Supporting Information

Divergent Synthesis of Functionalized Pyrrolidines and γ-Amino Ketones by Rhodium-Catalyzed Switchable Reactions of Vinyl Aziridines and Silyl Enol Ethers

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1. General Information

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under nitrogen. \(^1\)H NMR, \(^{13}\)C NMR spectra were measured at 400 MHz (or 500 MHz) and 100 MHz (or 125 MHz) in CDCl\(_3\) (or (CD\(_3\))\(_2\)CO, C\(_6\)D\(_6\)) using TMS signal, \(\delta\) 0.00 ppm ((CD\(_3\))\(_2\)CO: \(\delta\) 2.05 ppm; C\(_6\)D\(_6\): \(\delta\) 7.16 ppm), and the residual signals from CHCl\(_3\), \(\delta\) 77.0 ppm ((CH\(_3\))\(_2\)CO: \(\delta\) 206.8 ppm; C\(_6\)H\(_6\): \(\delta\) 128.7 ppm), as internal references for \(^1\)H and \(^{13}\)C NMR respectively.

Data for \(^1\)H NMR spectra are reported as follows: chemical shift (\(\delta\), ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, qd = quartet of doublets, ddd = doublet of doublet of doublets, m = multiplet), coupling constant (Hz), and integration.

Tetrahydrofuran and toluene were distilled from sodium and benzophenone prior to use. Dichloromethane and 1,2-dichloroethane (DCE) was distilled from CaH\(_2\) prior to use.

The catalysts [Rh(\(\eta^6\)-C\(_{10}\)H\(_8\))(COD)]SbF\(_6\), [Rh(dnCOT)(MeCN)\(_2\)]SbF\(_6\), RhCl(IPr)(COD) and chiral vinylaziridines were synthesized according to the literature procedures. All other chemicals and solvents were purchased from commercial company and used as received.
2. Table S1. Optimization of the Ring-Opening Reaction Conditions\textsuperscript{a}

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>time (h)</th>
<th>Conversion (%)</th>
<th>Yield (%)\textsuperscript{b}</th>
<th>ee (%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>IPrRh(COD)Cl/AgSbF\textsubscript{6}</td>
<td>0.25</td>
<td>100</td>
<td>66</td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td>[Rh(η\textsuperscript{6}-C\textsubscript{10}H\textsubscript{8})(COD)]SbF\textsubscript{6}</td>
<td>0.25</td>
<td>100</td>
<td>55</td>
<td>97</td>
</tr>
<tr>
<td>3</td>
<td>[Rh(COD)\textsubscript{2}]BF\textsubscript{4}</td>
<td>18</td>
<td>60</td>
<td>30</td>
<td>98</td>
</tr>
<tr>
<td>4</td>
<td>[Rh(NBD)\textsubscript{2}]BF\textsubscript{4}</td>
<td>18</td>
<td>100</td>
<td>50</td>
<td>82</td>
</tr>
<tr>
<td>5</td>
<td>[Rh(NBD)Cl]\textsubscript{2}/AgClO\textsubscript{4}</td>
<td>0.25</td>
<td>100</td>
<td>62</td>
<td>94</td>
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<td>6</td>
<td>[Rh(NBD)Cl]\textsubscript{2}/AgSbF\textsubscript{6}</td>
<td>0.25</td>
<td>100</td>
<td>82</td>
<td>94</td>
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<tr>
<td>7</td>
<td>[Rh(NBD)Cl]\textsubscript{2}/AgPF\textsubscript{6}</td>
<td>0.25</td>
<td>100</td>
<td>91</td>
<td>95</td>
</tr>
<tr>
<td>8</td>
<td>[Rh(NBD)Cl]\textsubscript{2}/AgPF\textsubscript{6}</td>
<td>3</td>
<td>100</td>
<td>95(86)</td>
<td>98</td>
</tr>
<tr>
<td>9</td>
<td>[Rh(NBD)Cl]\textsubscript{2}/AgOTf</td>
<td>0.25</td>
<td>100</td>
<td>61</td>
<td>68</td>
</tr>
<tr>
<td>10</td>
<td>[Rh(NBD)Cl]\textsubscript{2}/AgOMs</td>
<td>18</td>
<td>50</td>
<td>20</td>
<td>25</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions: To a solution of catalyst (5 mol%, the mole ratio of [Rh]:[Ag] = 1:1) in 1,2-dichloroethane (DCE) (0.5 mL) was added a mixture of (R)-1\textit{a} (0.1 mmol), 2\textit{o} (1.5 equiv) in DCE (1 mL) dropwise over a period of 3 mins at room temperature.\textsuperscript{b} Determined by H\textsuperscript{1}-NMR with CH\textsubscript{2}Br\textsubscript{2} as an internal standard.\textsuperscript{c} The reaction was run at 0 \textdegree C, the value in the parentheses was isolated yield.

3. Experimental Procedures and Characterization Data

3.1 Preparation of Enol Silyl Ethers\textsuperscript{[5]}

Enol silyl ethers 2 were facilely synthesized according to the known procedure and the physical data are identical in all respects to those previously reported.\textsuperscript{[5]} The new enolsilane substrates were also prepared from corresponding ketones according to the reported procedure and the physical data are showed as following:

**tert-butyldiphenyl((1-(m-tolyl)vinyl)oxy)silane: 2b**

Colorless oil. 60% yield.

\[^{1}\text{H} \text{NMR (400 MHz, CDCl}_3\text{): } \delta 7.79-7.77 \text{ (m, 4H), 7.58-7.56} \text{ (m, 2H), 7.44-7.36} \text{ (m, 6H), 7.29-7.25} \text{ (m, 1H), 7.16-7.14} \text{ (m, 1H), 4.73} \text{ (s, 1H), 4.00} \text{ (s, 1H), 2.38} \text{ (s, 3H), 1.10} \text{ (s, 9H).} \[^{13}\text{C} \text{NMR (100 MHz, CDCl}_3\text{): } \delta 155.2, 137.7, 137.5, 135.5, 132.5, 129.9, 129.1, 128.2, 127.8, 126.0, 122.4, 92.1, 26.6, 21.6, 19.5. \text{HRMS (EI) calcd for C}_{25}\text{H}_{28}\text{O}_{2}\text{Si: 372.1909, found: 372.1907.}

**tert-butyl((1-(3-methoxyphenyl)vinyl)oxy)diphenylsilane: 2c**

Colorless oil. 65% yield.

\[^{1}\text{H} \text{NMR (400 MHz, CDCl}_3\text{): } \delta 7.79-7.77 \text{ (m, 4H), 7.43-7.26} \text{ (m, 9H), 6.90-6.88} \text{ (m, 1H), 4.75} \text{ (s, 1H), 4.03} \text{ (s, 1H), 3.83} \text{ (s, 3H), 1.10} \text{ (s, 9H).} \[^{13}\text{C} \text{NMR (100 MHz, CDCl}_3\text{): } \delta 159.6, 154.8, 139.1, 135.5, 132.4, 129.9, 129.2, 127.8, 117.8, 114.1, 110.7, 92.5, 55.2, 26.6, 19.5. \text{HRMS (EI) calcd for C}_{25}\text{H}_{28}\text{O}_{2}\text{Si: 388.1859, found: 388.1860.}
(1-(3-bromophenyl)vinyl)oxy(tert-butyl)diphenylsilane: 2d

Colorless oil. 54% yield.

