl 3-(4-methylbenzamido)-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ah): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1a (32.9 mg, 0.1 mmol), azlactone 2h (37.1 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol) Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 3ah (45.2 mg) in 85% yield as light yellow solid.

m.p. 88-89 °C; inseparable diastereomers (dr = 95:5); ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 8.2 Hz, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.39 – 7.34 (m, 3H), 7.23 – 7.13
ethyl 3-(4-methoxybenzamido)-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ai): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1a (32.9 mg, 0.1 mmol), azlactone 2i (39.5 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 3ai (51 mg) in 93% yield as light yellow solid. m.p. 87-88 °C; inseparable diastereomers (dr = 92:8); ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 8.3 Hz, 2H), 7.73 (d, J = 8.1 Hz, 1H), 7.58 (d, J = 8.7 Hz, 2H), 7.38 – 7.34 (m, 3H), 7.23 – 7.18 (m, 1H), 7.14 (d, J = 7.6 Hz, 1H), 6.94 (s, 1H), 6.87 (d, J = 8.7 Hz, 2H), 5.85 – 5.66 (m, 1H), 5.45 (d, J = 10.1 Hz, 1H), 5.31 (d, J = 16.8 Hz, 1H), 4.95 (d, J = 8.8 Hz, 1H), 4.01 – 3.89 (m, 1H), 3.85 – 3.77 (m, 4H), 2.47 (s, 3H), 0.70 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.2, 165.6, 165.3, 162.5, 145.0, 135.7, 135.2, 130.9, 129.6, 129.3, 128.9, 128.4, 127.5, 126.1, 126.0, 125.6, 123.6, 122.1, 113.7, 68.3, 62.8, 55.4, 45.6, 21.7, 13.2; IR (KBr): 2985, 1732, 1667, 1487, 1263, 1176, 933, 747 cm⁻¹; HRMS (ESI-TOF) m/z: [M - H] Calcd for C₂₉H₂₇N₂O₇S 531.1590, found 531.1596.

ethyl 3-(4-fluorobenzamido)-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3aj): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1a (32.9 mg, 0.1 mmol), azlactone 2j (37.7 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction
mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 3aj (49.3 mg) in 92% yield as light yellow solid.

m.p. 79-80 °C; inseparable diastereomers (dr = 91:9); ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 8.2 Hz, 2H), 7.73 (d, J = 8.1 Hz, 1H), 7.67 – 7.57 (m, 2H), 7.36 (d, J = 7.9 Hz, 3H), 7.23 – 7.19 (m, 1H), 7.14 (d, J = 7.8 Hz, 1H), 7.09 – 7.03 (m, 2H), 6.98 (s, 1H), 5.85 – 5.70 (m, 1H), 5.47 (d, J = 10.0 Hz, 1H), 5.32 (d, J = 16.7 Hz, 1H), 4.94 (d, J = 9.1 Hz, 1H), 4.00 – 3.88 (m, 1H), 3.86 – 3.74 (m, 1H), 2.47 (s, 3H), 0.70 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.1, 165.4, 164.8, 145.1, 135.7, 135.1, 130.9, 129.6, 129.5, 129.4 (J = 10 Hz), 129.3, 128.2, 127.6, 126.2, 126.1, 123.7, 122.2, 115.6 (J = 20 Hz), 68.4, 63.0, 45.5, 21.7, 13.2; IR (KBr): 2987, 1734, 1653, 1489, 1384, 762 cm⁻¹; HRMS (ESI-TOF) m/z: [M - H]⁺ Calcd for C₂₈H₂₄FN₂O₆S 535.1339, found 535.1339.

*ethyl 3-(4-chlorobenzamido)-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ak):* Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1a (32.9 mg, 0.1 mmol), azlactone 2k (40.1 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH.H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 3ak (48.6 mg) in 88% yield as light yellow solid.

m.p. 87-88 °C; inseparable diastereomers (dr = 95:5); ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, J = 8.2 Hz, 2H), 7.73 (d, J = 8.1 Hz, 1H), 7.55 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.1 Hz, 5H), 7.25 – 7.19 (m, 1H), 7.14 (d, J = 7.5 Hz, 1H), 6.99 (s, 1H), 5.83 – 5.67 (m, 1H), 5.46 (d, J = 10.1 Hz, 1H), 5.31 (d, J = 16.8 Hz, 1H), 4.94 (d, J = 9.4 Hz, 1H), 4.02 – 3.89 (m, 1H), 3.84 – 3.74 (m, 1H), 2.47 (s, 3H), 0.71 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.1, 165.3, 164.8, 145.1, 138.2, 135.7, 135.1, 131.7, 130.8, 129.6, 129.3, 128.8, 128.4, 128.2, 127.6, 126.1, 123.7, 122.2, 68.4, 63.0, 45.5, 21.7, 13.1; IR (KBr): 2981, 1733, 1670, 1481, 1363, 1160, 933, 755 cm⁻¹; HRMS (ESI-TOF) m/z: [M - H]⁺ Calcd for C₂₈H₂₄ClN₂O₆S 551.1044, found 551.1055.
ethyl 3-(4-bromobenzamido)-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3al): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1a (32.9 mg, 0.1 mmol), azlactone 2l (46.8 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 3al (50.7 mg) in 85% yield as light yellow solid.

m.p. 78-79 °C; inseparable diastereomers (dr = 95:5); ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, J = 8.2 Hz, 2H), 7.73 (d, J = 8.1 Hz, 1H), 7.52 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 7.39 – 7.33 (m, 3H), 7.23 – 7.18 (m, 1H), 7.13 (d, J = 7.6 Hz, 1H), 7.00 (s, 1H), 5.83 – 5.67 (m, 1H), 5.46 (d, J = 10.1 Hz, 1H), 5.31 (d, J = 16.8 Hz, 1H), 4.94 (d, J = 9.4 Hz, 1H), 4.00 – 3.90 (m, 1H), 3.84 – 3.74 (m, 1H), 2.46 (s, 3H), 0.70 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.0, 165.3, 164.9, 145.1, 135.7, 135.1, 132.2, 131.8, 130.8, 129.6, 129.3, 128.6, 128.2, 127.6, 126.7, 126.1, 123.7, 122.2, 68.4, 63.0, 45.5, 21.7, 13.1; IR (KBr): 2981, 1733, 1670, 1479, 1367, 1160, 1010, 844 cm⁻¹; HRMS (ESI-TOF) m/z: [M - H]⁻ Calcd for C₂₈H₂₄BrN₂O₆S 595.0539, found 595.0532.

ethyl 2-oxo-1-tosyl-3-(4-(trifluoromethyl)benzamido)-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3am): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1a (32.9 mg, 0.1 mmol), azlactone 2m (45.2 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 3am (48.6 mg) in 83% yield as light yellow solid.

