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Article

Rhodium-Catalyzed Tandem Asymmetric Allylic Decarboxylative Addition and Cyclization of Vinylethylene Carbonates with *N*-Nosylimines

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Abstract: A enantioselective tandem transformation concerning asymmetric allylic decarboxylative addition and cyclization of *N*-nosylimines with vinylethylene carbonates (VECs) in the presence of $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$, chiral sulfoxide-*N*-olefin tridentate ligand has been developed. The reaction of VECs with various substituted *N*-nosylimines proceeded smoothly under mild conditions, giving highly functionalized oxazolidine frameworks in good to high yields with good to excellent enantioselectivity.

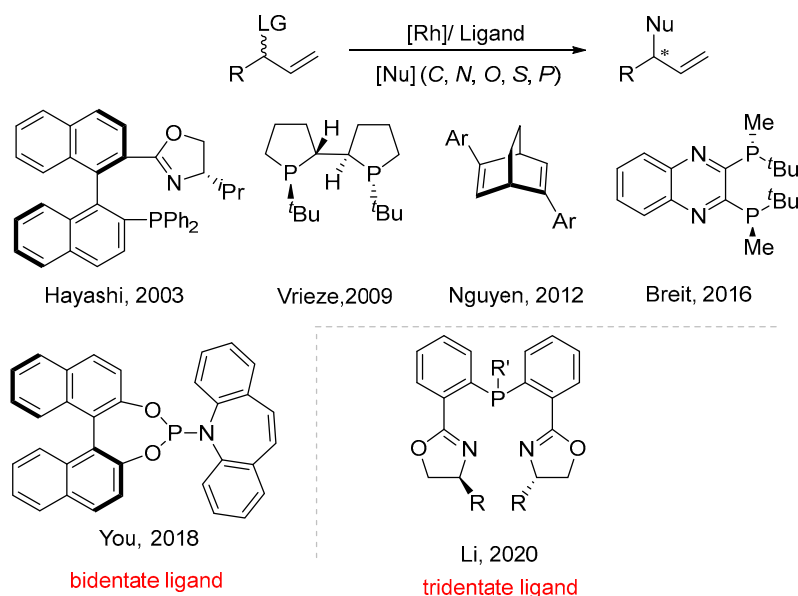
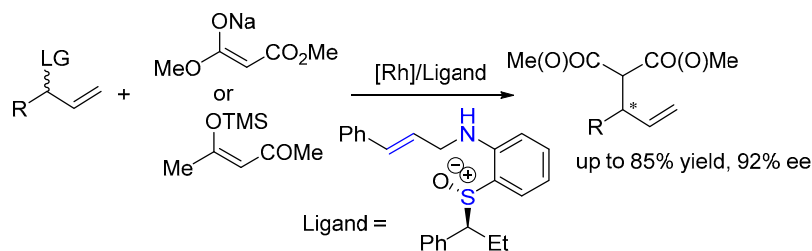
Keywords: rhodium; tridentate ligand; tandem reaction; allylic decarboxylation; cycloaddition; C–N Bond Formation

1. Introduction

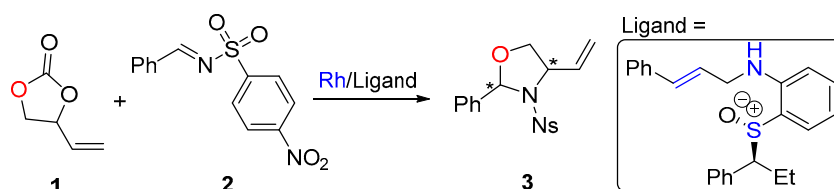
Rhodium, among the efficient transition-metal catalysts, catalyzed asymmetric allylic substitution has gained increasing attention due to the development of chiral ligands in recent years [1–5]. Since Hayashi [6] reported the first Rh-catalyzed asymmetric allylic alkylation employing a bidentate *N,P*-ligand in 2003, a variety of bidentate ligands has been discovered or designed to succeed in the asymmetric allylic substitution reaction [7–14]. Recently, Li [15–19] developed a Rh/*N,P,N*-tridentate ligand [20] catalysis system, which has proven to be a powerful tool for catalyzing asymmetric allylic alkylation (AAA) reaction. A broad spectrum of nucleophiles including C, N, O, S, even P [21] are compatible, showing a vigorousness of the tridentate ligand for allylic reaction (Scheme 1a). Very recently, we designed a tridentate sulfoxide-*N*-olefin hybrid Ligands and applied them in Rh catalyzed asymmetric allylic alkylation [22] (Scheme 1b). In this study, the coordination of the olefin to rhodium is crucial to the enantioselectivity but becomes hemilabile once the catalytic cycle is finished.