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.88-7.87 (m, 1H), 7.77-7.74 (m, 4H), 7.67-7.65 (m, 1H), 7.46-7.37 (m, 7H), 7.26-7.22 (m, 1H), 4.73 (d, $J = 2.8$ Hz, 1H), 4.05 (d, $J = 2.4$ Hz, 1H), 1.10 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 153.7, 139.7, 135.5, 132.2, 131.2, 130.0, 129.8, 128.4, 127.8, 123.8, 122.5, 93.3, 26.6, 19.5. HRMS (EI) calcd for C$_{24}$H$_{25}$SiBr: 436.0858, found: 436.0856.

tert-butyl diphenyl(1-(p-tolyl)vinyl)oxy) silane: 2e

Colorless oil. 65% yield.

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.89-7.87 (m, 4H), 7.75 (d, $J = 8.5$ Hz, 2H), 7.43-7.35 (m, 6H), 7.18 (d, $J = 8.0$ Hz, 2H), 4.70 (d, $J = 2.0$ Hz, 1H), 3.97 (d, $J = 2.5$ Hz, 1H), 2.47 (s, 3H), 1.20 (s, 9H).

$^{13}$C NMR (125 MHz, CDCl$_3$): δ 155.2, 138.2, 135.6, 134.8, 132.6, 129.9, 129.0, 127.8, 125.2, 91.5, 26.7, 21.3, 19.6. HRMS (EI) calcd for C$_{25}$H$_{28}$Si: 372.1909, found: 372.1912.

((1-[[1,1'-biphenyl]-4-yl)vinyl]oxy)(tert-butyl) diphenylsilane: 2f

White solid. 58% yield.

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.84-7.79 (m, 6H), 7.64-7.61 (m, 4H), 7.44-7.33 (m, 9H), 4.80 (s, 1H), 4.05 (s, 1H), 1.12 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 154.8, 141.0, 140.7, 136.4, 135.5, 132.4, 129.9, 128.8, 127.8, 127.4, 127.0, 126.9, 125.6, 92.3, 26.6, 19.5. HRMS (EI) calcd for C$_{30}$H$_{30}$Si: 434.2066, found: 434.2063.

tert-butyl((1-(4-chlorophenyl)vinyl)oxy)diphenylsilane: 2g

Colorless oil. 70% yield.

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.76-7.75 (m, 4H), 7.71 (d, $J = 8.4$ Hz, 2H), 7.46-7.37 (m, 6H), 7.33 (d, $J = 8.4$ Hz, 2H), 4.72 (d, $J = 2.4$ Hz, 1H), 4.03 (d, $J = 2.0$ Hz, 1H), 1.09 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 154.1, 136.0, 135.4, 134.0, 132.2, 129.9, 128.3, 127.8, 126.5, 92.6, 26.5, 19.5. HRMS (EI) calcd for C$_{24}$H$_{25}$OSiCl: 392.1363, found: 392.1362.

tert-butyl((1-(3,4-dimethylphenyl)vinyl)oxy)diphenylsilane: 2h

Colorless oil. 55% yield.

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.66-7.64 (m, 4H), 7.39-7.36 (m, 2H), 7.27-7.23 (m, 6H), 7.01 (d, $J = 7.2$ Hz, 1H), 4.57 (s, 1H), 3.82 (s, 1H), 2.16 (s, 3H), 2.15 (s, 3H), 0.96 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 155.2, 136.9, 136.3, 135.5, 135.2, 132.6, 129.8, 129.6, 127.7, 126.6, 122.8, 91.3, 26.6, 20.0, 19.6, 19.5. HRMS (EI) calcd for C$_{26}$H$_{30}$Si: 386.2066, found: 386.2065.

tert-butyl diphenyl((1-(3,4,5-trimethoxyphenyl)vinyl)oxy)silane: 2i

Colorless oil. 58% yield.

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.79-7.77 (m, 4H), 7.46-7.38 (m, 6H), 7.00 (s, 2H), 4.70 (s, 1H), 4.04 (s, 1H), 3.88 (s, 3H), 3.87 (s, 6H), 1.11 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 154.7, 152.9, 138.2, 135.5, 133.1, 132.3, 129.9, 127.8, 102.5, 91.7, 60.9, 56.0, 26.6, 19.5. HRMS (EI) calcd for C$_{27}$H$_{24}$O$_4$Si: 448.2070, found: 448.2073.

((1-(benzo[d][1,3]dioxol-5-yl)vinyl)oxy)(tert-butyl)diphenylsilane: 2j

Colorless oil. 68% yield.
1H NMR (400 MHz, CDCl3): δ 7.78-7.76 (m, 4H), 7.45-7.37 (m, 6H), 7.30-7.28 (m, 1H), 7.20 (s, 1H), 6.81 (d, J = 8.0 Hz, 1H), 5.97 (s, 2H), 4.60 (s, 1H), 3.93 (s, 1H), 1.09 (s, 9H). 13C NMR (100 MHz, CDCl3): δ 154.7, 147.7, 147.6, 135.5, 132.4, 132.0, 129.9, 127.8, 119.2, 108.0, 105.9, 101.2, 91.1, 26.6, 19.5.


To a stirred solution of [Rh(NBD)2]BF4 in DCE (0.5 mL) at room temperature under argon atmosphere was added a solution of vinylaziridine 1 (0.20 mmol) and enol silyl ether 2 (0.3 mmol) in DCE (1.5 mL) via syringe. The resulting mixture was then stirred at room temperature for about 0.25-19 h. Upon complete consumption of 1 (TLC monitoring), the solvent was removed under reduced pressure, and the residue was purified by chromatography on a triethylamine-deactivated silica gel column, eluting with hexane:ethyl acetate:triethylamine (200:10:1) to afford the desired [3+2] cycloadduct 3.

(2S,4S)-2-((tert-butyldiphenylsilyloxy)-2-phenyl-4-(prop-1-en-2-yl)-1-tosylpyrrolidine: 3aa

Colorless oil. 80% yield.

1H NMR (500 MHz, CDCl3): δ 8.07-8.05 (m, 2H), 7.71-7.69 (m, 2H), 7.49-7.38 (m, 6H), 7.34-7.31 (m, 2H), 7.27-7.25 (m, 1H), 7.21-7.18 (m, 2H), 7.00 (s, 4H), 4.51 (s, 1H), 4.23 (s, 1H), 3.60 (t, J = 8.0 Hz, 1H), 2.88 (dd, J = 10.5 and 8.5 Hz, 1H), 2.40 (dd, J = 14.0 and 7.5 Hz, 1H), 2.34 (s, 3H), 2.22 (dd, J = 14.0 and 12.0 Hz, 1H), 1.87-1.79 (m, 1H), 1.31 (s, 3H), 1.22 (s, 9H).

13C NMR (125 MHz, CDCl3): δ 144.2, 143.1, 142.2, 136.9, 136.5, 136.0, 134.0, 130.0, 129.5, 128.8, 127.8, 127.7, 127.6, 127.2, 127.1, 126.8, 110.4, 96.1, 53.4, 49.5, 40.0, 27.1, 21.4, 20.7, 20.1. HRMS (ESI) calcd for C36H41NNaO3Si [(M+Na+)]: 618.2469, found: 618.2475. [α]27D = -5.0 (c 1.0, CHCl3).

98% ee. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 12.19 min (minor), 15.94 min (major).