m.p. 104-105 °C; inseparable diastereomers (dr = 94:6); ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 8.3 Hz, 2H), 7.76 – 7.70 (m, 3H), 7.66 (d, J = 8.3 Hz, 2H), 7.41 – 7.35 (m, 3H), 7.25 – 7.20 (m,
1H), 7.14 (d, J = 7.6 Hz, 1H), 7.08 (s, 1H), 5.83 – 5.68 (m, 1H), 5.47 (d, J = 10.6 Hz, 1H), 5.33 (d, J = 16.8 Hz, 1H), 4.96 (d, J = 9.7 Hz, 1H), 4.00 – 3.91 (m, 1H), 3.86 – 3.76 (m, 1H), 2.47 (s, 3H), 0.71 (t, J = 7.1 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 166.0, 165.1, 164.6, 145.2, 136.6, 135.4 (J = 60 Hz), 133.6 (J = 40 Hz), 130.8, 129.6, 129.3, 128.1, 127.7, 127.5, 126.2, 125.6 (J = 3 Hz), 123.7, 122.2, 68.5, 63.1, 45.4, 21.7, 13.1; IR (KBr): 2984, 1734, 1670, 1522, 1325, 1162, 933, 856 cm⁻¹; HRMS (ESI-TOF) m/z: [M - H]+ Calcd for C29H24F3N2O6S 585.1307, found 585.1325.
5. Procedure for the synthesis of chiral 3 and characterization data

Under an argon atmosphere, bromobenzene (4 mL) was added to the mixture of vinyl benzoxazinanone 1 (0.1 mmol), azlactone 2a (0.05 mmol), [Ir(COD)Cl]₂ (0.0025 mmol) and L20 (0.005 mmol). Then, the reaction mixture was stirred at -15 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography to afford pure product chiral 3.

**ethyl (3R,4S)-3-benzamido-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (chiral 3aa):** Following the general procedure, under an argon atmosphere, bromobenzene (4 mL) was added to the mixture of vinyl benzoxazinanone 1a (32.9 mg, 0.1 mmol), azlactone 2a (11.2 mg, 0.05 mmol), [Ir(COD)Cl]₂ (1.7 mg, 0.0025 mmol) and L20 (3.0 mg, 0.005 mmol). Then, the reaction mixture was stirred at -15 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 15:1) to afford pure product chiral 3aa (20.7 mg) in 80% yield as light yellow solid.

m.p. 75-77 °C; [α]D²⁰ = +11.1 (c 0.38, Acetone); inseparable diastereomers (dr = 84:16); ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, J = 8.3 Hz, 2H), 7.74 (d, J = 8.1 Hz, 1H), 7.60 (d, J = 7.4 Hz, 2H), 7.51 – 7.45 (m, 1H), 7.40 – 7.34 (m, 5H), 7.20 (d, J = 7.5 Hz, 1H), 7.14 (d, J = 7.6 Hz, 1H), 7.02 (s, 1H), 5.82 – 5.69 (m, 1H), 5.47 (d, J = 10.1 Hz, 1H), 5.33 (d, J = 16.9 Hz, 1H), 4.97 (d, J = 9.5 Hz, 1H), 4.01 – 3.91 (m, 1H), 3.86 – 3.76 (m, 1H), 2.47 (s, 3H), 0.71 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.1, 165.9, 165.4, 145.1, 135.6, 135.1, 133.4, 131.9, 130.9, 129.7, 129.2, 128.5, 128.3, 127.6, 127.0, 126.2, 126.1, 123.7, 122.2, 68.3, 62.9, 45.5, 21.8, 13.2; IR (KBr): 2986, 1733, 1669, 1506, 1265, 1159, 933, 740 cm⁻¹; HRMS (ESI-TOF) m/z: [M - H]⁻ Calcd for C₂₈H₂₆N₂O₆S 517.1434, found 517.1422; Enantiomeric ratio: 93:7, determined by HPLC (Daicel Chiralpak AS-H, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): tₘ = 41.560 min (minor), tᵣ = 20.360 min (major).
ethyl

(3R,4S)-3-benzamido-6-methoxy-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (chiral 3ea): Following the general procedure, under an argon atmosphere, bromobenzene (4 mL) was added to the mixture of vinyl benzoxazinanone 1e (35.9 mg, 0.1 mmol), azlactone 2a (11.2 mg, 0.05 mmol), [Ir(COD)Cl]₂ (1.7 mg, 0.0025 mmol) and L20 (3.0 mg, 0.005 mmol). Then, the reaction mixture was stirred at -15 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 15:1) to afford pure product chiral 3ea (18.2 mg) in 66% yield as light yellow solid.

m.p. 77-79 °C; [α]D⁻²⁰ = +9.9 (c 0.36, Acetone); inseparable diastereomers (dr = 83:17); ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, J = 8.3 Hz, 2H), 7.65 (d, J = 8.9 Hz, 1H), 7.60 (d, J = 7.3 Hz, 2H), 7.51 – 7.46 (m, 1H), 7.42 – 7.33 (m, 4H), 7.00 (s, 1H), 6.91 – 6.86 (m, 1H), 6.69 (d, J = 1.9 Hz, 1H), 5.82 – 5.68 (m, 1H), 5.46 (d, J = 10.1 Hz, 1H), 5.31 (d, J = 16.8 Hz, 1H), 4.89 (d, J = 8.9 Hz, 1H), 4.02 – 3.94 (m, 1H), 3.89 – 3.81 (m, 1H), 3.80 (s, 3H), 2.48 (s, 3H), 0.79 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.1, 165.9, 165.3, 157.7, 145.0, 135.6, 133.4, 131.9, 130.8, 130.0, 129.6, 129.2, 128.5, 128.2, 127.0, 123.7, 123.6, 112.5, 111.8, 68.3, 62.9, 55.6, 45.7, 21.7, 13.3; IR (KBr): 2982, 1733, 1670, 1489, 1219, 1152, 936, 710 cm⁻¹; HRMS (ESI-TOF) m/z: [M - H] Calcd for C₂₉H₂₈N₂O₇S 547.1539, found 547.1536; Enantiomeric excess: 86:14, determined by HPLC (Daicel Chiralpak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): tᵣ = 36.187 min (minor), tᵣ = 25.073 min (major).