Tandem reactions involving transition metal catalyzed decarboxylative addition and cyclozation of vinylethylene carbonates (VECs) are efficient ways to construct heterocycles. The key to these conversions is reckoned the *in situ* formation of zwitterionic π -allyl palladium intermediates during CO_2 extrusion [23]. These intermediates consistently act as efficient C, O-dipoles, facilitating [3+n] [24–31] and [5+n] [32–39] annulation reactions for the construction of structurally diverse five- to medium-membered rings. However, Rh has rarely been reported in such enantioselective transformations despite the blooming allylic substitution reaction developed. As a continuous interest in the tridentate ligand applied in Rh catalysis, herein we report a rhodium-catalyzed tandem asymmetric allylic decarboxylative addition and allylic substitution of vinylethylene carbonates with *N*-nosylimines (Scheme 1c).

a) Development of rhodium catalyzed asymmetric allylation

b) Previous work: tridentate Sulfoxide-*N*-Olefin ligand for asymmetric allylation

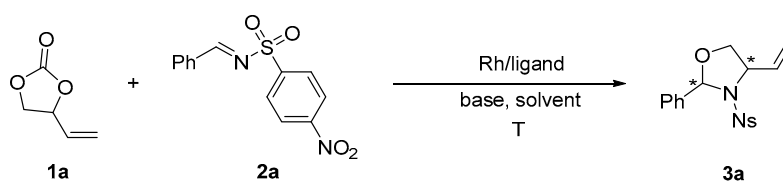
c) This work: rhodium catalyzed asymmetric tandem reaction



Scheme 1. Background for rhodium catalyzed allylic substitution.

2. Results and Discussion

We performed our initial study using 4-Vinyl-1,3-dioxolan-2-one **1a** with *N*-nosylimines **2a** for this reaction. In the presence of 1 mmol% of $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$, 2 mmol% of Sulfoxide ligand **L1** and Cs_2CO_3 in dichloromethane (DCM) at 25 °C, the expected cycloadduct **3** as diastereomers could be obtained in 32% yield with 41%/37% ee (Table 1, entry 1). And the diastereomers **3a** and **3a'** can be separated through a column chromatograph.

Table 1. Optimization Study ^a.

Entry	Rh	L	Base	Solvent	T (°C)	Yield ^b (%)	ee ^c (%)	dr ^d
1	[Rh(C ₂ H ₄) ₂ Cl] ₂	L1	Cs ₂ CO ₃	DCM	rt	32	41/37	1.1/1
2	[Rh(C ₂ H ₄) ₂ Cl] ₂	L1	Cs ₂ CO ₃	Tol.	rt	9	50/51	1.8/1
3	[Rh(C ₂ H ₄) ₂ Cl] ₂	L1	Cs ₂ CO ₃	THF	rt	47	12/23	1.1/1
4	[Rh(C ₂ H ₄) ₂ Cl] ₂	L1	Cs ₂ CO ₃	MeCN	rt	24	16/31	2/1
5	[Rh(C ₂ H ₄) ₂ Cl] ₂	L1	Cs ₂ CO ₃	DCE	rt	35	53/73	1.2/1
6	[Rh(C ₂ H ₄) ₂ Cl] ₂	L1	CsF	DCE	rt	24	60/77	2/1
7	[Rh(C ₂ H ₄) ₂ Cl] ₂	L1	K ₂ CO ₃	DCE	rt	29	31/35	2.2/1
8	[Rh(C ₂ H ₄) ₂ Cl] ₂	L1	CsCl	DCE	rt	19	53/51	1.5/1
9	[Rh(C ₂ H ₄) ₂ Cl] ₂	L1	Et ₃ N	DCE	rt	65	45/89	1.2/1
10	[Rh(C ₂ H ₄) ₂ Cl] ₂	L1	DBU	DCE	rt	61	23/25	2/1
11	[Rh(C ₂ H ₄) ₂ Cl] ₂	L1	TMEDA	DCE	rt	39	65/69	1.4/1
12	[Rh(C ₂ H ₄) ₂ Cl] ₂	L1	Et ₃ N	DCE	0	65	60/88	1.2/1
13	[Rh(C ₂ H ₄) ₂ Cl] ₂	L1	Et ₃ N	DCE	-10	61	81/91	1.2/1
14	[Rh(C ₂ H ₄) ₂ Cl] ₂	L1	Et ₃ N	DCE	-25	52	57/91	1.2/1
15	Rh(acac)(C ₂ H ₄) ₂	L1	Et ₃ N	DCE	-10	42	15/65	2/1
16	[Rh(cod)Cl] ₂	L1	Et ₃ N	DCE	-10	nr	-	-
17 ^e	[Rh(C₂H₄)₂Cl]₂	L1	Et₃N	DCE	-10	65	87/98	1.2/1
18	[Rh(C ₂ H ₄) ₂ Cl] ₂	L2	Et ₃ N	DCE	-10	32	7/5	2/1
19	[Rh(C ₂ H ₄) ₂ Cl] ₂	L3	Et ₃ N	DCE	-10	26	7/9	1.4/1
20	[Rh(C ₂ H ₄) ₂ Cl] ₂	L4	Et ₃ N	DCE	-10	25	rac	1.7/1
21	[Rh(C ₂ H ₄) ₂ Cl] ₂	L5	Et ₃ N	DCE	-10	51	59/61	1.4/1
22	[Rh(C ₂ H ₄) ₂ Cl] ₂	L6	Et ₃ N	DCE	-10	66	33/37	1.5/1