(2S,4S)-2-((tert-butyldiphenylsilyloxy)-2-phenyl-1-tosyl-4-vinylpyrrolidine: 3ba
White solid. 69% yield.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.07-8.06 (m, 2H), 7.69 (d, $J = 6.8$ Hz, 2H), 7.50-7.18 (m, 11H), 6.99 (s, 4H), 5.31-5.22 (m, 1H), 4.74 (d, $J = 10.4$ Hz, 1H), 4.49 (d, $J = 17.2$ Hz, 1H), 3.55 (t, $J = 8.4$ Hz, 1H), 2.80 (t, $J = 9.6$ Hz, 1H), 2.44 (dd, $J = 14.8$ and 8.0 Hz, 1H), 2.34 (s, 3H), 2.11 (dd, $J = 14.4$ and 12.0 Hz, 1H), 1.77-1.65 (m, 1H), 1.22 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 144.1, 142.3, 137.1, 136.8, 136.5, 136.0, 133.98, 133.96, 130.0, 129.5, 128.8, 127.8, 127.7, 127.6, 127.3, 127.1, 126.8, 116.4, 96.0, 54.3, 51.4, 38.1, 27.1, 21.4, 20.1. HRMS (ESI) calcd for C$_{35}$H$_{39}$NaN$_2$O$_5$Si: 604.2312, found: 604.2319. $\left[\alpha\right]_{D}^{27} = +11.3$ (c 1.0, CHCl$_3$). 97% ee. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 12.50 min (minor), 16.73 min (major).

(2S,4S)-2-((tert-butyldiphenylsilyl)oxy)-1-((4-nitrophenyl)sulfonyl)-2-phenyl-4-vinylpyrrolidine: 3ca

White solid. 66% yield.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.07-8.05 (m, 2H), 8.01 (d, $J = 8.8$ Hz, 2H), 7.65 (d, $J = 8.0$ Hz, 2H), 7.52-7.48 (m, 3H), 7.43-7.28 (m, 6H), 7.20-7.16 (m, 4H), 5.31-5.22 (m, 1H), 4.79 (d, $J = 10.4$ Hz, 1H), 4.52 (d, $J = 17.2$ Hz, 1H), 3.63 (t, $J = 8.4$ Hz, 1H), 2.80 (t, $J = 10.4$ Hz, 1H), 2.48 (dd, $J = 14.4$ and 8.0 Hz, 1H), 2.14 (dd, $J = 14.4$ and 11.6 Hz, 1H), 1.79-1.69 (m, 1H), 1.22 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 145.1, 143.5, 149.3, 136.5, 136.4, 136.0, 133.7, 133.6, 130.3, 129.6, 128.1, 128.0, 127.9, 127.8, 127.7, 126.8, 123.4, 116.9, 96.1, 54.7, 50.8, 38.1, 27.1, 20.1. HRMS (ESI) calcd for C$_{34}$H$_{36}$N$_2$NaOSi: 635.2006, found: 635.2011. $\left[\alpha\right]_{D}^{27} = +23.6$ (c 1.0, CHCl$_3$). 81% ee. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 11.17 min (minor), 17.46 min (major).
(2S,4S)-2-(tert-butyldiphenylsilyloxy)-1-(methylsulfonyl)-2-phenyl-4-vinylpyrrolidine: 3da

Yellow oil. 73% yield.

\[ \text{1H NMR (500 MHz, CDCl}_3\text{): } \delta 8.00-7.98 \text{ (m, 2H), 7.74-7.73 \text{ (m, 2H), 7.69-7.67 \text{ (m, 2H), 7.48-7.40 \text{ (m, 6H), 7.36-7.33 \text{ (m, 3H), 5.44-5.37 \text{ (m, 1H), 4.82 \text{ (d, } J = 9.5 \text{ Hz, 1H), 4.60-4.57 \text{ (m, 1H), 3.46 \text{ (t, } J = 8.5 \text{ Hz, 1H), 2.98 \text{ (t, } J = 9.5 \text{ Hz, 1H), 2.52 \text{ (dd, } J = 14.5 \text{ and 8.0 Hz, 1H), 2.30 \text{ (dd, } J = 14.5 \text{ and 11.5 Hz, 1H), 2.26 \text{ (s, 3H), 1.83-1.74 \text{ (m, 1H), 1.31 \text{ (s, 3H), 1.16 \text{ (s, 9H).}}\]

\[ \text{13C NMR (125 MHz, CDCl}_3\text{): } \delta 144.1, 136.9, 136.4, 136.0, 133.9, 133.8, 130.1, 129.5, 128.0, 127.9, 127.8, 127.6, 126.6, 116.5, 95.5, 54.8, 38.3, 37.7, 27.1, 20.0. \]

HRMS (ESI) calcd for C\text{29}H\text{35}NNaO\text{3}S\text{Si}\[(\text{M+Na}^+)]: 528.199, found: 528.2009. \[ [\alpha]_D^{28} = +11.6 \text{ (c 1.0, CHCl}_3\text{).} \]

87% ee. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 12.78 min (minor), 18.61 min (major).

(2S,4S)-2-(tert-butyldiphenylsilyloxy)-4-(3-methylbut-1-en-2-yl)-2-phenyl-1-tosylpyrrolidine: 3ea

White solid. 60% yield.

\[ \text{1H NMR (400 MHz, CDCl}_3\text{): } \delta 8.10-8.07 \text{ (m, 2H), 7.73-7.71 \text{ (m, 2H), 7.47-7.31 \text{ (m, 2H), 7.26-7.24 \text{ (m, 1H), 7.20-7.18 \text{ (m, 2H), 7.01 \text{ (s, 4H), 4.61 \text{ (s, 1H), 4.38 \text{ (s, 1H), 3.73 \text{ (t, } J = 8.4 \text{ Hz, 1H), 2.92-2.87 \text{ (m, 1H), 2.45 \text{ (dd, } J = 13.6 \text{ and 6.8 Hz, 1H), 2.34 \text{ (s, 3H), 2.25-2.08}}\]

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(m, 2H), 1.71-1.64 (m, 1H), 1.20 (s, 9H), 0.66 (d, \( J = 6.8 \) Hz, 3H), 0.63 (d, \( J = 6.8 \) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 155.1, 144.2, 142.2, 137.1, 136.4, 136.1, 134.1, 133.9, 130.0, 129.5, 128.8, 127.8, 127.7, 127.6, 127.2, 127.1, 126.9, 106.4, 96.0, 55.0, 51.1, 38.0, 33.3, 27.1, 21.9, 21.8, 20.1. HRMS (ESI) calcd for C\(_{38}\)H\(_{45}\)NNaO\(_3\)Si\([\text{M+Na}^+]\): 646.2782, found: 646.2791. \([\alpha]^{27}\)D = -4.0 (c 1.0, CHCl\(_3\)). 91% ee.

HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 11.09 min (minor), 13.70 min (major).