ethyl

(3R,4S)-3-benzamido-6-chloro-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (chiral 3ga): Following the general procedure, under an argon atmosphere, bromobenzene (4 mL) was added to the mixture of vinyl benzoxazinanone 1g (36.3 mg, 0.1 mmol), azlactone 2a (11.2 mg, 0.05 mmol), [Ir(COD)Cl]₂ (1.7 mg, 0.0025 mmol) and L20 (3.0 mg, 0.005 mmol). Then, the reaction mixture was stirred at -15 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 15:1) to afford pure product chiral 3ga (19.2mg) in 70% yield as light yellow solid.
m.p. 74-76 °C; [α]_D^{20} = +14.1 (c 0.38, Acetone); inseparable diastereomers (dr = 83:17); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, $J$ = 8.3 Hz, 2H), 7.70 (d, $J$ = 8.7 Hz, 1H), 7.57 (d, $J$ = 7.3 Hz, 2H), 7.53 – 7.47 (m, 1H), 7.43 – 7.33 (m, 5H), 7.13 (s, 1H), 7.08 (s, 1H), 5.73 – 5.61 (m, 1H), 5.49 (d, $J$ = 10.0 Hz, 1H), 5.33 (d, $J$ = 16.7 Hz, 1H), 4.99 (d, $J$ = 9.6 Hz, 1H), 4.07 – 4.00 (m, 1H), 3.91 – 3.82 (m, 1H), 2.49 (s, 3H), 0.79 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.9, 165.8, 164.9, 145.4, 135.1, 133.5, 133.2, 132.0, 131.7, 130.5, 130.1, 129.9, 129.3, 128.5, 127.4, 127.0, 126.3, 124.5, 123.4, 68.1, 63.3, 45.2, 21.8, 13.3; IR (KBr): 3124, 1734, 1670, 1479, 1399, 1154, 935, 810 cm$^{-1}$; HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for C$_{28}$H$_{25}$ClN$_2$O$_6$S 551.1044, found 551.1040; Enantiomeric excess: 89:11, determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t$_R$ = 11.963 min (minor), t$_R$ = 17.737 min (major).

**ethyl (3R,4S)-3-benzamido-7-fluoro-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (chiral 3ia):** Following the general procedure, under an argon atmosphere, bromobenzene (4 mL) was added to the mixture of vinyl benzoazinanone 1i (34.7 mg, 0.1 mmol), azlactone 2a (11.2 mg, 0.05 mmol), [Ir(COD)Cl]$_2$ (1.7 mg, 0.0025 mmol) and L20 (3.0 mg, 0.005 mmol). Then, the reaction mixture was stirred at -15 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 15:1) to afford pure product chiral 3ia (18.7 mg) in 70% yield as light yellow solid. m.p. 127-129 °C; [α]_D^{20} = +10.7 (c 0.37, Acetone); inseparable diastereomers (dr = 74:26); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.07 (d, $J$ = 8.3 Hz, 2H), 7.60 (d, $J$ = 7.5 Hz, 2H), 7.57 – 7.52 (m, 1H), 7.49 (d, $J$ = 7.2 Hz, 1H), 7.42 – 7.36 (m, 4H), 7.13 - 7.07 (m, 1H), 7.05 (s, 1H), 6.97 – 6.90 (m, 1H), 5.78 – 5.63 (m, 1H), 5.47 (d, $J$ = 10.0 Hz, 1H), 5.32 (d, $J$ = 16.8 Hz, 1H), 4.92 (d, $J$ = 9.5 Hz, 1H), 4.07 – 3.96 (m, 1H), 3.89 – 3.80 (m, 1H), 2.48 (s, 3H), 0.79 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.0, 165.8, 165.1, 145.4, 136.1, 135.3, 133.2, 132.0, 130.6, 129.7, 129.3, 128.5, 127.0, 124.0, 112.6 ($J$ = 20 Hz), 110.2 ($J$ = 30 Hz), 68.2, 63.1, 45.0, 21.8, 13.3; IR (KBr): 2988, 1748, 1670, 1507, 1275, 1177, 847, 750 cm$^{-1}$; HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for C$_{28}$H$_{25}$FN$_2$O$_6$S 535.1339, found 535.1351; Enantiomeric
excess: 88:12, determined by HPLC (Daicel Chiralpak OD-H, hexane/ isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t<sub>R</sub> = 19.283 min (minor), t<sub>R</sub> = 27.760 min (major).

6. Procedure for the synthesis of product 5 and characterization data

![Chemical structures](image)

Under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanones 1 (0.1 mmol), azlactones 4 (0.15 mmol), [Ir(COD)Cl]<sub>2</sub> (3.4 mg, 0.005 mmol) and TsOH·H<sub>2</sub>O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography to afford pure products 5.

(E)-4-methyl-N-(2-(3-(5-oxo-2,4-diphenyl-4,5-dihydrooxazol-4-yl)prop-1-en-1-yl)phenyl)benz enesulfonamide (5aa): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1a (32.9 mg, 0.1 mmol), azlactone 4a (35.6 mg, 0.15 mmol), [Ir(COD)Cl]<sub>2</sub> (3.4 mg, 0.005 mmol) and TsOH·H<sub>2</sub>O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 5aa (48 mg) in 92% yield as light yellow solid.

m.p. 60-61 °C; E/Z = 83:17; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.45 – 8.35 (m, 2H), 7.67 – 7.61 (m, 2H), 7.61 – 7.53 (m, 3H), 7.53 – 7.38 (m, 4H), 7.34 (s, 1H), 7.28 – 7.25 (m, 1H), 7.22 (d, J = 6.2 Hz, 2H), 7.19 – 7.12 (m, 1H), 7.12 – 7.02 (m, 2H), 6.26 (s, 1H), 6.09 (d, J = 15.7 Hz, 1H), 5.77 – 5.64 (m, 1H), 3.07 – 2.88 (m, 2H), 2.39 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.0, 156.2, 143.9, 138.2, 136.6, 133.1, 132.7, 131.6, 131.2, 129.6, 129.2, 128.9, 128.8, 128.7, 128.6, 128.3, 127.3, 127.2, 126.3, 126.0, 125.7, 124.7, 106.0, 45.3, 21.6; IR (KBr): 2923, 1772, 1338, 1161, 963, 750 cm<sup>-1</sup>; HRMS (ESI-TOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>31</sub>H<sub>27</sub>N<sub>2</sub>O<sub>4</sub>S 523.1692, found 523.1693.
(E)-N-(2-(3-(2-(2-chlorophenyl)-5-oxo-4-phenyl-4,5-dihydrooxazol-4-yl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (5ab): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1a (32.9 mg, 0.1 mmol), azlactone 4b (40.7 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 5ab (52.8 mg) in 95% yield as light yellow solid.

m.p. 70-71 °C; E/Z = 95:5; ¹H NMR (400 MHz, CDCl₃) δ 8.50 – 8.39 (m, 2H), 7.67 (dd, J = 7.8, 1.7 Hz, 1H), 7.63 – 7.46 (m, 6H), 7.40 – 7.34 (m, 1H), 7.33 – 7.27 (m, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.19 – 7.14 (m, 1H), 7.08 – 7.00 (m, 2H), 6.13 (s, 1H), 6.03 (d, J = 15.7 Hz, 1H), 5.75 – 5.61 (m, 1H), 3.36 – 3.13 (m, 2H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.7, 156.6, 143.9, 136.6, 135.2, 133.1, 132.9, 132.3, 132.0, 131.7, 131.3, 130.7, 129.7, 129.2, 128.9, 128.6, 128.2, 127.3, 127.1, 127.0, 126.4, 125.9, 125.0, 105.3, 41.5, 21.6; IR (KBr): 2963, 1778, 1337, 1162, 961, 749 cm⁻¹; HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₃₁H₂₆ClN₂O₄S 557.1302, found 557.1320.