^a Reaction conditions: Rh salt (0.001 mmol), ligand (0.002 mmol), **1a** (0.20 mmol), **2a** (0.10 mmol), base (0.15 mmol), and solvent (1 mL). ^b Isolated yield. ^c Determined by a chiral HPLC. ^d Determined by ¹H NMR analysis of the crude product. ^e Rh salt (0.002 mmol), ligand (0.004 mmol).

Solvents such as toluene, THF, MeCN and DCE (1,2-dichloroethane) were next screened (entries 2–5). This investigation led to the finding that DCE was optimal in terms of reactivity and enantioselectivity, giving the desired product **3** as in a 35% total yield, 53%/73% ee and 1.2/1 dr (entry 5 vs. entries 1–5). Base played an important role in the cycloaddition, and a series of bases including CsF, K₂CO₃, CsCl, Et₃N, 1,8-diazabicyclo [5.4.0]-7-undecene (DBU) and *N,N,N,N'*-tetramethyl ethylenediamine (TMEDA) were tested (entries 5–11), CsF gave **3a/3a'** in a poor yield but with good enantioselectivity and diastereoselectivity (entry 6). Et₃N was identified as the optimal base that could dramatically improve the yield and enantioselectivity (entry 9). The reaction was performed at a temperature ranging from -25 °C to 25 °C (entries 9, 12–14), and we found that the reaction at -10

$^{\circ}\text{C}$ gave superior results, giving rise to desired products in 61% yield with with good ee values (entry 13). Rhodium salts such as $\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2$ and $[\text{Rh}(\text{cod})\text{Cl}]_2$ were surveyed. $\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2$ gave **3a/3a'** in a poor yield and low ee value (entry 15). While $[\text{Rh}(\text{cod})\text{Cl}]_2$ was not suitable for this reaction (entry 16).

When the catalyst loading was increased to 2 mol%, the yield and enantioselectivity of the reaction was increased (entry 17). Ligand is crucial to asymmetric allylic substitution. Therefore, structurally varying Sulfoxide ligands such as **L1**, **L2**, **L3**, **L4**, **L5** and **L6** were explored (Figure 1). The bidentate sulfoxide ligands **L2** and **L4** were less reactive, and the compounds **3a/3a'** were obtained with low yield and enantioselectivity (entry 18 and entry 20). Chirality only at sulfoxide (**L3**) led to decreased yield and enantioselectivity (entry 19). When the sulfoxide ligands containing imine fragments was used, the enantioselectivity dropped despite of the good yield (entry 21 and 22).