\((2\text{S,4S})-2-((\text{tert-butyldiphenylsilyl})\text{oxy})-4-(\text{hex-1-en-2-yl})-2\text{-phenyl-1-tosylpyrrolidine}: 3\text{fa}\)

Colorless oil. 74% yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.10-8.07 (m, 2H), 7.73-7.71 (m, 2H), 7.48-7.31 (m, 8H), 7.25-7.16 (m, 3H), 7.00 (s, 4H), 4.54 (s, 1H), 4.32 (s, 1H), 3.70 (t, \( J = 8.0 \) Hz, 1H), 2.89 (dd, \( J = 10.4 \) and 8.8 Hz, 1H), 2.43 (dd, \( J = 14.0 \) and 7.2 Hz, 1H), 2.33 (s, 3H), 2.24-2.17 (m, 1H), 2.08-1.99 (m, 1H), 1.56-1.53 (m, 2H), 1.21 (s, 9H), 1.12-1.05 (m, 2H), 0.99-0.93 (m, 2H), 0.79 (d, \( J = 7.2 \) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 148.1, 144.0, 142.2, 137.0, 136.4, 136.0, 134.0, 133.8, 130.0, 129.5, 128.7, 127.7, 127.64, 127.59, 127.2, 127.0, 126.8, 108.5, 96.0, 54.1, 49.9, 38.5, 35.2, 29.7, 27.1, 22.2, 21.3, 20.1, 13.8. HRMS (ESI) calcd for C\(_{39}\)H\(_{47}\)NNaO\(_3\)Si\([\text{M+Na}^+]\): 660.2938, found: 660.2945. \([\alpha]^{27}\)D = -1.4 (c 1.0, CHCl\(_3\)). 82% ee. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 10.31 min (minor), 12.84 min (major).
(2S,4S)-2-((tert-butyldiphenylsilyl)oxy)-4-(prop-1-en-2-yl)-2-(m-tolyl)-1-tosylpyrrolidine: 3ab

White solid. 61% yield.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.08-8.05 (m, 2H), 7.73-7.71 (m, 2H), 7.47-7.45 (m, 4H), 7.39-7.32 (m, 3H), 7.18-7.14 (m, 1H), 7.06-7.01 (m, 5H), 6.87 (s, 1H), 4.51 (s, 1H), 4.24 (s, 1H), 3.64 (t, $J = 8.0$ Hz, 1H), 2.89 (dd, $J = 10.4$ and 8.4 Hz, 1H), 2.40-2.37 (m, 1H), 2.34 (s, 3H), 2.21-2.14 (m, 1H), 2.11 (s, 3H), 1.93-1.83 (m, 1H), 1.31 (s, 3H), 1.22 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 144.0, 143.2, 142.1, 137.0, 136.9, 136.5, 136.1, 134.13, 134.07, 130.0, 129.4, 128.7, 128.0, 127.8, 127.5, 127.1, 124.1, 110.3, 96.1, 53.6, 49.6, 40.0, 27.2, 21.4, 21.3, 20.8, 20.1. HRMS (ESI) calcd for C$_{37}$H$_{44}$NNaO$_3$Si [(M+Na$^+$)]: 632.2625, found: 632.2623. $\left[\alpha\right]_{D}^{28} = +15.8$ (c 1.0, CHCl$_3$). 97% ee. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 11.47 min (minor), 17.20 min (major).

(2S,4S)-2-((tert-butyldiphenylsilyl)oxy)-2-(3-methoxyphenyl)-4-(prop-1-en-2-yl)-1-tosylpyrrolidine: 3ac

Colorless oil. 75% yield.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.07-7.05 (m, 2H), 7.73-7.71 (m, 2H), 7.49-7.44 (m, 3H), 7.42-7.32 (m, 3H), 7.11-7.07 (m, 1H), 7.05 (s, 4H), 6.97-6.92 (m, 2H), 6.81-6.79 (m, 1H), 4.51 (s, 1H), 4.23 (s, 1H), 3.63-3.58 (m, 4H), 2.87 (dd, $J = 10.4$ and 8.8 Hz, 1H), 2.40 (dd, $J = 14.4$ and 8.0 Hz, 1H), 2.35 (s, 3H), 2.24-2.17 (m, 1H), 1.87-1.78 (m, 1H), 1.31 (s, 3H), 1.22 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 158.9, 145.8, 143.1, 142.3, 136.8, 136.5, 136.0, 133.95, 133.86, 130.0, 129.5, 128.7, 128.6, 127.8, 127.6, 127.1, 119.2, 113.4, 112.2, 110.5, 95.9, 54.9, 53.5, 49.6, 39.9, 27.1, 21.3, 20.6, 20.1. HRMS (ESI) calcd for C$_{37}$H$_{44}$NO$_3$Si [(M+H$^+$)]: 626.2755, found: 626.2757. $\left[\alpha\right]_{D}^{28} = +8.5$ (c 1.0, CHCl$_3$). 98% ee. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 14.49 min (minor), 21.81 min (major).
(2S,4S)-2-(3-bromophenyl)-2-((tert-butylidiphenylsilyl)oxy)-4-(prop-1-en-2-yl)-1-tosylpyrrolidine: 3ad

White solid. 64% yield.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.06-8.04 (m, 2H), 7.70-7.68 (m, 2H), 7.65-7.64 (m, 1H), 7.49-7.46 (m, 3H), 7.41-7.33 (m, 4H), 7.18-7.15 (m, 2H), 7.09-7.06 (m, 4H), 4.53 (s, 1H), 4.24 (s, 1H), 3.64 (t, $J$ = 8.5 Hz, 1H), 2.89 (dd, $J$ = 10.5 and 8.5 Hz, 1H), 2.40-2.36 (m, 4H), 2.12-2.06 (m, 1H), 1.95-1.88 (m, 1H), 1.30 (s, 3H), 1.21 (s, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 146.4, 142.9, 142.8, 136.7, 136.5, 136.0, 133.8, 133.7, 130.4, 130.1, 129.9, 129.6, 129.3, 129.1, 127.8, 127.7, 126.7, 125.7, 121.9, 110.5, 95.3, 53.4, 49.4, 39.9, 27.1, 21.4, 20.8, 20.1. HRMS (ESI) calcd for C$_{36}$H$_{40}$BrN$_3$O$_3$Si [(M+Na$^+$)]: 696.1574, found: 696.1591. [α]$_D^{26}$ = +26.2 (c 1.0, CHCl$_3$). 85% ee. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 95/5, 0.5 mL/min. Retention times: 11.69 min (minor), 18.09 min (major).

(2S,4S)-2-((tert-butylidiphenylsilyl)oxy)-4-(prop-1-en-2-yl)-2-(p-tolyl)-1-tosylpyrrolidine: 3ae

Colorless oil. 60% yield.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.05 (d, $J$ = 6.5 Hz, 2H), 7.69 (d, $J$ = 7.5 Hz, 2H), 7.46-7.44 (m, 3H), 7.40-7.29 (m, 5H), 7.04-6.98 (m, 6H), 4.50 (s, 1H), 4.23 (s, 1H), 3.58 (t, $J$ = 8.0 Hz, 1H), 2.88 (t, $J$ = 9.5 Hz, 1H), 2.41-2.35 (m, 7H), 2.23-2.17 (m, 1H), 1.85-1.78 (m,
1H), 1.30 (s, 3H), 1.20 (s, 9H). $^1$C NMR (125 MHz, CDCl$_3$): $\delta$ 143.2, 142.2, 141.3, 137.1, 136.9, 136.5, 136.1, 134.1, 130.0, 129.4, 128.6, 128.3, 127.8, 127.6, 127.2, 126.7, 110.4, 96.1, 53.4, 49.4, 40.0, 27.1, 21.4, 21.0, 20.7, 20.1. HRMS (ESI) calcd for C$_{37}$H$_{43}$NNaO$_3$SSi [(M+Na$^+$)]: 632.2625, found: 632.2631. [$\alpha$]$^{28}_D$ = -9.4 (c 1.0, CHCl$_3$). 98% ee. HPLC analysis of the product: Daicel Chiralpak IF column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 21.34 min (minor), 24.57 min (major).