(ESI-TOF) m/z: [M + H]⁺ Calcd for C₃₁H₂₆ClN₂O₄S 557.1302, found 557.1320.

(E)-N-(2-(3-(2-(3-chlorophenyl)-5-oxo-4-phenyl-4,5-dihydrooxazol-4-yl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (5ac): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1a (32.9 mg, 0.1 mmol), azlactone 4c (40.7 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 5ac (28.1 mg) in 51% yield as light yellow solid.

m.p. 63-64 °C; E/Z = 91:9; ¹H NMR (400 MHz, CDCl₃) δ 8.48 – 8.33 (m, 2H), 7.68 – 7.63 (m, 1H), 7.62 – 7.44 (m, 6H), 7.42 – 7.35 (m, 2H), 7.25 – 7.19 (m, 3H), 7.19 – 7.03 (m, 3H), 6.28 (s, 1H), 6.18 (d, J = 15.7 Hz, 1H), 5.75 – 5.61 (m, 1H), 3.08 – 2.87 (m, 2H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.7, 156.5, 143.9, 140.2, 136.6, 134.7, 133.1, 133.0, 131.7, 130.0, 129.7, 129.3, 128.9, 128.8, 128.7, 128.1, 127.3, 127.2, 126.4, 124.9, 124.8, 124.2, 105.1, 45.1, 21.6; IR
(KBr): 2922, 1779, 1337, 1160, 965, 751 cm\(^{-1}\); HRMS (ESI-TOF) m/z: \([M + H]^+\) Calcd for C\(_{31}\)H\(_{26}\)ClN\(_2\)O\(_4\)S 557.1302, found 557.1318.

\((E)-4\)-methyl-N-(2-((3-(5-oxo-4-phenyl-2-(p-tolyl)-4,5-dihydrooxazol-4-yl)prop-1-en-1-yl)phenyl)benzenesulfonamide (5ad): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone \(1a\) (32.9 mg, 0.1 mmol), azlactone \(4d\) (37.7 mg, 0.15 mmol), \([\text{Ir}(\text{COD})\text{Cl}]_2\) (3.4 mg, 0.005 mmol) and TsOH\(\text{H}_2\text{O}\) (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product \(5ad\) (46.6 mg) in 87% yield as light yellow solid.

m.p. 68-69 °C; \(E/Z = 91:9\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.45 – 8.35 (m, 2H), 7.60 – 7.54 (m, 3H), 7.53 – 7.45 (m, 4H), 7.31 – 7.26 (m, 2H), 7.25 (s, 1H), 7.21 (d, \(J = 8.0\) Hz, 2H), 7.18 – 7.14 (m, 1H), 7.11 – 7.03 (m, 2H), 6.25 (s, 1H), 6.04 (d, \(J = 15.7\) Hz, 1H), 5.76 – 5.65 (m, 1H), 3.03 – 2.87 (m, 2H), 2.40 (s, 3H), 2.38 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 164.0, 156.1, 143.9, 139.2, 136.6, 135.3, 133.1, 132.7, 131.6, 131.1, 129.6, 129.3, 128.8, 128.7, 128.6, 128.4, 127.3, 127.2, 126.3, 126.0, 125.9, 124.8, 106.1, 45.2, 21.6, 21.2; IR (KBr): 2925, 1774, 1338, 1162, 967, 753 cm\(^{-1}\); HRMS (ESI-TOF) m/z: \([M + H]^+\) Calcd for C\(_{32}\)H\(_{29}\)N\(_2\)O\(_4\)S 537.1848, found 537.1835.

\((E)-N-(2-(3-(4-(3-chlorophenyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (5ae): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone \(1a\) (32.9 mg, 0.1 mmol), azlactone \(4e\) (40.7 mg, 0.15 mmol), \([\text{Ir}(\text{COD})\text{Cl}]_2\) (3.4 mg, 0.005 mmol) and TsOH\(\text{H}_2\text{O}\) (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product \(5ae\) (52.8 mg) in 95% yield as light yellow solid.

m.p. 65-66 °C; \(E/Z = 83:17\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.43 – 8.37 (m, 1H), 8.36 – 8.29 (m, 1H), 7.67 – 7.61 (m, 2H), 7.61 – 7.56 (m, 2H), 7.55 – 7.50 (m, 1H), 7.49 – 7.39 (m, 4H), 7.26 – 7.18 (m, 3H), 7.18 – 7.12 (m, 1H), 7.12 – 7.03 (m, 2H), 6.36 (s, 1H), 6.15 (d, \(J = 15.7\) Hz, 1H),
5.77 – 5.62 (m, 1H), 3.08 – 2.89 (m, 2H), 2.39 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.5, 155.2, 143.9, 137.9, 136.6, 135.0, 133.1, 132.8, 131.6, 131.4, 130.2, 129.9, 129.6, 129.3, 128.7, 128.6, 127.2, 126.9, 126.4, 126.0, 125.2, 124.8, 106.2, 45.2, 21.6; IR (KBr): 2923, 1777, 1333, 1162, 967, 756 cm\(^{-1}\); HRMS (ESI-TOF) m/z: [M + H]\(^+\) Calcd for C\(_{31}\)H\(_{26}\)ClN\(_2\)O\(_4\)S 5557.1302, found 557.1313.

