# Palladium-Catalyzed Cyclization Reactions of 2-Vinylthiiranes with Heterocumulenes. Regioselective and Enantioselective Formation of Thiazolidine, Oxathiolane, and Dithiolane Derivatives

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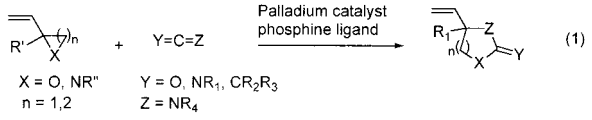
The first palladium-catalyzed ring-expansion reaction of 2-vinylthiiranes with heterocumulenes to form sulfur-containing five-membered-ring heterocycles is described. This regioselective reaction requires 5 mol % of $Pd_2(dba)_3$·$CHCl_3$ and 10 mol % of bidendate phosphine ligand (dppp, BINAP), at 50−80 °C, in THF. The reaction of 2-vinylthiiranes with carbodiimides, isocyanates, and ketenimines affords 1,3-thiazolidine derivatives, whereas the reaction with diphenylketene or isothiocyanates results in the formation of 1,3-oxathiolane or 1,3-dithiolane compounds in good to excellent isolated yields and in up to 78% ee.

## Introduction

Palladium-catalyzed ring-expansion reactions of heterocyclic compounds have attracted considerable attention in recent years. The substrates for this type of reaction commonly are small rings such as oxiranes, oxetanes, aziridines, and azetidines.[1] We previously reported the regio- and stereoselective formation of five- and six-membered heterocycles by the palladium-catalyzed ring-opening cycloaddition reactions of vinyloxiranes,[2,3] vinyloxetanes,[4] and vinylaziridines[5] with heterocumulenes (eq 1). However, to our knowledge, there




(1)

are no examples of ring expansion reactions of thiiranes catalyzed by transition metal complexes[6,7] presumably because of the supposed poisoning of the catalyst by the organic sulfur reactant.[8,9] Sulfur-containing heterocycles are of particular interest, especially the thiazolidine and the oxathiolane moieties that are found in a wide range of products possessing biological activity.[10−12]

Herein, we describe the first palladium-catalyzed ring-opening reaction of 2-vinylthiiranes with heterocumulenes for the formation of thiazolidine, oxathiolane, and dithiolane derivatives. Moreover, this methodology could be used to synthesize these five-membered heterocycles in fair-good enantioselectivity, by adding a chiral ligand to the reaction mixture.

## Results and Discussion

**Cycloaddition Reactions of 2-Vinylthiirane with Various Heterocumulenes.** The reaction of 2-vinylthiirane (**1a**, 1.5 mmol) with bis(*p*-chlorophenyl)carbodiimide (**2a**, 1 mmol) was first investigated by using reaction conditions similar to those described for the reaction of 2-vinyloxiranes with heterocumulenes, i.e., 3 mol % of $Pd_2(dba)_3$·$CHCl_3$ and 6 mol % of dppp in 5 mL of THF under $N_2$ at room temperature for 24 h. However, no conversion of the carbodiimide (by IR determination) was observed. Complete conversion of the carbodiimide (1 mmol) in 24 h resulted when **1a** (2 mmol) was reacted at 50 °C in the presence of 5 mol % of $Pd_2(dba)_3$·$CHCl_3$ and 10 mol % of dppp. The product, *N*-(4-chlorophenyl)-*N*-[3-(4-chlorophenyl)-4-vinyl-1,3-thiazolidin-2-ylidene]-amine (**4a**) was isolated in 97% yield. The reaction