(2S,4S)-2-[(1,1'-biphenyl)-4-yl]-2-((tert-butylidiphenylsilyl)oxy)-4-(prop-1-en-2-yl)-1-tosylpyrrolidine: 3af

White solid. 65% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.10-8.07 (m, 2H), 7.73-7.72 (m, 2H), 7.62-7.60 (m, 2H), 7.49-7.46 (m, 7H), 7.42-7.32 (m, 6H), 7.07 (d, $J$ = 8.4 Hz, 2H), 6.97 (d, $J$ = 8.0 Hz, 2H), 4.53 (s, 1H), 4.26 (s, 1H), 3.65 (t, $J$ = 8.0 Hz, 1H), 2.95 (dd, $J$ = 10.4 and 8.8 Hz, 1H), 2.44 (dd, $J$ = 14.0 and 7.6 Hz, 1H), 2.31 (s, 3H), 2.27-2.23 (m, 1H), 1.90-1.80 (m, 1H), 1.33 (s, 3H), 1.24 (s, 9H). $^1$C NMR (100 MHz, CDCl$_3$): $\delta$ 143.2, 143.1, 142.2, 140.6, 140.1, 137.1, 136.5, 136.0, 134.01, 133.97, 130.0, 129.5, 128.81, 128.76, 127.8, 127.6, 127.4, 127.3, 127.1, 126.9, 126.2, 110.5, 95.9, 53.6, 49.3, 40.0, 27.2, 21.3, 20.7, 20.1. HRMS (ESI) calcd for C$_{42}$H$_{45}$NNaO$_3$SSi [(M+Na$^+$)]: 694.2782, found: 694.2785. [$\alpha$]$^{27}_D$ = -46.2 (c 1.0, CHCl$_3$). 98% ee. HPLC analysis of the product: Daicel Chiralpak IF column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 22.03 min (minor), 27.04 min (major).
(2S,4S)-2-((tert-butyldiphenylsilyl)oxy)-2-(4-chlorophenyl)-4-(prop-1-en-2-yl)-1-tosylpyrrolidine: 3ag

Colorless oil. 77% yield.

1H NMR (400 MHz, CDCl3): δ 8.04-8.02 (m, 2H), 7.67-7.65 (m, 2H), 7.49-7.33 (m, 8H), 7.15-7.13 (m, 2H), 7.06 (s, 4H), 4.52 (s, 1H), 4.23 (s, 1H), 3.60 (t, J = 8.0 Hz, 1H), 2.90 (dd, J = 10.4 and 9.2 Hz, 1H), 2.42-2.40 (m, 1H), 2.37 (s, 3H), 2.17-2.10 (m, 1H), 1.88-1.79 (m, 1H), 1.31 (s, 3H), 1.20 (s, 9H). 13C NMR (100 MHz, CDCl3): δ 142.9, 142.8, 142.6, 137.0, 136.4, 135.9, 133.8, 133.7, 133.2, 130.1, 129.6, 128.9, 128.2, 127.8, 127.70, 127.68, 126.9, 110.5, 95.5, 53.4, 49.2, 39.9, 27.1, 21.4, 20.7, 20.1. HRMS (ESI) calcd for C36H41ClNOSi [(M+H+)]: 630.2259, found: 630.2270. [α]28D = -20.1 (c 1.0, CHCl3). 89% ee. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 95/5, 0.5 mL/min. Retention times: 11.53 min (minor), 12.87 min (major).

(2S,4S)-2-((tert-butyldiphenylsilyl)oxy)-2-(3,4-dimethylphenyl)-4-(prop-1-en-2-yl)-1-tosylpyrrolidine: 3ah

Colorless oil. 44% yield.

1H NMR (400 MHz, CDCl3): δ 8.07-8.04 (m, 2H), 7.73-7.71 (m, 2H), 7.48-7.44 (m, 3H), 7.40-7.31 (m, 4H), 7.04-6.98 (m, 5H), 6.81 (s, 1H), 4.51 (s, 1H), 4.24 (s, 1H), 3.62 (t, J = 8.0 Hz, 1H), 2.90 (dd, J = 10.4 and 8.4 Hz, 1H), 2.38-2.33 (m, 4H), 2.26 (s, 3H), 2.20-2.13 (m, 1H), 2.00 (s, 3H), 1.91-1.82 (m, 1H), 1.31 (s, 3H), 1.21 (s, 9H). 13C NMR (100 MHz, CDCl3): δ 143.3, 142.0, 141.5, 137.2, 136.5, 136.1, 135.6, 135.3, 134.2, 134.1, 130.0, 129.4, 128.9, 128.6, 128.0, 127.8, 127.6, 127.1, 124.4, 110.3, 96.1, 53.6, 49.5, 40.0, 27.1, 21.3, 20.8, 20.2, 19.8, 19.4. HRMS (ESI) calcd for C35H45NNaO3Si [(M+Na+)]: 646.2782, found: 646.2791. [α]27D = +9.1 (c 1.0, CHCl3). 95% ee. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 95/5, 0.5 mL/min. Retention times: 11.31 min (minor), 15.71 min (major).
(2S,4S)-2-((tert-butyldiphenylsilyl)oxy)-4-(prop-1-en-2-yl)-1-tosyl-2-(3,4,5-trimethoxyphenyl)pyrrolidine: 3ai

White solid. 73% yield.

\[\text{H NMR (500 MHz, CDCl}_3\text{): } \delta \text{ 8.07-8.05 (m, 2H), 7.76-7.74 (m, 2H), 7.50-7.36 (m, 6H), 7.08 (s, 4H), 6.55 (s, 2H), 4.53 (s, 1H), 4.25 (s, 1H), 3.91 (s, 3H), 3.64 (t, } J = 8.5 \text{ Hz, 1H), 3.53 (s, 6H), 2.90 (dd, } J = 10.5 \text{ and 9.0 Hz, 1H), 2.42 (dd, } J = 14.0 \text{ and 7.5 Hz, 1H), 2.35 (s, 3H), 2.20 (dd, } J = 14.0 \text{ and 12.0 Hz, 1H), 1.86-1.78 (m, 1H), 1.33 (s, 3H), 1.23 (s, 9H).}\]

\[\text{C NMR (125 MHz, CDCl}_3\text{): } \delta \text{ 152.1, 143.1, 142.4, 139.6, 136.9, 136.8, 136.5, 136.0, 133.9, 133.6, 130.1, 129.5, 128.7, 127.9, 127.6, 127.0, 110.5, 104.0, 95.8, 60.8, 55.4, 53.6, 49.7, 39.9, 27.0, 21.3, 20.6, 20.1. HRMS (ESI) calcd for C_{39}H_{47}NO_{17}S\text{Si }[(M+Na^+)]: 708.2786, found: 708.2780.}\]

\[\text{[α]}_D^{26} = +44.4 (c 1.0, CHCl}_3\text{). 98% ee. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 15.09 min (minor), 20.55 min (major).}\]

(2S,4S)-2-(benzo[d][1,3]dioxol-5-yl)-2-((tert-butyldiphenylsilyl)oxy)-4-(prop-1-en-2-yl)-1-tosylpyrrolidine: 3aj

White solid. 71% yield.

\[\text{H NMR (500 MHz, CDCl}_3\text{): } \delta \text{ 8.06-8.04 (m, 2H), 7.70-7.69 (m, 2H), 7.48-7.44 (m, 3H), 7.40-7.38 (m, 1H), 7.36-7.33 (m, 2H), 7.13 (d, } J = 8.0 \text{ Hz, 2H), 7.07 (d, } J = 8.5 \text{ Hz, 1H), 6.85-6.76 (m, 1H), 6.59-6.54 (m, 2H), 6.47-6.42 (m, 2H), 6.29-6.23 (m, 2H), 6.09-6.05 (m, 2H), 6.02-5.97 (m, 2H), 5.85-5.81 (m, 2H), 5.73-5.69 (m, 2H), 5.62-5.58 (m, 2H).}\]