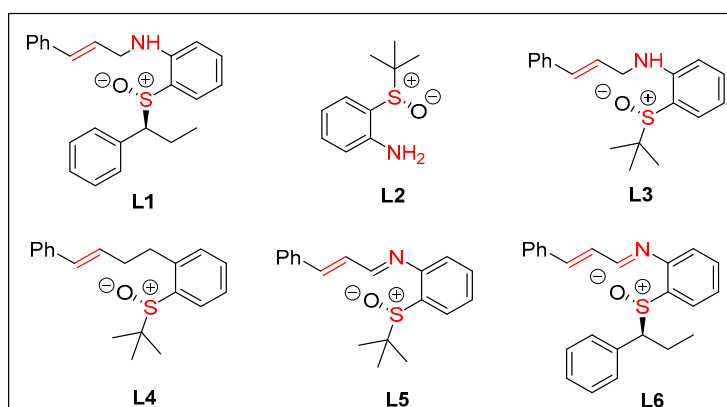
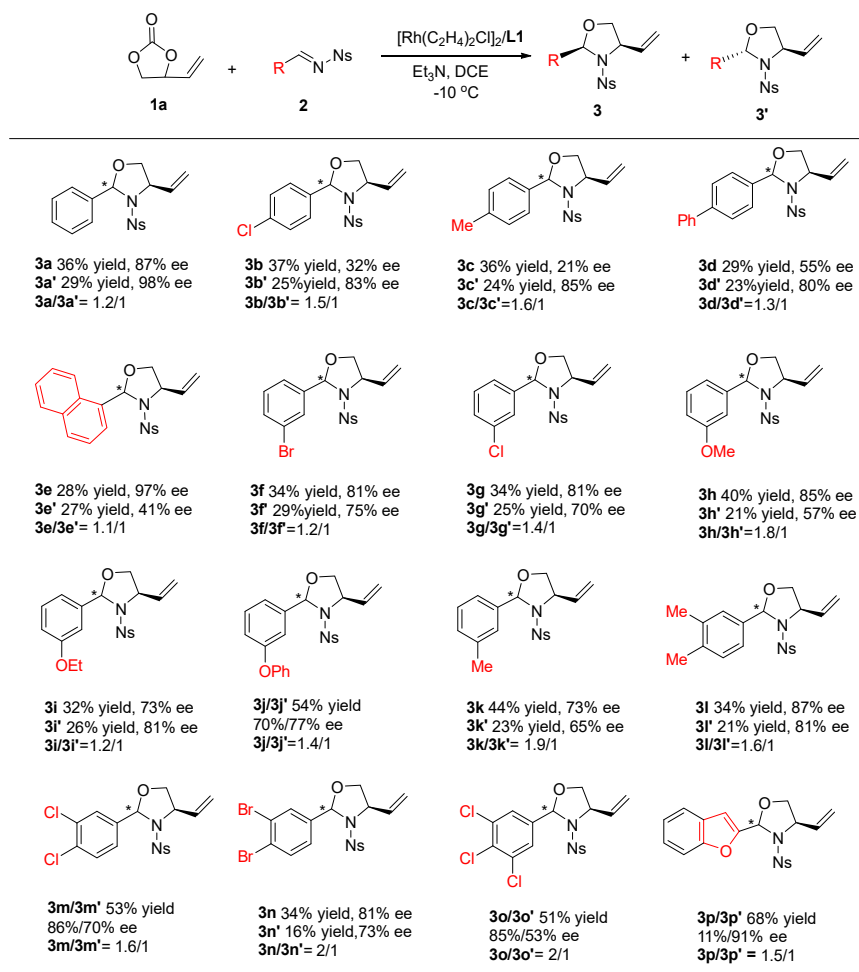


Figure 1. Ligands used in this reaction.

Having optimized reaction conditions in hand, the generality of the Rh-catalyzed asymmetric cycloaddition was examined using various *N*-nosylimines **2** (Scheme 2). The substrates **2b**, **2f**, **2g** containing the electron-withdrawing substituent (e.g., *p*-Cl, *m*-Br and *m*-Cl) on the phenyl ring resulted in allyl products **3b'**, **3f/3f'** and **3g/3g'** in moderate to good yields with slight decreased ee values. **3c'**, **3d'** were all isolated in good enantioselectivity. The steric hindrance from the para of the phenyl substituent led to a decreased yield (**3d/3d'**). 1-naphthyl substituted imine was also suited for the protocol, and **3e/3e'** were garnered in a 55% total yield with 97% ee and 41% ee, respectively. Similarly, *N*-nosylphenylimines bearing ether substituents (-OMe, -OEt, -OPh) on the phenyl ring were well tolerated under these catalytic conditions, leading to **3h-3j** in good yields (up to 61%) and enantioselectivities (up to 85% ee). In contrast, the *N*-nosylimines bearing a *m*-Me substituent showed low enantioselectivities but provided good yield in 67%. Interestingly, attaching multi-substituted groups on the phenyl ring, **3m/3m'**, **3n/3n'** and **3o** were also achieved in good to high yield with a high level of enantioselectivities. Heteroaryl- substrates **2p** gave **3p/3p'** in an excellent yield and enantioselectivity (Scheme 2).



Scheme 2. Scope of the allylic substrates **2**^{ab}. a: Reaction conditions: $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$ (0.004 mmol), **L1** (0.008 mmol), **1a** (0.40 mmol), **2** (0.20 mmol), Et_3N (0.30 mmol), and DCE (2.0 mL). b: Yield referred to isolated yield and ee was determined by a chiral HPLC.