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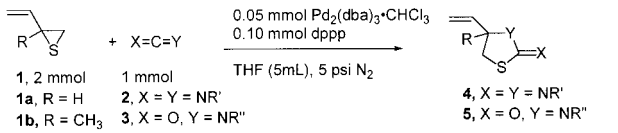
**Table 1. Cycloaddition Reactions of 2-Vinylthiiranes (1) with Carbodiimides (2) or Isocyanates (3)[a]**




| entry | 1 | 2 or 3 | reaction conditions | product | isolated yield[b] (%) |
|---|---|---|---|---|---|
| 1 | **1a** | X = Y = $NC_6H_4CL$-*p*, **2a** | 50 °C, 24 h | **4a** | 97 |
| 2 | **1a** | X = Y = $NC_6H_4Br$-*p*, **2b** | 70 °C, 24 h | **4b** | 98 |
| 3 | **1a** | X = Y = $NC_6H_4Cl$-*o*, **2c** | 80 °C, 24 h | **4c** | 95 |
| 4 | **1a** | X = Y = $NC_6H_4NO_2$-*p*, **2d** | 80 °C, 24 h | **4d** | 85 |
| 5 | **1b** | X = Y = $NC_6H_4Cl$-*p*, **2a** | 60 °C, 48 h | **4e** | 60 |
| 6 | **1b** | X = Y = $NC_6H_4Br$-*p*, **2b** | 60 °C, 24 h | **4f** | 43 |
| 7 | **1b** | X = Y = $NC_6H_4NO_2$-*p*, **2d** | 80 °C, 24 h | **4g** | 80 |
| 8 | **1a** | X = O, Y = $NC_6H_4Cl$-*p*, **3a** | 50 °C, 20 h | **5a** | 75 |
| 9 | **1a** | X = O, Y = $NC_6H_4Br$-*p*, **3b** | 50 °C, 20 h | **5b** | 57 |
| 10 | **1b** | X = O, Y = $NC_6H_4NO_2$-*p*, **3c** | 50 °C, 24 h | **5c** | 47 |
| 11 | **1a** | X = Y = $NC_6H_4CH_3$-*p*, **2e** | 80 °C, 24 h | | 0 |
| 12 | **1a** | X = Y = $NC_6H_5$, **2f** | 80 °C, 24 h | | 0 |

[a] All reactions were conducted in THF (5 mL) using **1** (2 mmol), **2** or **3** (1 mmol), $Pd_2(dba)_3$•$CHCl_3$ (0.05 mmol), and dppp (0.10 mmol) in a glass autoclave. [b] Isolated yield by preparative silica gel TLC with *n*-pentane/$Et_2O$ as the developer.

proceeds smoothly when carbodiimides containing electron withdrawing substituents on the aromatic ring (i.e., **2b**−**d)** were used for the reaction with **1a**, resulting in the formation of (4-vinyl-1,3-thiazolidin-2-ylidene)amine, **4b**−**d**, in 85−98% yields (Table 1, entries 2−4). Slightly lower product yields of **4e**−**g** (43−80% yield) were obtained from the reactions of **2a**,**b** and **2d** with 2-methyl-2-vinylthiirane (**1b**) under the same reaction conditions (entries 5−7). Utilizing isocyanates (**3a**−**c**) for the reaction with **1a** or **1b** afforded 4-vinyl-1,3-thiazolidin-2-ones (**5a**−**c**) in fine yields (entries 8−10). No conversion occurred when carbodiimides **2e** and **2f** were used in reaction with **1a** (entries 11, 12), possibly due to the lower electrophilicity of the carbon center of the carbodiimides as well as the strong coordination of the sulfur anion to the palladium in the $\pi$-allyl palladium intermediate (via infra). Performing the reaction using other palladium catalysts such as $Pd(PhCN)_2Cl_2$ or $Pd(PPh_3)_4$ also did not afford the products. When other 2-vinylthiiranes such as 3-phenyl-2-vinylthiirane or 2-styrylthiirane[13] were used to react with bis(*p*-chlorophenyl)carbodiimide (**2a**) in the presence of 5 mol % of $Pd_2(dba)_3$•$CHCl_3$−dppp catalyst in THF at 80 °C for 24 h, none of the desired products was obtained.