\((E)-N-(2-(3-(4-(4-fluorophenyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide\) (5af): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1a (32.9 mg, 0.1 mmol), azlactone 4f (38.3 mg, 0.15 mmol), [Ir(COD)Cl\(_2\)] (3.4 mg, 0.005 mmol) and TsOH\(\cdot\)H\(_2\)O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 5af (44.8 mg) in 83% yield as light yellow solid.

m.p. 60-61 °C; E/Z = 83:17; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.55 – 8.37 (m, 2H), 7.66 – 7.55 (m, 4H), 7.49 – 7.39 (m, 3H), 7.26 – 7.13 (m, 6H), 7.11 – 7.03 (m, 2H), 6.30 (s, 1H), 6.13 (d, \(J = 15.8\) Hz, 1H), 5.76 – 5.64 (m, 1H), 3.04 – 2.92 (m, 2H), 2.39 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 165.6(\(J = 253\) Hz), 163.9, 155.1, 143.9, 138.2, 136.6, 133.1, 131.6, 131.3, 131.2, 129.6, 129.2, 128.7, 128.6, 127.3, 127.2, 126.3, 126.0, 125.5, 124.7, 124.6, 116.1(\(J = 21.8\) Hz), 45.3, 21.6; IR (KBr): 2923, 1774, 1509, 1333, 1157, 964, 753 cm\(^{-1}\); HRMS (ESI-TOF) m/z: [M + H]\(^+\) Calcd for C\(_{31}\)H\(_{26}\)ClN\(_2\)O\(_4\)S 541.1597, found 541.1599.

\((E)-4-methyl-N-(4-methyl-2-(3-(5-oxo-2,4-diphenyl-4,5-dihydrooxazol-4-yl)prop-1-en-1-yl)phenyl)benzenesulfonamide\) (5da): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1d (34.3 mg, 0.1 mmol), azlactone 4a (35.6 mg, 0.15 mmol), [Ir(COD)Cl\(_2\)] (3.4 mg, 0.005 mmol) and TsOH\(\cdot\)H\(_2\)O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 5da (42.9 mg) in 80% yield as light yellow solid.
m.p. 45-49 °C; E/Z > 95:5; \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.41 (d, \( J = 7.3 \) Hz, 2H), 7.64 (d, \( J = 6.7 \) Hz, 2H), 7.60 – 7.53 (m, 3H), 7.53 – 7.32 (m, 5H), 7.21 (d, \( J = 8.1 \) Hz, 2H), 7.11 (d, \( J = 8.1 \) Hz, 1H), 6.95 (d, \( J = 8.1 \) Hz, 1H), 6.89 (s, 1H), 6.14 (s, 1H), 6.04 (d, \( J = 15.8 \) Hz, 1H), 5.76 – 5.59 (m, 1H), 3.10 – 2.84 (m, 2H), 2.39 (s, 3H), 2.20 (s, 3H); \( ^{13} \)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 164.0, 156.2, 143.7, 138.3, 136.7, 132.1, 131.5, 130.4, 129.3, 129.1, 128.9, 128.7, 128.4, 127.7, 126.0, 124.4, 108.6, 45.2, 21.6, 20.9; IR (KBr): 2923, 1773, 1396, 1162, 962, 749 cm\(^{-1}\); HRMS (ESI-TOF) m/z: [M + H]\(^+\) Calcd for C\(_{32}\)H\(_{29}\)N\(_2\)O\(_4\)S 537.1848, found 537.1848.

\( (E)\)-N-(4-methoxy-2-(3-(5-oxo-2,4-diphenyl-4,5-dihydrooxazol-4-yl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (5ea): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1e (35.9 mg, 0.1 mmol), azlactone 4a (35.6 mg, 0.15 mmol), [Ir(COD)Cl]\(_2\) (3.4 mg, 0.005 mmol) and TsOH.H\(_2\)O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 5ea (45.8 mg) in 83% yield as light yellow solid.

m.p. 79-80 °C; inseparable E/Z-isomers (E/Z = 93:7); \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.49 – 8.28 (m, 2H), 7.63 (dd, \( J = 7.9 \), 1.4 Hz, 2H), 7.59 – 7.41 (m, 8H), 7.21 (d, \( J = 8.1 \) Hz, 2H), 7.08 (d, \( J = 8.8 \) Hz, 1H), 6.69 (dd, \( J = 8.8 \), 2.9 Hz, 1H), 6.60 (d, \( J = 2.8 \) Hz, 1H), 6.03 (d, \( J = 15.8 \) Hz, 1H), 5.97 (s, 1H), 5.73 – 5.61 (m, 1H), 3.66 (s, 3H), 3.02 – 2.83 (m, 2H), 2.40 (s, 3H); \( ^{13} \)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 164.0, 158.4, 156.2, 143.7, 138.3, 136.7, 134.8, 132.1, 131.6, 129.3, 129.6, 129.1, 128.9, 128.8, 128.7, 128.3, 126.0, 125.9, 125.0, 114.2, 111.5, 105.9, 55.3, 45.1, 21.9; IR (KBr): 2962, 1773, 1494, 1160, 803, 749 cm\(^{-1}\); HRMS (ESI-TOF) m/z: [M + H]\(^+\) Calcd for C\(_{32}\)H\(_{26}\)N\(_2\)O\(_5\)S 553.1797, found 553.1805.

\( (E)\)-N-(4-fluoro-2-(3-(5-oxo-2,4-diphenyl-4,5-dihydrooxazol-4-yl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (5fa): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1f (34.7 mg, 0.1 mmol), azlactone 4a (35.6 mg, 0.15 mmol), [Ir(COD)Cl]\(_2\) (3.4 mg, 0.005 mmol) and TsOH.H\(_2\)O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 5fa (45.8 mg) in 83% yield as light yellow solid.

m.p. 79-80 °C; inseparable E/Z-isomers (E/Z = 93:7); \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.49 – 8.28 (m, 2H), 7.63 (dd, \( J = 7.9 \), 1.4 Hz, 2H), 7.59 – 7.41 (m, 8H), 7.21 (d, \( J = 8.1 \) Hz, 2H), 7.08 (d, \( J = 8.8 \) Hz, 1H), 6.69 (dd, \( J = 8.8 \), 2.9 Hz, 1H), 6.60 (d, \( J = 2.8 \) Hz, 1H), 6.03 (d, \( J = 15.8 \) Hz, 1H), 5.97 (s, 1H), 5.73 – 5.61 (m, 1H), 3.66 (s, 3H), 3.02 – 2.83 (m, 2H), 2.40 (s, 3H); \( ^{13} \)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 164.0, 158.4, 156.2, 143.7, 138.3, 136.7, 134.8, 132.1, 131.6, 129.3, 129.6, 129.1, 128.9, 128.8, 128.7, 128.3, 126.0, 125.9, 125.0, 114.2, 111.5, 105.9, 55.3, 45.1, 21.9; IR (KBr): 2962, 1773, 1494, 1160, 803, 749 cm\(^{-1}\); HRMS (ESI-TOF) m/z: [M + H]\(^+\) Calcd for C\(_{32}\)H\(_{26}\)N\(_2\)O\(_5\)S 553.1797, found 553.1805.
the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 5fa (27.5 mg) in 51% yield as light yellow solid.