An X-ray diffraction analysis of the compound **3b** enabled the determination of the absolute configuration of the two newly formed stereocenters [40] (Figure 2).

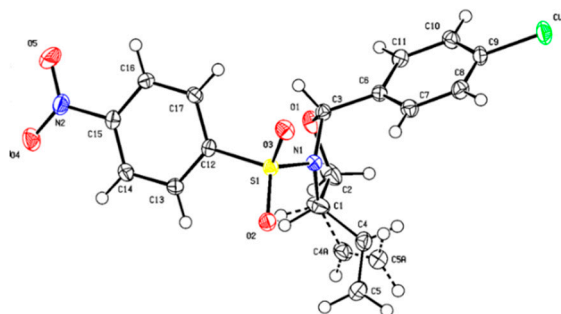
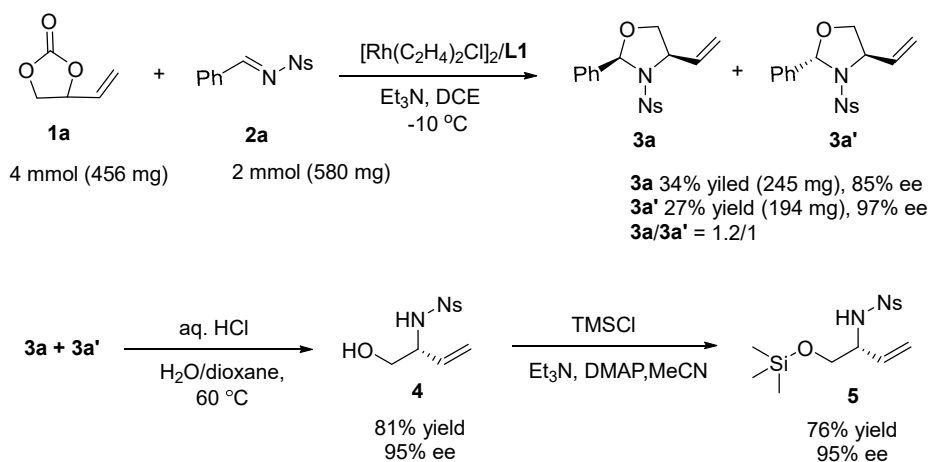


Figure 2. X-ray structure of **3b**.

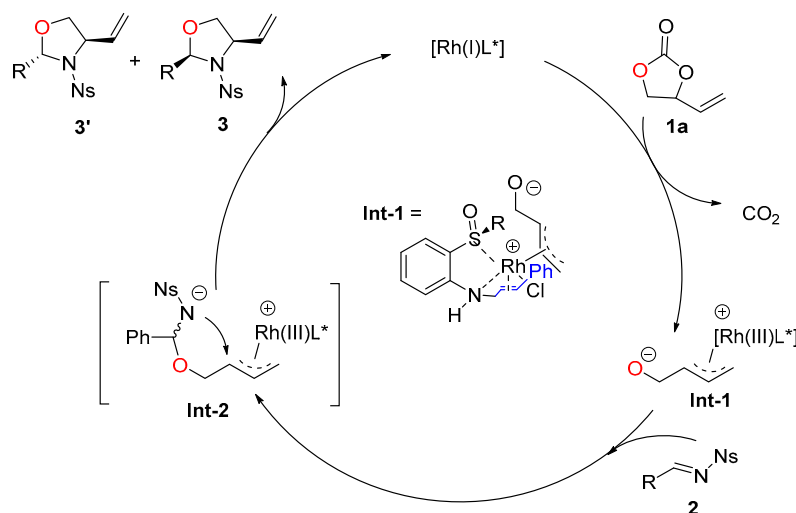
The scale-up synthesis of chiral oxazolidine products **3a/3a'** was conducted under the optimal conditions as shown in **Scheme 3**. **1a** (456 mg, 4 mmol) and **2a** (580 mg, 2 mmol) were employed and **3a/3a'** (440 mg, 61% yield, 85%/97% ee and 1.2/1 dr) was obtained (Scheme 3). To further demonstrate the synthetic utility of this approach, oxazolidine **3a/3a'** was successfully converted into the corresponding β -*tert*- β -amino alcohol under established conditions [41]. Direct hydrolysis of **3a/3a'**

under acidic conditions yielded amino alcohol **4** with 81% yield and 95% ee. Subsequent protection of the alcohol with chlorotrimethylsilane in acetonitrile gave **5** (76% yield and 95% ee) [42].