Ketenimines can also participate in these palladium-catalyzed cycloaddition reactions (Table 2). In particular, the reaction of 2-vinylthiirane (**1a**) with the ketenimine **6a** (respectively **6b**) gave only one regioisomer **7a** (respectively **7b**) in moderate to good yields (entries 1, 2). The cyclization is also totally stereoselective on the

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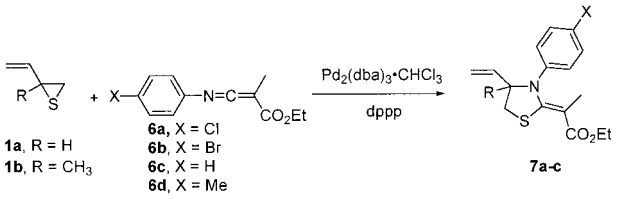
**Table 2. Cycloaddition Reactions of 2-Vinylthiiranes (1) with Ketenimines (6)[a]**




| entry | 1 | 6 | product | isolated yield (%) |
|---|---|---|---|---|
| 1 | **1a** | **6a** | **7a** | 73 |
| 2 | **1a** | **6b** | **7b** | 46 |
| 3 | **1a** | **6c** | | |
| 4 | **1a** | **6d** | | traces |
| 5 | **1b** | **6a** | **7c** | 81 |

[a] All reactions were conducted in THF (5 mL) at 70 °C under $N_2$ pressure (5 psi), using **1** (2 mmol), **6** (1 mmol), $Pd_2(dba)_3$•$CHCl_3$ (0.05 mmol), and dppp (0.10 mmol) in a glass autoclave.

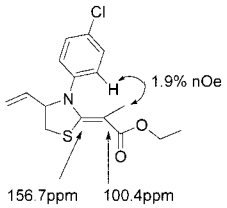
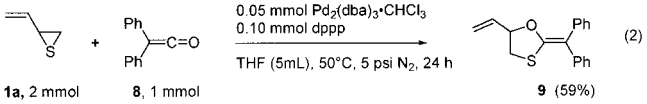



**Figure 1.** Characteristic NMR data of compound **7a**.

double bond: for instance, a 1.9% nuclear Overhauser effect was measured between the methyl group and one aromatic proton in **7a** (Figure 1).

As we already observed with the experiment involving **2f**, this reaction requires an electron-withdrawing group on the aromatic ring: no desired products or only traces were formed by the reaction of **1a** with **6c** or **6d** (entries 3, 4).

Ketenes are known to be more reactive heterocumulenes than ketenimines. The regioselective reaction of **1a** with diphenylketene (**8**) gave the oxathiolane derivative (**9**) in 59% yield, using $Pd_2(dba)_3$•$CHCl_3$−dppp in THF at 50 °C (eq 2). No cyclic thioester was isolated, perhaps due to the steric hindrance of the two phenyl groups near the vinyl substituent.




(2)

The palladium-catalyzed ring expansion enables one to synthesize not only oxathiolane but also dithiolane compounds. Treatment of 2-vinylthiirane (**1a**, 2 mmol) with *p*-chlorophenylisothiocyanate (**10a**) in the presence of 0.05 mmol $Pd_2(dba)_3$•$CHCl_3$, 0.1 mmol dppp in THF, under $N_2$ at 80 °C for 24 h, gave syn and anti isomers[14] of *N*-(4-chlorophenyl)-4-vinyl-1,3-dithiolan-2-ylideneamine (**11a**) in 77% yield (eq 3). For this reaction, the sulfur of the isothiocyanate is the nucleophile rather than nitrogen.[15−17] Other isothiocyanates such as **10b**−**d** re-

(14) A mixture of *E* and *Z* isomers of **9a**−**d** was detected by $^{13}C$ NMR spectroscopy. See the Supporting Information for their spectra.