S14
2-((tert-butyldiphenylsilyl)oxy)-2-(furan-2-yl)-4-(prop-1-en-2-yl)-1-tosylypyrrolidine: 3ak

Colorless oil. 71% yield. d.r. = 5:1. (The diastereomers can not be separated by chromatography)

1H NMR (the major product, 500 MHz, CDCl3): δ 8.00-7.98 (m, 2H), 7.73-7.71 (m, 2H), 7.48-7.34 (m, 6H), 7.25-7.24 (m, 2H), 7.13-7.11 (m, 2H), 6.96 (s, 1H), 6.80-6.79 (m, 1H), 6.37-6.36 (m, 1H), 4.51 (s, 1H), 4.25 (s, 1H), 3.54 (t, J = 8.0 Hz, 1H), 2.84 (dd, J = 11.0 and 8.5 Hz, 1H), 2.37 (s, 3H), 2.29-2.24 (m, 1H), 2.13 (dd, J = 13.5 and 6.5 Hz, 1H), 1.87-1.80 (m, 1H), 1.30 (s, 3H), 1.16 (s, 9H). 13C NMR (the major product, 125 MHz, CDCl3): δ 154.8, 142.9, 142.4, 141.1, 136.8, 136.5, 135.9, 133.9, 133.6, 130.0, 129.5, 129.0, 127.8, 127.6, 127.2, 110.6, 110.4, 109.3, 92.1, 52.8, 45.1, 40.0, 26.8, 21.4, 20.5, 19.8; 1H NMR (the minor product, 500 MHz, CDCl3): δ 8.00-7.98 (m, 2H), 7.69-7.68 (m, 2H), 7.48-7.34 (m, 6H), 7.25-7.24 (m, 2H), 7.13-7.11 (m, 2H), 7.03 (s, 1H), 6.78-6.77 (m, 1H), 6.40-6.39 (m, 1H), 4.51 (s, 1H), 4.25 (s, 1H), 3.29 (t, J = 8.0 Hz, 1H), 2.70 (dd, J = 11.0 and 9.0 Hz, 1H), 2.37 (s, 3H), 2.23-2.20 (m, 1H), 2.07 (dd, J = 13.0 and 6.0 Hz, 1H), 2.03-2.00 (m, 1H), 1.20 (s, 3H), 1.16 (s, 9H). 13C NMR (the minor product, 125 MHz, CDCl3): δ 156.2, 142.9, 142.4, 141.0, 136.8, 136.3, 135.8, 134.0, 133.6, 129.9, 129.5, 129.0, 127.7, 127.5, 127.1, 111.4, 110.2, 108.0, 92.8, 51.5, 46.9, 42.6, 26.8, 21.4, 20.0, 19.5. HRMS (ESI) calcld for C34H40NO4SSi [(M+H+']): 586.2442, found: 586.2450. [α]26D = +27.2 (c 1.0, CHCl3).

Note: the ee value of 3ak can not be determined by HPLC analysis using a chiral stationary phase.
2-((tert-butyldiphenylsilyl)oxy)-4-(prop-1-en-2-yl)-2-(thiophen-2-yl)-1-tosylpyrrolidine: 3al

Colorless oil. 56% yield. d.r. = 10:1

1H NMR (the major product, 400 MHz, CDCl₃): δ 8.05-8.04 (m, 2H), 7.75-7.73 (m, 2H), 7.47-7.33 (m, 6H), 7.21-7.19 (m, 1H), 7.10 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 6.81-6.79 (m, 1H), 6.67-6.66 (m, 1H), 4.52 (s, 1H), 4.24 (s, 1H), 3.51 (t, J = 8.0 Hz, 1H), 2.81 (dd, J = 10.8 and 9.2 Hz, 1H), 2.51 (dd, J = 14.0 and 7.2 Hz, 1H), 2.34 (s, 3H), 2.23-2.16 (m, 1H), 1.83-1.73 (m, 1H), 1.30 (s, 3H), 1.19 (s, 9H). 13C NMR (the major product, 100 MHz, CDCl₃): δ 149.8, 142.8, 142.3, 136.8, 136.6, 136.0, 133.8, 133.5, 130.0, 129.5, 128.8, 127.8, 127.6, 127.0, 126.3, 125.2, 124.6, 110.6, 94.1, 52.9, 50.2, 39.7, 26.9, 21.4, 20.6, 20.0. HRMS (ESI) calcd for C₃₄H₄₀N₂O₃S₂Si [(M+H)⁺]: 602.2213, found: 602.2221. [α]²⁷_D = +5.9 (c 1.0, CHCl₃). 96% ee (the major product). HPLC analysis of the major product: Daicel Chiralpak IF column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 22.45 min (minor), 25.99 min (major).

(2S,4S)-2-phenyl-4-(prop-1-en-2-yl)-1-tosyl-2-((triisopropylsilyl)oxy)pyrrolidine: 3am

Colorless oil. 25% yield.

1H NMR (500 MHz, CDCl₃): δ 7.28-7.26 (m, 2H), 7.22-7.19 (m, 1H), 7.16-7.13 (m, 2H), 7.05-7.01 (m, 4H), 4.84 (s, 1H), 4.73 (s, 1H), 4.14 (t, J = 8.5 Hz, 1H), 3.33-3.26 (m, 1H), 3.17 (dd, J = 11.0 and 9.0 Hz, 1H), 2.48-2.44 (m, 2H), 2.37 (s, 3H), 1.79 (s, 3H), 1.34-1.28 (m,
3H), 1.24-1.21 (m, 18H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 143.5, 143.3, 142.2, 137.3, 128.8, 127.4, 127.2, 127.0, 126.8, 111.0, 95.8, 53.4, 50.6, 41.3, 21.40, 21.37, 18.53, 18.48, 14.0. HRMS (ESI) calcd for C$_{26}$H$_{37}$NNaO$_3$Si [(M+Na$^+$)]: 494.2156, found: 494.2153. $[\alpha]_{D}^{28} = -45.0$ (c 0.5, CHCl$_3$). 92% ee. HPLC analysis of the product: Daicel Chiralpak IC column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 36.77 min (major), 38.89 min (minor).

**3.3 General Procedure for Ring-Opening Reaction of Vinyl Aziridines and Enol Silyl Ethers.**

**Condition A:**

A mixture of [Rh(NBD)Cl]$_2$ (5.0 mg, 5 mol%) and AgPF$_6$ (5.5 mg, 10 mol%) in DCE (0.5 mL) was stirred at room temperature under argon atmosphere for 30 min. Then a solution of vinylaziridine 1 (0.20 mmol) and enol silyl ethers 2 (0.3 mmol) in DCE (1.5 mL) was added dropwise to this mixture at 0°C. The resulting mixture was then stirred at 0°C for about 1-4 h. Upon complete consumption of 1 (TLC monitoring), the solvent was removed under reduced pressure, and the residue was purified by chromatography, eluting with hexane:ethyl acetate:dichloromethane (7:1:1) to afford the desired cycloadduct 4.
Condition B:

A mixture of [Rh(NBD)Cl]_2 (5.0 mg, 5 mol%) and AgSbF_6 (7.5 mg, 10 mol%) in DCE (0.5 mL) was stirred at room temperature under argon atmosphere for 30 min. Then a solution of vinylaziridine 1 (0.20 mmol) and enol silyl ethers 2 (0.3 mmol) in DCE (1.5 mL) was added dropwisely to this mixture at room temperature. The resulting mixture was then stirred at room temperature for about 0.5-2.5 h. Upon complete consumption of 1 (TLC monitoring), the solvent was removed under reduced pressure, and the residue was purified by chromatography, eluting with hexane:ethyl acetate:dichloromethane (7:1:1) to afford the desired cycloadduct 4.