Scheme 3. Scale-up synthesis of **3a/3a'** and the transformation for oxazolidines.

Based on known reports [13] and our previous work [22], a possible mechanism was proposed. The reaction starts from the ring opening of VECs **1a** by oxidative addition with a Rh(I) catalyst with the assistance of the tridentate ligand. the formed π -allyl-Rh(III) intermediate (**Int-1**), which already got 18 valence electrons and no vacant coordination for imine, could only attack the imine by oxide anion. This is a possible reason for the low diastereoselectivity. Subsequent *N* anion after the addition continued to proceed nucleophilic attack back to Rh(allyl) intermediate **Int-2**, providing allylic oxazolidines and regenerating the Rh(I) catalyst to furnish the catalytic cycle (Scheme 4).



Scheme 4. Possible mechanism.

3. Materials and Methods

3.1. Reagents and General Methods

All manipulations were carried out under the argon atmosphere using standard Schlenk techniques. All glassware were oven or flame dried immediately prior to use. All solvents were purified and dried according to standard methods prior to use, unless stated otherwise. ^1H NMR spectra were obtained at 400 MHz or 600 MHz and recorded relative to the tetramethylsilane signal (0 ppm) or residual protio-solvent (7.26 ppm for CDCl_3 , 1.94 ppm for CD_3CN). ^{13}C NMR spectra were obtained at 100 MHz or 150 MHz, and chemical shifts were recorded relative to the solvent resonance (CDCl_3 , 77.16 ppm, CD_3CN , 1.32 ppm). Data

for NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Infrared spectra were recorded on Nicolet FT-IR spectrometers. The accurate masses were measured by ESI-TOF using QTOF Ultima, G2-xs TOF from Waters, and microflex LRF MALDI-TOF. Optical rotations α_D were obtained with AUTOPOL VI from rudolph-research-analytical. HPLC using chiral stationary phase columns by comparing the samples with the appropriate racemic samples, column and elution details specified in each entry.

3.2. Synthetic Procedures

General Procedure for the Synthesis of **3** and **3'**

In a screw-cap Schlenk tube filled with argon, $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$ (0.004 mmol, 2 mol%), Sulfoxide ligand **L1** (0.008 mmol, 4 mol%), *N*-nosylimine **2** (0.20 mmol) were added. After that, 4-Vinyl-1,3-dioxolan-2-one **1** (0.40 mmol) and 1,2-Dichloroethane (DCE) (2.0 mL) were added. Finally, add triethylamine (0.30 mmol). After 24 h stirring at -10°C , the reaction mixture was filtered over silica (CH_2Cl_2) and concentrated under reduced pressure to afford the crude product. The crude residue was purified by flash column chromatography (petroleum ether/ethyl acetate) to give the desired products **3** and **3'**

Representative **3** and **3'**

(2*R*,4*R*)-3-((4-nitrophenyl)sulfonyl)-2-phenyl-4-vinylloxazolidine (**3a**)

White solid; **m.p.**: 101 - 104 $^\circ\text{C}$; 36% yield (26.0 mg); **HPLC ee**: 87% [Daicel CHIRALPAK AD-H (0.46 cm \times 25cm); *n*-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 18.02 (major), 22.33 (minor) min]. $[\alpha]_D^{20} = +16.9$ (c 1.0, CHCl_3). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.24 (d, J = 8.8 Hz, 2H), 7.79 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 6.7 Hz, 2H), 7.38 – 7.32 (m, 3H), 6.21 (s, 1H), 5.76 (ddd, J = 17.9, 10.1, 8.0 Hz, 1H), 5.33 (d, J = 17.1 Hz, 1H), 5.23 (d, J = 10.2 Hz, 1H), 4.50 (q, J = 7.3 Hz, 1H), 4.10 (dd, J = 9.1, 7.0 Hz, 1H), 3.82 (dd, J = 9.1, 5.0 Hz, 1H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 150.1, 144.7, 136.6, 135.4, 129.5, 128.9, 128.6, 127.5, 124.2, 119.3, 92.5, 71.2, 62.0. **IR** (CH_2Cl_2): ν_{max} (cm^{-1}) = 3055, 3005, 2972, 2875, 2304, 1715, 1530, 1347, 1274, 1262, 1171, 900, 767, 747, 735, 687. **HRMS** (ESI $^+$) calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 383.0672, Found: 383.0665.