m.p. 67-68 °C; inseparable E/Z-isomers (E/Z = 89:11); \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.40 (d, \(J = 7.4\) Hz, 2H), 7.65 – 7.40 (m, 10H), 7.25 – 7.15 (m, 3H), 6.92 – 6.77 (m, 2H), 6.06 (s, 1H), 6.01 (d, \(J = 15.8\) Hz, 1H), 5.78 – 5.66 (m, 1H), 3.02 – 2.86 (m, 2H), 2.40 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.9, 161.1 (\(J = 245\) Hz), 159.9, 156.3, 144.0, 138.1, 136.4, 134.9 (\(J = 8.3\) Hz), 132.8, 129.7, 129.2, 128.9, 128.8, 128.7, 127.2, 126.4, 126.0, 115.4 (\(J = 22.6\) Hz), 113.4 (\(J = 23.3\) Hz), 105.8, 45.1, 21.6; IR (KBr): 2916, 1773, 1507, 1261, 1161, 962, 750 cm\(^{-1}\); HRMS (ESI-TOF) m/z: [M + H]\(^+\) Calcd for C\(_{31}\)H\(_{26}\)FN\(_2\)O\(_4\)S 541.1597, found 541.1591.

\((E)-N-(4-chloro-2-(3-(5-oxo-2,4-diphenyl-4,5-dihydrooxazol-4-yl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (5ga): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1g (36.3 mg, 0.1 mmol), azlactone 4a (35.6 mg, 0.15 mmol), [Ir(COD)Cl]\(_2\) (3.4 mg, 0.005 mmol) and TsOH-H\(_2\)O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 5ga (38.9 mg) in 70% yield as light yellow solid.

m.p. 72-73 °C; inseparable E/Z-isomers (E/Z = 87:13); \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.49 – 8.31 (m, 2H), 7.67 – 7.61 (m, 2H), 7.60 – 7.41 (m, 8H), 7.25 – 7.17 (m, 3H), 7.15 – 7.08 (m, 1H), 7.06 (d, \(J = 2.3\) Hz, 1H), 6.22 (s, 1H), 5.98 (d, \(J = 15.8\) Hz, 1H), 5.79 – 5.65 (m, 1H), 3.05 – 2.86 (m, 2H), 2.39 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.9, 156.3, 144.1, 138.1, 136.3, 133.3, 132.8, 132.0, 131.7, 130.1, 130.0, 129.7, 129.3, 129.1, 128.9, 128.8, 128.7, 128.5, 128.3, 127.2, 127.1, 127.0, 126.9, 126.8, 126.3, 126.0, 105.8, 45.2, 21.6; IR (KBr): 2918, 1776, 1333, 1163, 963, 748 cm\(^{-1}\); HRMS (ESI-TOF) m/z: [M + H]\(^+\) Calcd for C\(_{31}\)H\(_{26}\)ClN\(_2\)O\(_4\)S 557.1302, found 557.1304.

\((E)-N-(4-bromo-2-(3-(5-oxo-2,4-diphenyl-4,5-dihydrooxazol-4-yl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (5ha): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone 1h (40.6 mg, 0.1 mmol),
azlactone 4a (35.6 mg, 0.15 mmol), [Ir(COD)Cl]_2 (3.4 mg, 0.005 mmol) and TsOH H_2O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 5ha (49.2 mg) in 82% yield as light yellow solid.

m.p. 81-82 °C; inseparable E/Z-isomers (E/Z = 83:17); 1H NMR (400 MHz, CDCl_3) δ 8.60 – 8.26 (m, 2H), 7.63 (dd, J = 8.0, 1.6 Hz, 2H), 7.59 – 7.43 (m, 8H), 7.26 – 7.19 (m, 4H), 7.16 (d, J = 8.6 Hz, 1H), 6.27 (s, 1H), 5.98 (d, J = 15.8 Hz, 1H), 5.80 – 5.63 (m, 1H), 3.07 – 2.84 (m, 2H), 2.39 (s, 3H); 13C NMR (100 MHz, CDCl_3) δ 163.9, 156.3, 144.1, 138.1, 136.3, 133.5, 132.8, 132.2, 131.5, 130.1, 129.8, 129.3, 129.1, 128.9, 128.8, 128.7, 128.5, 128.3, 127.2, 126.9, 126.8, 126.3, 126.0, 119.7, 105.8, 45.2, 21.6; IR (KBr): 2925, 1776, 1478, 1275, 1163, 962, 749 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]^+ Calcd for C_{31}H_{26}BrN_2O_4S 601.0797, found 601.0792.

(E)-N-(5-fluoro-2-(3-(5-oxo-2,4-diphenyl-4,5-dihydrooxazol-4-yl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonylamide (5ia): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoazinanone 1i (34.7 mg, 0.1 mmol), azlactone 4a (35.6 mg, 0.15 mmol), [Ir(COD)Cl]_2 (3.4 mg, 0.005 mmol) and TsOH H_2O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product 5ia (50.2 mg) in 93% yield as light yellow solid.

m.p. 66-67 °C; E/Z > 95:5; 1H NMR (400 MHz, CDCl_3) δ 8.49 – 8.35 (m, 2H), 7.68 – 7.59 (m, 4H), 7.57 (d, J = 7.4 Hz, 1H), 7.54 – 7.39 (m, 5H), 7.23 (d, J = 8.1 Hz, 2H), 7.10 (dd, J = 10.1, 2.6 Hz, 1H), 7.01 (dd, J = 8.6, 6.2 Hz, 1H), 6.78 – 6.66 (m, 1H), 6.45 (s, 1H), 6.04 (d, J = 15.7 Hz, 1H), 5.73 – 5.58 (m, 1H), 3.11 – 2.88 (m, 2H), 2.39 (s, 3H); 13C NMR (100 MHz, CDCl_3) δ 164.0, 162.3 (J = 246 Hz), 156.3, 144.2, 138.2, 136.3, 134.7 (J = 10.7 Hz), 132.8, 130.2, 129.8, 129.2, 128.9, 128.8, 128.7, 128.3, 127.2, 126.5 (J = 3.3 Hz), 126.2, 126.0, 112.8 (J = 21.5 Hz), 110.3 (J = 25.3 Hz), 105.9, 45.2, 21.6; IR (KBr): 2918, 1774, 1497, 1335, 1168, 981, 749 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]^+ Calcd for C_{31}H_{25}FN_2O_4S 541.1597, found 541.1591.
7. Procedure for one-mmol scale synthesis of product 3aa