(S)-4-methyl-N-(3-methyl-2-(2-oxo-2-phenylethyl)but-3-en-1-yl)benzenesulfonamide: 4ao

Colorless oil. 86% yield. Condition A.
The enantiomer of this compound has already been reported.[4a] \([\alpha]^{28}_D = -2.8\) (c 1.0, CHCl_3). 98% ee. HPLC analysis of the product: Daicel Chiralpak OD-H column; hexane/2-propanol = 70/30, 0.5 mL/min. Retention times: 12.75 min (minor), 14.87 min (major).

(S)-4-methyl-N-(2-(2-oxo-2-phenylethyl)but-3-en-1-yl)benzenesulfonamide: 4bo

Colorless oil. 70% yield. Condition A.

\(^1\)H NMR (500 MHz, CDCl_3): \(\delta 7.90-7.88\) (m, 2H), 7.72 (d, \(J = 8.0\) Hz, 2H), 7.58-7.55 (m, 1H), 7.46-7.43 (m, 2H), 7.26 (d, \(J = 9.0\) Hz, 2H), 5.69-5.62 (m, 1H), 5.10-5.04 (m, 2H), 4.83 (t, \(J = 6.0\) Hz, 1H), 3.11-2.91 (m, 5H), 2.39 (s, 3H). \(^{13}\)C NMR (125 MHz, CDCl_3): \(\delta 198.4, 143.4, 137.8, 136.8, 136.7, 133.2, 129.7, 128.6, 128.0, 127.0, 117.4, 46.3, 40.3, 38.5, 21.4\). HRMS (ESI) calcd for C_{19}H_{21}NNaO_3S [(M+Na^+)]: 366.1134, found: 366.1128. \([\alpha]^{27}_D = +1.7\) (c 1.0, CHCl_3). 96% ee. HPLC analysis of the product: Daicel Chiralpak OD-H column; hexane/2-propanol = 70/30, 0.5 mL/min. Retention times: 13.94 min (minor), 15.33 min (major).
(S)-4-nitro-N-(2-(2-oxo-2-phenylethyl)but-3-en-1-yl)benzenesulfonamide: 4co

Yellow oil. 67% yield. Condition A.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.29-8.27 (m, 2H), 8.04-8.01 (m, 2H), 7.88-7.86 (m, 2H), 7.59-7.55 (m, 1H), 7.46-7.43 (m, 2H), 5.72-5.65 (m, 1H), 5.28 (t, $J$ = 6.0 Hz, 1H), 5.13-5.07 (m, 2H), 3.22-3.18 (m, 1H), 3.11-3.06 (m, 3H), 2.98-2.92 (m, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 198.4, 149.9, 145.8, 137.5, 136.4, 133.5, 128.7, 128.2, 128.0, 124.3, 117.6, 46.3, 40.2, 38.5. HRMS (ESI) calcd for C$_{18}$H$_{18}$N$_2$NaO$_5$S [(M+Na$^+$)]: 397.0829, found: 397.0832. $[\alpha]^2$D = +4.0 ($c$ 1.0, CHCl$_3$). 71% ee. HPLC analysis of the product: Daicel Chiralpak AD-H column; hexane/2-propanol = 70/30, 0.5 mL/min. Retention times: 30.82 min (minor), 44.45 min (major).

(S)-4-methyl-N-(2-(2-oxo-2-phenylethyl)-3-phenylbut-3-en-1-yl)benzenesulfonamide: 4go

Colorless oil. 87% yield. Condition A.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.90-7.88 (m, 2H), 7.66 (d, $J$ = 8.4 Hz, 2H), 7.56-7.52 (m, 1H), 7.44-7.40 (m, 2H), 7.29-7.24 (m, 5H), 7.18 (d, $J$ = 8.4 Hz, 2H), 5.30 (s, 1H), 5.04 (s, 1H), 4.90 (t, $J$ = 6.4 Hz, 1H), 3.59-3.53 (m, 1H), 3.25-3.12 (m, 3H), 3.06-2.99 (m, 1H), 2.34 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 198.4, 149.0, 143.2, 141.0, 136.8, 136.7, 133.1, 129.6, 128.5, 128.0, 127.8, 126.9, 126.6, 113.9, 45.5, 40.2, 38.5, 21.4. HRMS (ESI) calcd for
C_{25}H_{25}NNaO_{3}S [(M+Na^+)]: 442.1447, found: 442.1454. [\alpha]^{28}D = -29.3 (c 1.0, CHCl_3). 97% ee. HPLC analysis of the product: Daicel Chiralpak OD-H column; hexane/2-propanol = 70/30, 0.5 mL/min. Retention times: 16.26 min (minor), 18.80 min (major).

(S)-4-methyl-N-(3-methyl-2-(2-oxo-2-(p-toly)ethyl)but-3-en-1-yl)benzenesulfonamide: 4ap

Yellow oil. 96% yield. Condition A.

\[^1^H\text{NMR} (400 \text{ MHz, CDCl}_3): \delta 7.78 \text{ (d, } J = 8.4 \text{ Hz, } 2H), 7.72 \text{ (d, } J = 8.4 \text{ Hz, } 2H), 7.25-7.22 \text{ (m, } 4H), 4.85 \text{ (s, } 1H), 4.79 \text{ (t, } J = 6.0 \text{ Hz, } 1H), 4.71 \text{ (s, } 1H), 3.10-2.95 \text{ (m, } 4H), 2.91-2.85 \text{ (m, } 1H), 2.40 \text{ (s, } 3H), 2.38 \text{ (s, } 3H), 1.64 \text{ (s, } 3H). \]

\[^{13}C\text{NMR} (100 \text{ MHz, CDCl}_3): \delta 198.0, 144.2, 143.9, 143.2, 136.8, 134.2, 129.6, 129.2, 128.1, 127.0, 113.3, 44.9, 41.2, 39.8, 21.5, 21.4, 20.2. \]

HRMS (ESI) calcul for C_{21}H_{23}NNaO_{3}S [(M+Na^+)]: 394.1447, found: 394.1450. [\alpha]^{27}D = -1.7 (c 1.0, CHCl_3). 95% ee. HPLC analysis of the product: Daicel Chiralpak OD-H column; hexane/2-propanol = 70/30, 0.5 mL/min. Retention times: 12.22 min (minor), 26.41 min (major).

(S)-N-(2-(2-(4-chlorophenyl)-2-oxoethyl)-3-methylbut-3-en-1-yl)-4-methylbenzenesulfonamide: 4aq

Yellow oil. 62% yield. Condition B.

\[^1^H\text{NMR} (400 \text{ MHz, CDCl}_3): \delta 7.83 \text{ (d, } J = 8.4 \text{ Hz, } 2H), 7.71 \text{ (d, } J = 8.0 \text{ Hz, } 2H), 7.41 \text{ (d, } J = 8.8 \text{ Hz, } 2H), 7.26 \text{ (d, } J = 8.4 \text{ Hz, } 2H), 4.87 \text{ (s, } 1H), 4.72 \text{ (s,} \]

S20
1H), 4.70-4.67 (m, 1H), 3.11-2.97 (m, 4H), 2.91-2.86 (m, 1H), 2.39 (s, 3H), 1.65 (s, 3H). 13C NMR (100 MHz, CDCl3): δ 197.2, 144.0, 143.4, 139.6, 136.8, 135.0, 129.7, 129.4, 128.9, 127.0, 113.5, 44.8, 41.1, 39.8, 21.4, 20.4. HRMS (ESI) calcd for C20H22ClNNaO3S [(M+Na+): 414.0901, found: 414.0900. [α]28D = +0.1 (c 1.0, CHCl3). 94% ee. HPLC analysis of the product: Daicel Chiralpak OD-3 column; hexane/2-propanol = 70/30, 0.5 mL/min. Retention times: 12.69 min (minor), 26.48 min (major).