(2*S*,4*R*)-3-((4-nitrophenyl)sulfonyl)-2-phenyl-4-vinylloxazolidine (**3a'**)

White solid; **m.p.**: 101 - 104 $^\circ\text{C}$; 29% yield (20.8 mg); **HPLC ee**: 98% [Daicel CHIRALPAK AD-H (0.46 cm \times 25cm); *n*-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 17.01 (major), 20.61 (minor) min]. $[\alpha]_D^{20} = -37.3$ (c 1.0, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.10 (d, J = 8.8 Hz, 2H), 7.49 (d, J = 8.8 Hz, 2H), 7.39 – 7.31 (m, 1H), 7.30 – 7.22 (m, 4H), 6.17 (s, 1H), 5.91 (ddd, J = 17.0, 10.1, 8.6 Hz, 1H), 5.42 (d, J = 17.0 Hz, 1H), 5.31 (d, J = 10.1 Hz, 1H), 4.44 (dt, J = 8.6, 5.7 Hz, 1H), 4.30 (dd, J = 8.7, 6.0 Hz, 1H), 3.86 (dd, J = 8.7, 5.4 Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 149.7, 146.1, 136.7, 134.4, 129.7, 128.4, 128.3, 128.1, 123.7, 119.3, 92.4, 71.7, 62.6. **IR** (CH_2Cl_2): ν_{max} (cm^{-1}) = 3053, 3009, 2977, 2871, 2301, 1713, 1531, 1341, 1273, 1262, 1174, 901, 769, 750, 741, 681. **HRMS** (ESI $^+$) calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 383.0672, Found: 383.0665.

(2*R*,4*R*)-2-(4-chlorophenyl)-3-((4-nitrophenyl)sulfonyl)-4-vinylloxazolidine (**3b**)

White solid; **m.p.**: 149 - 151 $^\circ\text{C}$; 37% yield (29.1 mg); **HPLC ee**: 32% [Daicel CHIRALPAK AD-H (0.46 cm \times 25cm); *n*-hexane/2-propanol = 90/10; flow rate = 0.5 mL/min; detection wavelength = 214 nm; t_R = 39.58 (major), 46.06 (minor) min]. $[\alpha]_D^{20} = +14.8$ (c 1.0, CHCl_3). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.32 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 6.20 (s, 1H), 5.70 (ddd, J = 17.5, 10.2, 7.7 Hz, 1H), 5.31 (d, J = 17.0 Hz, 1H), 5.23 (d, J = 10.2 Hz, 1H), 4.41 (q, J = 6.8 Hz, 1H), 4.06 (dd, J = 9.1, 7.1 Hz, 1H), 3.75 (dd, J = 9.3, 5.4 Hz, 1H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 150.4, 144.1, 135.6, 135.5, 135.0, 129.0, 128.8, 128.8, 124.4, 119.5, 91.7, 71.0, 61.9. **IR** (CH_2Cl_2): ν_{max} (cm^{-1}) = 3105, 3064, 2963, 2925, 2872, 2298, 1763, 1603, 1536, 1350, 1265, 1174, 1118, 856, 757, 697, 632, 576. **HRMS** (ESI $^+$) calcd for $\text{C}_{17}\text{H}_{15}\text{ClN}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 417.0282, Found: 417.0294.

(2*S*,4*R*)-2-(4-chlorophenyl)-3-((4-nitrophenyl)sulfonyl)-4-vinylloxazolidine (**3b'**)

White solid; **m.p.**: 149 - 151 $^\circ\text{C}$; 25% yield (19.7 mg); **HPLC ee**: 83% [Daicel CHIRALPAK AD-H (0.46 cm \times 25cm); *n*-hexane/2-propanol = 90/10; flow rate = 0.5 mL/min; detection wavelength = 214 nm; t_R = 42.76 (major), 54.28 (minor) min]. $[\alpha]_D^{20} = -22.5$ (c 1.0, CHCl_3). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ

8.19 (d, $J = 8.5$ Hz, 2H), 7.61 (d, $J = 8.5$ Hz, 2H), 7.26 (d, $J = 2.2$ Hz, 5H), 6.15 (s, 1H), 5.87 – 5.77 (m, 1H), 5.42 (d, $J = 17.0$ Hz, 1H), 5.30 (d, $J = 10.0$ Hz, 1H), 4.48 – 4.41 (m, 1H), 4.25 (dd, $J = 8.9, 6.1$ Hz, 1H), 3.84 (dd, $J = 8.9, 5.2$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 149.9, 146.1, 135.8, 135.5, 133.9, 129.4, 128.6, 128.6, 123.9, 119.9, 91.5, 71.6, 62.5. IR (CH_2Cl_2): ν_{max} (cm^{-1}) = 3101, 3067, 2966, 2922, 2871, 2293, 1761, 1600, 1532, 1356, 1264, 1172, 1120, 851, 754, 699, 638, 577. HRMS (ESI⁺) calcd for $\text{C}_{17}\text{H}_{15}\text{ClN}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 417.0282, Found: 417.0294.