Under an argon atmosphere, acetone (40 mL) was added to the mixture of vinyl benzoazinanone 1a (329 mg, 1 mmol), azlactone 2a (350 mg, 1.5 mmol), [Ir(COD)Cl]₂ (34 mg, 0.05 mmol) and TsOH·H₂O (40 mg, 0.2 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through flash chromatography to afford pure product 3aa (471 mg) in 91% yield as light yellow solid.
8. NMR spectra of products 3, 5 and chiral 3

$^1$H NMR (400 MHz, CDCl$_3$) of compound 3aa: inseparable diastereomers (dr = 94:6)

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3aa: inseparable diastereomers (dr = 94:6)
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3ba: inseparable diastereomers (dr > 95:5)

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ba: inseparable diastereomers (dr > 95:5)
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3ca: inseparable diastereomers (dr > 95:5)

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ca: inseparable diastereomers (dr > 95:5)
\[^1\text{H} \text{NMR (400 MHz, CDCl}_3\text{)} \text{ of compound 3}\text{da: inseparable diastereomers (dr} > 95:5\text{)}\]

\[^{13}\text{C} \text{NMR (100 MHz, CDCl}_3\text{)} \text{ of compound 3}\text{da: inseparable diastereomers (dr} > 95:5\text{)}\]
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3ea: inseparable diastereomers (dr > 95:5)

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ea: inseparable diastereomers (dr > 95:5)
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3fa: inseparable diastereomers (dr = 95:5)

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3fa: inseparable diastereomers (dr = 95:5)
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3ga: inseparable diastereomers (dr > 95:5)

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ga: inseparable diastereomers (dr > 95:5)
$^{1}H$ NMR (400 MHz, CDCl$_3$) of compound 3ha: inseparable diastereomers (dr > 95:5)

$^{13}C$ NMR (100 MHz, CDCl$_3$) of compound 3ha: inseparable diastereomers (dr > 95:5)
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3ia: inseparable diastereomers (dr = 92:8)

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ia: inseparable diastereomers (dr = 92:8)
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3ja: inseparable diastereomers (dr = 91:9)

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ja: inseparable diastereomers (dr = 91:9)
\(^1\)H NMR (400 MHz, CDCl\(_3\)) of compound 3ka: inseparable diastereomers (dr = 95:5)

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) of compound 3ka: inseparable diastereomers (dr = 95:5)
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3la: inseparable diastereomers (dr = 95:5)

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3la: inseparable diastereomers (dr = 95:5)
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3ma: inseparable diastereomers (dr = 93:7)

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ma: inseparable diastereomers (dr = 93:7)
\(^1\)H NMR (400 MHz, CDCl\(_3\)) of compound \textbf{3ab}: inseparable diastereomers (dr > 95:5)

\[^{13}\text{C} \text{NMR} \ (100 \text{ MHz, CDCl}_3) \text{ of compound } \textbf{3ab}: \text{ inseparable diastereomers (dr > 95:5)}
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3ac: inseparable diastereomers (dr = 95:5)

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ac: inseparable diastereomers (dr = 95:5)
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3ad: inseparable diastereomers (dr=88:12)

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ad: inseparable diastereomers (dr= 88:12)
$^{1}$H NMR (400 MHz, CDCl$_3$) of compound 3ae: inseparable diastereomers (dr = 95:5)

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ae: inseparable diastereomers (dr = 95:5)
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3af: inseparable diastereomers (dr > 95:5)

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3af: inseparable diastereomers (dr > 95:5)
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3ag: inseparable diastereomers (dr = 95:5)

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ag: inseparable diastereomers (dr = 95:5)
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3ah: inseparable diastereomers (dr = 95:5)

13C NMR (100 MHz, CDCl$_3$) of compound 3ah: inseparable diastereomers (dr= 95:5)
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3ai: inseparable diastereomers (dr = 92:8)

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ai: inseparable diastereomers (dr = 92:8)
$^1$H NMR (400 MHz, CDCl$_3$) of compound **3aj**: inseparable diastereomers (dr = 91:9)

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound **3aj**: inseparable diastereomers (dr = 91:9)
$^1$H NMR (400 MHz, CDCl$_3$) of compound **3ak**: inseparable diastereomers (dr = 95:5)

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound **3ak**: inseparable diastereomers (dr = 95:5)
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3al: inseparable diastereomers (dr = 95:5)

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3al: inseparable diastereomers (dr = 95:5)
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3am: inseparable diastereomers (dr = 94:6)

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3am: inseparable diastereomers (dr = 94:6)
$^1$H NMR (400 MHz, CDCl$_3$) of compound 5aa:

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 5aa:
$^1$H NMR (400 MHz, CDCl$_3$) of compound 5ab:

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 5ab:
$^1$H NMR (400 MHz, CDCl$_3$) of compound 5ac:

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 5ac:
$^{1}H$ NMR (400 MHz, CDCl$_3$) of compound 5ad:

$^{13}C$ NMR (100 MHz, CDCl$_3$) of compound 5ad:
$^1$H NMR (400 MHz, CDCl$_3$) of compound 5ae:

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 5ae:
$^1$H NMR (400 MHz, CDCl$_3$) of compound 5af:

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 5af:
$^1$H NMR (400 MHz, CDCl$_3$) of compound 5da:

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 5da:
$^1$H NMR (400 MHz, CDCl$_3$) of compound 5ea: inseparable $E/Z$-isomers ($E/Z = 93:7$)

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 5ea: inseparable $E/Z$-isomers ($E/Z = 93:7$)
$^1$H NMR (400 MHz, CDCl$_3$) of compound 5fa: inseparable $E$/Z-isomers ($E$/Z = 89:11)

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 5fa: inseparable $E$/Z-isomers ($E$/Z = 89:11)
$^1$H NMR (400 MHz, CDCl$_3$) of compound 5ga: inseparable $E$/Z-isomers ($E$/Z=87:13)

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 5ga: inseparable $E$/Z-isomers ($E$/Z=87:13)
$^1$H NMR (400 MHz, CDCl$_3$) of compound 5ha: inseparable $E/Z$-isomers ($E/Z=83:17$)

$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 5ha: inseparable $E/Z$-isomers ($E/Z=83:17$)
\(^1\text{H NMR (400 MHz, CDCl}_3\text{)}\) of compound 5ia:

\[^{13}\text{C NMR (100 MHz, CDCl}_3\text{)}\) of compound 5ia:
$^1$H NMR (400 MHz, CDCl$_3$) of chiral 3aa: inseparable diastereomers (dr = 84:16)

$^{13}$C NMR (100 MHz, CDCl$_3$) of chiral 3aa: inseparable diastereomers (dr = 84:16)
$^1$H NMR (400 MHz, CDCl$_3$) of **chiral 3ea**: inseparable diastereomers (dr = 83:17)