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**Scheme 1**

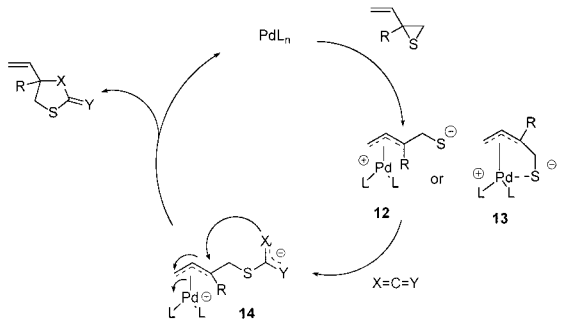
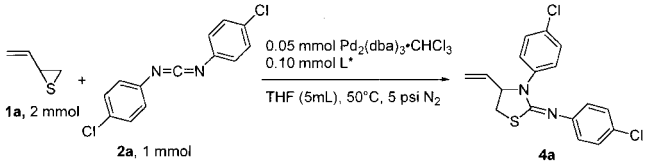


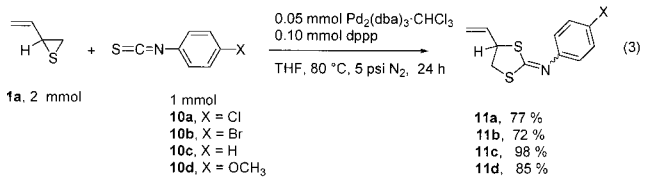

**Table 3. Asymmetric Cycloaddition Reactions of 1a with 2a Using Various Chiral ligands**




| entry | chiral ligand L* | reaction time (h) | isolated yield (%) | ee[a] (%) |
|---|---|---|---|---|
| 1 | (*S*)-tol-BINAP | 24 | 84 | 63 |
| 2 | (*R*)-BINAP | 24 | 68 | −68[b] |
| 3 | (*R*,*R*)-BDPP | 24 | 91 | −27 |
| 4 | (−) DIOP | 24 | 48 | −17 |
| 5 | (*R*,*R*)-NORPHOS | 72 | 59 | 64 |
| 6 | (*R*,*R*)-Me-DUPHOS | 24 | 29 | −25 |
| 7 | Trost ligand | 72 | *c* | |
| 8 | Fe* | 24 | 90 | −47 |

[a] ee determined by chiral HPLC (Chiralcel OD column, hexane/2-propanol 95/5). [b] The negative sign indicates the opposite chirality. [c] Conversion less than 10%.

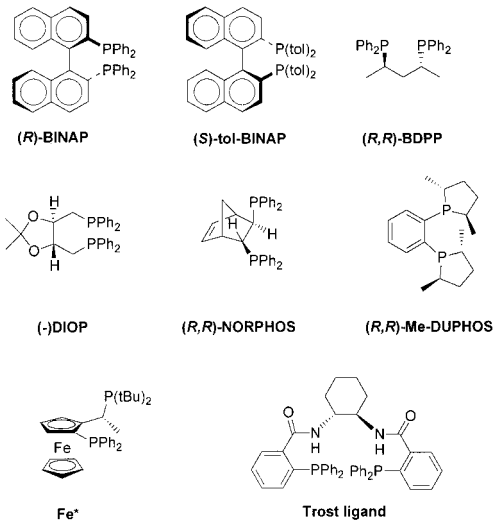
actedwith **1a**, affording **11b**−**d** in high yields. In these cases, the cyclization products were obtained irrespective of whether the aromatic ring contained electron-donating or electron-withdrawing groups.




All these cyclization reactions may proceed via the formation of a $\pi$-allyl palladium complex (**12**), generated by oxidative addition of 2-vinylthiiranes to a palladium(0) species (Scheme 1). It is conceivable that the sulfur may coordinate to palladium to form intermediate **13** as it is known that sulfur bonds strongly to metals. Reaction of **12** or **13** with heterocumulenes affords the palladium complex **14**. Nucleophilic addition of either nitrogen (of carbodiimides, isocyanates, and ketenimines), oxygen (of ketene), or sulfur (of isothiocyanates) to the $\pi$-allyl palladium moiety may afford the product, with regeneration of the palladium(0) catalyst.