(S)-N-(2-(2-(3-methoxyphenyl)-2-oxoethyl)-3-methylbut-3-en-1-yl)-4-methylbenzenesulfonamide: 4ar

Yellow oil. 83% yield. Conditon B.

1H NMR (400 MHz, CDCl3): δ 7.71 (d, J = 8.4 Hz, 2H), 7.47-7.45 (m, 1H), 7.42-7.41 (m, 1H), 7.36-7.32 (m, 1H), 7.25 (d, J = 8.0 Hz, 2H), 7.12-7.09 (m, 1H), 4.86 (s, 1H), 4.72 (s, 1H), 4.69 (t, J = 6.0 Hz, 1H), 3.84 (s, 3H), 3.12-2.96 (m, 4H), 2.92-2.85 (m, 1H), 2.39 (s, 3H), 1.64 (s, 3H). 13C NMR (100 MHz, CDCl3): δ 198.2, 159.8, 144.1, 143.3, 138.1, 136.9, 129.65, 129.55, 127.0, 120.6, 119.6, 113.5, 112.3, 55.4, 44.9, 41.3, 40.0, 21.4, 20.2. HRMS (ESI) calcd for C21H25NNaO3S [(M+Na+): 410.1396, found: 410.1403. [α]27D = -2.0 (c 1.0, CHCl3). 95% ee. HPLC analysis of the product: Daicel Chiralpak OD-H column; hexane/2-propanol = 70/30, 0.5 mL/min. Retention times: 14.61 min (minor), 16.96 min (major).

(S)-4-methyl-N-(2-methyl-3-(2-oxo-2-(o-tolyl)ethyl)but-3-en-1-yl)benzenesulfonamide: 4as

Yellow oil. 55% yield. Conditon B.
$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.72 (d, $J = 8.4$ Hz, 2H), 7.56-7.54 (m, 2H), 7.38-7.34 (m, 1H), 7.28-7.22 (m, 4H), 4.86 (s, 1H), 4.70 (s, 1H), 4.57 (t, $J = 6.4$ Hz, 1H), 3.09-2.95 (m, 4H), 2.88-2.84 (m, 1H), 2.43 (s, 3H), 2.40 (s, 3H), 1.62 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 202.4, 144.0, 143.4, 138.1, 137.7, 136.9, 131.9, 131.3, 129.7, 128.3, 127.1, 125.7, 113.7, 44.8, 42.8, 41.5, 21.4, 21.1, 20.1. HRMS (ESI) calcd for C$_{21}$H$_{25}$NNaO$_3$ [(M+Na$^+$)]: 394.1447, found: 394.1457. $[^\alpha]_{28}^D = -3.1$ (c 1.0, CHCl$_3$). 89% ee. HPLC analysis of the product: Daicel Chiralpak AD-H column; hexane/2-propanol = 70/30, 0.5 mL/min. Retention times: 16.40 min (minor), 20.26 min (major).

4-methyl-N-(3-methyl-2-(1-oxo-1-phenylpropan-2-yl)but-3-en-1-yl)benzenesulfonamide: 4at

Colorless oil. 84% yield. $d.r. = 1.5:1$. (Z)-2t was used. Conditon A (10 mol% AgClO$_4$ was used) (The diastereomers can not be separated by chromatography).

$^{1}$H NMR (the major product, 500 MHz, CDCl$_3$): $\delta$ 7.91-7.89 (m, 2H), 7.74 (d, $J = 8.0$ Hz, 2H), 7.59-7.54 (m, 1H), 7.48-7.43 (m, 2H), 7.30 (d, $J = 8.0$ Hz, 2H), 4.80 (s, 1H), 4.66 (s, 1H), 4.61 (s, 1H), 3.76-3.70 (m, 1H), 3.10 (t, $J = 6.0$ Hz, 2H), 2.64-2.60 (m, 1H), 2.42 (s, 3H), 1.57 (s, 3H), 1.15 (d, $J = 7.0$ Hz, 3H). $^{13}$C NMR (the major product, 125 MHz, CDCl$_3$): $\delta$ 203.1, 144.0, 141.8, 136.6, 136.1, 133.1, 129.7, 128.7, 128.1, 127.0, 113.9, 46.9, 41.5, 40.4, 21.6, 21.4, 15.2; $^{1}$H NMR (the minor product, 500 MHz, CDCl$_3$): $\delta$ 7.91-7.89 (m, 2H), 7.66 (d, $J = 8.0$ Hz, 2H), 7.59-7.54 (m, 1H), 7.48-7.43 (m, 2H), 7.24 (d, $J = 8.0$ Hz, 2H), 4.98 (s, 1H), 4.80 (s, 1H), 4.50 (s, 1H), 3.46-3.40 (m, 1H), 2.97-2.92 (m, 1H), 2.84-2.78 (m, 1H), 2.72-2.67 (m, 1H), 2.39 (s, 3H), 1.59 (s, 3H), 1.05 (d, $J = 7.0$ Hz, 3H). $^{13}$C NMR (the minor product, 125 MHz, CDCl$_3$): $\delta$ 202.6, 143.4, 143.2, 136.7, 136.4, 133.2, 129.5, 128.7, 128.2, 127.0, 116.7, 49.0, 43.4, 40.7, 21.4, 18.4, 16.7. HRMS (ESI) calcd for C$_{21}$H$_{25}$NNaO$_3$ [(M+H$^+$)]: 394.1448, found: 394.1447. $[^\alpha]_{28}^D = -15.0$ (c 1.0, CHCl$_3$). HPLC analysis of the product: Daicel Chiralpak IE column; hexane/2-propanol = 70/30, 0.5 mL/min. The major product: 98% ee: Retention times: 44.20 min (minor), 47.84 min (major);
The minor product: 98% ee: Retention times: 39.20 min (major), 42.38 min (minor).

4. References:
5. Crystal Structure of (S,S)-3ba

Datablock: z

Bond precision: C-C = 0.0056 Å
Wavelength=0.71073

Cell: a=8.4529(13) b=8.8371(16) c=38.949(6)
alpha=90 beta=90 gamma=90

Temperature: 296 K

Calculated Reported
Volume 3337.6(9) 3337.6(9)
Space group P 21 21 21 P 2(1) 2(1) 2(1)
Hall group F 2ac 2ab ?
Molity formula C35 H38 N O3 S Si
Sum formula C35 H38 N O3 S Si
Mr 591.02 591.02
Dx, g cm^-3 1.158 1.158
Z 4 4
Mu (mm^-1) 0.166 0.166
F000 1240.0 1240.0
F000' 1241.28
h,k,lmax 10,11,47 10,11,47
Nref 5854[ 3383] 5852
Tmin,Tmax 0.538,0.558 0.524,0.558
Tmin' 0.923

Correction method: # Reported T Limits: Tmin=0.924 Tmax=0.958
AbsCorr = MULTI-SAN
Data completeness= 1.74/1.00 Theta(max)= 25.010
R(reflections)= 0.0470( 4014) wR2(reflections)= 0.1086( 5892)
S = 1.014 Npar= 370
6. $^1$H and $^{13}$C NMR Spectra for New Compounds