$^{13}$C NMR (100 MHz, CDCl$_3$) of **chiral 3ea**: inseparable diastereomers (dr = 83:17)
$^1$H NMR (400 MHz, CDCl$_3$) of chiral 3ga: inseparable diastereomers (dr = 83:17)

$^{13}$C NMR (100 MHz, CDCl$_3$) of chiral 3ea: inseparable diastereomers (dr = 83:17)
$^1$H NMR (400 MHz, CDCl$_3$) of chiral 3ia: inseparable diastereomers (dr = 74:26)

$^{13}$C NMR (100 MHz, CDCl$_3$) of chiral 3ia: inseparable diastereomers (dr = 74:26)
9. HPLC spectra of chiral 3

chiral 3aa:

Racemic:

Enantioselective:
chiral 3ea:
Racemic:

<table>
<thead>
<tr>
<th>Integration Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
</tr>
<tr>
<td>-----</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>Total:</td>
</tr>
</tbody>
</table>

Enantioselective:

<table>
<thead>
<tr>
<th>Integration Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
</tr>
<tr>
<td>-----</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>Total:</td>
</tr>
</tbody>
</table>
**chiral 3ga:**

**Racemic:**

<table>
<thead>
<tr>
<th>No.</th>
<th>Peak Name</th>
<th>Retention Time (min)</th>
<th>Area (mAU·min)</th>
<th>Height (mAU)</th>
<th>Relative Area (%)</th>
<th>Relative Height (%)</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>12.650</td>
<td>451.737</td>
<td>881.603</td>
<td>37.76</td>
<td>47.11</td>
<td>n.a.</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>18.730</td>
<td>454.843</td>
<td>660.925</td>
<td>38.02</td>
<td>32.09</td>
<td>n.a.</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>31.280</td>
<td>141.349</td>
<td>112.804</td>
<td>11.82</td>
<td>6.03</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

Total: 1196.204 1871.452 100.00 100.00

**Enantioselective:**

<table>
<thead>
<tr>
<th>No.</th>
<th>Peak Name</th>
<th>Retention Time (min)</th>
<th>Area (mAU·min)</th>
<th>Height (mAU)</th>
<th>Relative Area (%)</th>
<th>Relative Height (%)</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td></td>
<td>17.737</td>
<td>245.464</td>
<td>348.295</td>
<td>69.17</td>
<td>84.93</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

Total: 275.279 416.295 100.00 100.00
chiral 3ia:

Racemic:

<table>
<thead>
<tr>
<th>No.</th>
<th>Peak Name</th>
<th>Retention Time</th>
<th>Area mAU</th>
<th>Height mAU</th>
<th>Relative Area %</th>
<th>Relative Height %</th>
<th>Amount n.a.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>18.227</td>
<td>87.998</td>
<td>82.783</td>
<td>41.11</td>
<td>49.28</td>
<td>n.a.</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>26.230</td>
<td>88.143</td>
<td>58.000</td>
<td>41.18</td>
<td>34.53</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

Total: 214.030 167.969 100.00 100.00

Enantioselective:

<table>
<thead>
<tr>
<th>No.</th>
<th>Peak Name</th>
<th>Retention Time</th>
<th>Area mAU</th>
<th>Height mAU</th>
<th>Relative Area %</th>
<th>Relative Height %</th>
<th>Amount n.a.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td></td>
<td>27.700</td>
<td>101.805</td>
<td>62.958</td>
<td>87.55</td>
<td>81.46</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

Total: 116.250 77.288 100.00 100.00
10. X-ray single crystal data for compounds 3aa and chiral 3aa

The thermal ellipsoid was drawn at the 30% probability level.

Empirical formula  C_{28} H_{26} N_{2} O_{6} S
Formula weight  518.57
Temperature  296.15 K
Wavelength  0.71073 Å
Crystal system  Monoclinic
Space group  P 1 21/ n 1
Unit cell dimensions  
\[a = 9.4926(15) \text{ Å}\]
\[b = 12.1584(19) \text{ Å}\]
\[c = 22.925(4) \text{ Å}\]
\[\alpha = 90^\circ.\]
\[\beta = 94.409(2)^\circ.\]
\[\gamma = 90^\circ.\]
Volume  2638.1(7) Å³
Z  4
Density (calculated)  1.306 Mg/m³
Absorption coefficient  0.167 mm⁻¹
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(000)</td>
<td>1088</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.35 x 0.25 x 0.2 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.392 to 27.000°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-12&lt;=h&lt;=12, -15&lt;=k&lt;=15, -26&lt;=l&lt;=29</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>17967</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>5729 [R(int) = 0.0790]</td>
</tr>
<tr>
<td>Completeness to theta = 25.242°</td>
<td>99.7 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.7532 and 0.5578</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>5729 / 0 / 336</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.027</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0555, wR2 = 0.1512</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0717, wR2 = 0.1626</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>n/a</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.574 and -0.456 e.Å⁻³</td>
</tr>
</tbody>
</table>
The thermal ellipsoid was drawn at the 30% probability level.

Empirical formula  
C31 H34 N2 O7 S

Formula weight  
578.66

Temperature  
296.15 K

Wavelength  
0.71073 Å

Crystal system  
Orthorhombic
Space group  
P2₁2₁2₁

Unit cell dimensions  
\[ a = 7.8782(19) \, \text{Å} \quad \alpha = 90^\circ. \]
\[ b = 10.747(3) \, \text{Å} \quad \beta = 90^\circ. \]
\[ c = 35.997(8) \, \text{Å} \quad \gamma = 90^\circ. \]

Volume  
3047.8(12) Å³

Z  
4

Density (calculated)  
1.261 Mg/m³

Absorption coefficient  
0.154 mm⁻¹

F(000)  
1224

Crystal size  
0.3 x 0.2 x 0.15 mm³

Theta range for data collection  
2.544 to 28.484°.

Index ranges  
-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -47 ≤ l ≤ 29

Reflections collected  
22026

Independent reflections  
7198 [R(int) = 0.0953]

Completeness to theta = 25.242°  
99.8 %

Absorption correction  
None

Refinement method  
Full-matrix least-squares on F²

Data / restraints / parameters  
7198 / 0 / 375

Goodness-of-fit on F²  
1.081

Final R indices [I>2sigma(I)]  
R1 = 0.0565, wR2 = 0.1332

R indices (all data)  
R1 = 0.0780, wR2 = 0.1412

Absolute structure parameter  
0.09(4)

Extinction coefficient  
n/a

Largest diff. peak and hole  
0.360 and -0.288 e Å⁻³