**Asymmetric Cycloaddition Reactions of 2-Vinylthiirane Using Several Chiral Ligands.** The enantioselective variant of the reaction was next investigated. To determine the best chiral phosphine ligand for the process, we examined the cycloaddition reaction of the 2-vinylthiirane **1a** with the carbodiimide **2a** (Table 3).

It was shown that the BINAP-type ligands were very efficient (ee up to 94%) in the cycloaddition reaction of the 2-vinyloxirane with **2a**. With 2-vinylthiirane as the substrate, (*S*)-tol-BINAP and (*R*)-BINAP afforded the thiazolidine compound **4a** in good yields and 63−68% ee (entries 1, 2). The Trost ligand, which is known to give good enantiomeric excess in asymmetric allylic alkylation,[19] was then tested. However, no reaction occurred when it was added to the palladium(0) catalyst (entry 7). Reactions involving (*R*,*R*)-BDPP, (−)-DIOP, or (*R*,*R*)-Me-DUPHOS proceeded in low asymmetric induction (entries 3, 4, and 6). Use of (*R*,*R*)-NORPHOS gave 64% ee, comparable to results obtained with BINAP or tol-BINAP, but this cycloaddition reaction proceeded appreciably slower with complete conversion of the reactants requiring 72 h (entry 5). A chiral ferrocenyl diphosphine Fe*, which belongs to another class of chiral ligands, was also investigated. This type of ligand has been used in a variety of reactions, including enantioselective hydrogenation and hydroboration reactions,[20] asymmetric alcoholysis, and aminolysis of oxabenzonorbornadiene.[21] The reaction of 2-vinylthiirane with **2a** led to the desired product in 90% yield but only in 47% ee (entry 8). In summary, BINAP-type ligands were found to provide **4a** in good yields and in up to 68% ee.




The experimental conditions were varied in attempting to increase the enantioselectivity of the cycloaddition reaction of **1a** and **2a** in the presence of 5 mol % $Pd_2(dba)_3$•$CHCl_3$ and 10 mol % (*S*)-tol-BINAP. All changes—in temperature (from 25 to 65 °C), solvent (benzene, dichloromethane, DMF) and concentration of the substrates—had little impact on the % ee of the reaction.

The influence of the heterocumulene on the stereoselectivity of the ring-expansion reaction of **1a** was then assessed, using (*R*)-BINAP as the chiral ligand (Table 4). The isocyanate (**3a**) and the diphenylketene (**8**) gave the thiazolidine (**5a**) and the oxathiolane derivative (**9**), respectively, in good yields but in low enantiomeric excess (entries 4, 7). This poor enantioselectivity may be explained by a $\eta^3-\eta^1-\eta^3$ pathway involving intermediates **15** and **16**. The latter interconversion may be faster than

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(19) Trost, B. M.; Van Vranken, D. L.; Bingel, C. *J. Am. Chem. Soc.* **1992**, *114*, 9327.
(20) Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Landert, H.; Tijani, A. *J. Am. Chem. Soc.* **1994**, *116*, 4062.
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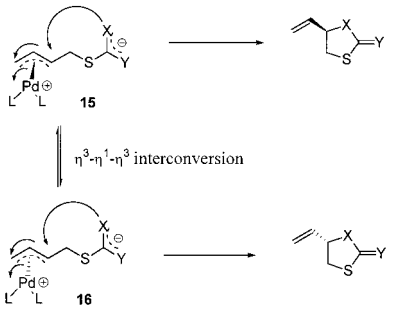
**Table 4. Asymmetric Cycloaddition Reactions of 1a with Various Heterocumulenes Using (*R*)-BINAP as the Chiral Ligand[a]**

| entry | heterocumulene | reaction conditions | isolated yield (%) | ee[b] (%) |
|---|---|---|---|---|
| 1 | **2a** | 50 °C, 24 h | 84 | 68 |
| 2 | **2b** | 70 °C, 48 h | 76 | 60 |
| 3 | **2c** | 80 °C, 30 h | 48 | 65 |
| 4 | **3a** | 50 °C, 17 h | 60 | 10[c] |
| 5 | **6a** | 70 °C, 24 h | 51 | 78 |
| 6 | **6b** | 70 °C, 24 h | 55 | 78 |
| 7 | **10** | 50 °C, 24 h | 92 | 10 |

[a] All reactions were conducted in THF (5 mL) under $N_2$ (5 psi), using **1a** (2 mmol), heterocumulene (1 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (0.05 mmol), and (*R*)-BINAP (0.10 mmol) in a glass autoclave. [b] ee determined by chiral HPLC (Chiralcel OD column, hexane/2-propanol mixture). [c] ee determined by chiral GC (Chiraldex B-PH, $T = 190$ °C).

**Scheme 2**




the intramolecular nucleophilic attack of the nitrogen atom (for **3a**) or the oxygen atom (for **8**) (Scheme 2). Using different carbodiimides, such as *p*-chlorophenylcarbodiimide (**2a**), *o*-chlorophenylcarbodiimide (**2b**), or *p*-bromophenylcarbodiimide (**2b**), in the cycloaddition reaction with **1a** did not significantly change the % ee of the reaction (entries 1−3). However, when the reaction was carried out with the ketenimines **6a**,**b**, the thiazolidine products **7a**,**b** were synthesized in 51−55% yield and in 78% ee in both cases (entries 5, 6). Therefore, the enantioselectivity of the cycloaddition reaction with 2-vinylthiirane is dependent, to some extent, on the type of the heterocumulene.

## Conclusions

It is easy to prepare thiazolidine, oxathiolane, and dithiolane derivatives by the regioselective reaction of 2-vinylthiiranes with heterocumulenes in the presence of 5 mol % $Pd_2(dba)_3{\cdot}CHCl_3$ and 10 mol % dppp. This methodology using chiral BINAP-type ligands affords products in up to 78% ee, the enantiomeric excess of this cyclization reaction depending on the nature of the heterocumulene. This study represents the first palladium-catalyzed ring opening of 2-vinylthiiranes with heterocumulenes to give heterocyclic compounds in fine yields and good enantioselectivity.

## Experimental Section

**General Methods.** All NMR spectra were recorded in $CDCl_3$ on Bruker AMX 500, Varian XL-300, and/or Gemini 200 spectrometers. Infrared spectra were recorded on a Bomem MB 100-C15 Fourier transform spectrometer. All reactions were carried out under a nitrogen atmosphere. Organic solvents were dried and distilled prior to use. $Pd_2(dba)_3{\cdot}CHCl_3$, phosphine ligands, isocyanates (**3a**−**c**), and isothiocyanates (**10a**−**d**) were purchased from commercial sources and were used as received. 2-Vinylthiiranes,[22] carbodiimides (**2a**−**f**),[23] ketenimines (**6a**−**d**),[24] and diphenylketene (**8**)[25] were prepared according to literature procedures.

**General Procedure for the Palladium-Catalyzed Cycloaddition Reaction of Vinylthiiranes and Heterocumulenes.** A mixture of $Pd_2(dba)_3{\cdot}CHCl_3$ (0.05 mmol), phosphine ligand (0.10 mmol), and THF (3 mL) was stirred under a $N_2$ atmosphere in a glass autoclave at room temperature for 30 min. Then 2-vinylthiirane (**1**, 2 mmol), the heterocumulene (**2**, **3**, **6**, **8**, or **10**, 1 mmol), and another 2 mL of THF were added, and the mixture was stirred under 5 psi of $N_2$, at a given temperature (see the tables and equations for the reaction time and temperature in each case) until the conversion of the heterocumulene was complete (monitored by IR). The reaction was then filtered through Celite and concentrated. The product was purified by silica gel preparative TLC using a mixture of *n*-pentane/$Et_2O$ as the developer.

***N*-(4-Chlorophenyl)-*N*-[3-(4-chlorophenyl)-4-vinyl-1,3-thiazolidin-2-ylidene]amine (4a):** mp = 75−76 °C; IR 1621 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz) 3.03 (dd, 1H, $J = 10.9$, 6.1 Hz), 3.42 (dd, 1H, $J = 10.9$, 6.7 Hz), 4.70 (brq, 1H, $J = 6.7$ Hz), 5.24 (dt, 1H, $J = 10.1$, 0.9 Hz), 5.29 (dt, 1H, $J = 17.2$, 0.9 Hz), 5.85 (ddd, 1H, $J = 17.2$, 10.1, 7.4 Hz), 6.85 (d, 2H, $J = 8.7$ Hz), 7.21 (d, 2H, $J = 8.7$ Hz), 7.32 (AB, 4H); $^{13}C$ NMR ($CDCl_3$, 75 MHz) 32.9, 66.4, 119.5, 123.2, 126.8, 128.8, 128.9, 135.4, 128.6, 130.9, 138.7, 150.1, 158.3; MS (*m*/*e*) 348 $[M]^+$. Anal. Calcd for $C_{17}H_{14}Cl_2N_2S$: C, 58.46; H, 4.04; N, 8.02. Found: C, 58.47; H, 4.04; N, 7.98.

***N*-(4-Chlorophenyl)-*N*-[3-(4-chlorophenyl)-4-methyl-4-vinyl-1,3-thiazolidin-2-ylidene]amine (4e):** mp = 58−59 °C; IR 1618 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz) 1.43 (s, 3H), 3.17 (s, 2H), 5.19 (d, 1H, $J = 17.2$ Hz), 5.24 (d, 1H, $J = 10.7$ Hz), 6.12 (dd, 1H, $J = 17.2$, 10.7 Hz), 6.81 (d, 2H, $J = 8.5$ Hz), 7.17 (d, 2H, $J = 8.5$ Hz), 7.19 (d, 2H, $J = 8.5$ Hz), 7.27 (2H, $J = 8.5$ Hz); $^{13}C$ NMR ($CDCl_3$, 75 MHz) 22.5, 40.4, 67.5, 116.3, 123.3, 128.7, 129.1, 130.8, 139.7, 128.4, 133.1, 137.5, 150.2, 159.6; MS (*m*/*e*) 362 $[M]^+$; HRMS calcd for $C_{18}H_{16}Cl_2N_2S$ 362.0411, found 362.0414.

**3-(4-Chlorophenyl)-4-vinyl-1,3-thiazolidin-2-one (5a):** oily liquid; IR 1673 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz) 3.09 (dd, 1H, $J = 11.0$, 6.1 Hz), 3.55 (dd, 1H, $J = 11.0$, 7.3 Hz), 4.67−4.78 (brq, 1H, $J = 7.0$ Hz), 5.23 (d, 1H, $J = 10.0$ Hz), 5.27 (d, 1H, $J = 17.2$ Hz), 5.82 (ddd, 1H, $J = 17.2$, 10.0, 6.6 Hz), 7.20 (d, 2H, $J = 8.9$ Hz), 7.29 (d, 2H, $J = 8.9$ Hz); $^{13}C$ NMR ($CDCl_3$, 50 MHz) 31.7, 64.1, 119.7, 125.8, 128.8, 134.7, 131.4, 136.4, 171.0; MS (*m*/*e*) 239 $[M]^+$; HRMS calcd for $C_{11}H_{10}ClNOS$ 239.0172, found 239.0142.

**Ethyl 2-[3-(4-chlorophenyl)-4-vinyl-1,3-thiazolidin-2-ylidene]propanoate (7a):** oily liquid; IR 1675, 1552 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz) 1.26 (t, 3H, $J = 7.1$ Hz), 1.52 (s, 3H), 2.80 (dd, 1H, $J = 10.9$, 1.5 Hz), 3.29 (dd, 1H, $J = 10.9$, 7.2 Hz), 4.19 (q, 2H, $J = 7.1$ Hz), 4.60 (m, 1H), 5.21−5.34 (m, 2H), 5.95 (ddd, 1H, $J = 17.0$, 10.2, 4.8 Hz), 6.87 (d, 2H, $J = 8.8$ Hz), 7.20 (d, 2H, $J = 8.8$ Hz); $^{13}C$ NMR ($CDCl_3$, 50 MHz) 14.4, 16.1, 33.8, 60.1, 70.2, 110.4, 116.6, 122.7, 128.4, 128.9, 136.4, 144.0, 156.7, 169.3; MS (*m*/*e*) 323 $[M]^+$; HRMS calcd for $C_{16}H_{18}ClNO_2S$ 323.0747, found 323.0747.

**Ethyl 2-[3-(4-chlorophenyl)-4-methyl-4-vinyl-1,3-thiazolidin-2-ylidene]propanoate (7c):** oily liquid; IR 1671, 1536 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz) 1.23 (t, 3H, $J = 7.1$ Hz), 1.31 (s, 3H), 1.34 (s, 3H), 2.97 (d, 2H, $J = 4.0$ Hz), 4.18 (q, 2H, $J = 7.1$ Hz), 5.12 (d, 1H, $J = 10.4$ Hz), 5.20 (d, 1H, $J = 17.3$ Hz), 5.77−5.91 (dd, 1H, $J = 17.3$, 10.4 Hz), 6.93 (d, 2H, $J = 8.5$ Hz), 7.21(d, 2H, $J = 17.0$ Hz), $^{13}C$ NMR ($CDCl_3$, 50 MHz) 14.5, 15.0, 23.8, 41.4, 59.8, 70.1, 97.1, 115.1, 128.7, 130.8, 141.2, 142.0, 160.2, 170.0; MS (*m*/*e*) 337 $[M]^+$; HRMS calcd for $C_{17}H_{20}ClN_2O_2S$ 337.0903, found 337.0890.

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**2-Benzhydrylidene-5-vinyl[1,3]oxathiolane (9):** oily liquid; IR 1616, 1596 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) 3.01 (dd, 1H, $J$ = 10.8, 8.4 Hz), 3.22 (dd, 1H, $J$ = 10.8, 5.5 Hz), 5.05 (brq, 1H, $J$ = 6.9 Hz), 5.29−5.51 (m, 4H), 6.01 (ddd, 1H, $J$ = 17.2, 10.4, 6.4 Hz), 7.11(m, 1H), 7.22−7.38 (m, 9H); $^{13}C$ NMR ($CDCl_3$, 125 MHz) 36.2, 85.6 118.7, 125.3, 126.9, 127.8, 128.0, 128.4, 130.7, 134.2, 139.2, 141.6, 152.14; MS (*m*/*e*) 280 $[M]^+$; HRMS calcd for $C_{18}H_{16}OS$ 280.0922, found 280.0918.

***N*-(4-Chlorophenyl)-*N*-[(2*E*,2*Z*)-4-vinyl-1,3-dithiolan-2-ylidene]amine (11a):** oily liquid; IR 1580, 1593 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz) 3.31−3.64 (m, 4H), 4.46−4.62 (m, 2H), 5.18−5.45 (m, 4H), 5.83−6.01 (m, 2H), 6.87−6.91 (m, 2H), 7.22−7.29 (m, 2H); $^{13}C$ NMR ($CDCl_3$, 75 MHz) 39.9, 42.5, 53.9, 57.1, 119.3, 119.4, 121.6, 121.7, 129.1, 133.6, 129.9, 125.2, 128.3, 150.1, 150.3, 171.0, 171.4; MS (*m*/*e*) 255 $[M]^+$; HRMS calcd for $C_{11}H_{10}ClN_2S_2$ at $[M + 2]^+$ 256.9943, found 256.9910.

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**Supporting Information Available:** Spectroscopic data for compounds **4b**−**d**,**f**,**g**, **5b**,**c**, **7b**, **11b**−**d**; $^1H$ and $^{13}C$ NMR spectra for compounds **4c**,**e**, **5a**−**c**, **7a**−**c**, **9**, **11a**−**d**; HPLC chromatograms showing the determination of % ee for **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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