(2*R*,4*R*)-3-((4-nitrophenyl)sulfonyl)-2-(*p*-tolyl)-4-vinyloxazolidine (3c)

White solid; **m.p.**: 124 - 126 °C; 36% yield (26.9 mg); HPLC *ee*: 21% [Daicel CHIRALPAK IA-H (0.46 cm × 25cm); *n*-hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 254 nm; $t_{\text{R}} = 21.33$ (major), 29.94 (minor) min]. $[\alpha]_{\text{D}}^{20} = +62.7$ (c 1.0, CHCl_3). ^1H NMR (600 MHz, CDCl_3) δ 8.24 (d, $J = 8.5$ Hz, 2H), 7.79 (d, $J = 8.5$ Hz, 2H), 7.30 (d, $J = 7.8$ Hz, 2H), 7.12 (d, $J = 7.8$ Hz, 2H), 6.17 (s, 1H), 5.77 (ddd, $J = 17.6, 10.1, 8.0$ Hz, 1H), 5.33 (d, $J = 17.0$ Hz, 1H), 5.23 (d, $J = 10.1$ Hz, 1H), 4.48 (td, $J = 7.4, 4.9$ Hz, 1H), 4.08 (dd, $J = 9.1, 7.0$ Hz, 1H), 3.82 (dd, $J = 9.1, 4.9$ Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 150.1, 144.8, 139.6, 135.5, 133.6, 129.2, 128.9, 127.5, 124.1, 119.2, 92.5, 71.1, 61.9, 21.3. IR (CH_2Cl_2): ν_{max} (cm^{-1}) = 3101, 3034, 2973, 2915, 2842, 2278, 1721, 1608, 1516, 1349, 1263, 1171, 876, 751, 687, 639. HRMS (ESI⁺) calcd for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 397.0829, Found: 397.08421.

(2*S*,4*R*)-3-((4-nitrophenyl)sulfonyl)-2-(*p*-tolyl)-4-vinyloxazolidine (3c')

White solid; **m.p.**: 124 - 126 °C; 24% yield (17.9 mg); HPLC *ee*: 85% [Daicel CHIRALPAK IA-H (0.46 cm × 25cm); *n*-hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 254 nm; $t_{\text{R}} = 23.94$ (minor), 25.75 (major) min]. $[\alpha]_{\text{D}}^{20} = -20.6$ (c 1.0, CHCl_3). ^1H NMR (600 MHz, CDCl_3) δ 8.10 (d, $J = 8.8$ Hz, 2H), 7.51 (d, $J = 8.8$ Hz, 2H), 7.14 (d, $J = 7.8$ Hz, 2H), 7.03 (d, $J = 7.7$ Hz, 2H), 6.12 (s, 1H), 5.91 (dt, $J = 18.1, 9.1$ Hz, 1H), 5.42 (d, $J = 17.0$ Hz, 1H), 5.31 (d, $J = 10.1$ Hz, 1H), 4.45 (dt, $J = 8.5, 5.8$ Hz, 1H), 4.29 (dd, $J = 8.8, 6.1$ Hz, 1H), 3.85 (dd, $J = 8.8, 5.4$ Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 149.6, 146.2, 139.9, 134.5, 133.8, 128.9, 128.5, 128.1, 123.6, 119.3, 92.3, 71.7, 62.6, 21.3. IR (CH_2Cl_2): ν_{max} (cm^{-1}) = 3110, 3031, 2979, 2911, 2848, 2281, 1722, 1608, 1522, 1350, 1269, 1172, 878, 752, 688, 644. HRMS (ESI⁺) calcd for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 397.0829, Found: 397.08421.

(2*R*,4*R*)-2-([1,1'-biphenyl]-4-yl)-3-((4-nitrophenyl)sulfonyl)-4-vinyloxazolidine (3d)

White solid; **m.p.**: 140 - 143 °C; 29% yield (25.2mg); HPLC *ee*: 55% [Daicel CHIRALPAK AD-H (0.46 cm × 25cm); *n*-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; $t_{\text{R}} = 25.06$ (major), 29.58 (minor) min]. $[\alpha]_{\text{D}}^{20} = +13.2$ (c 1.0, CHCl_3). ^1H NMR (600 MHz, CDCl_3) δ 8.26 (d, $J = 8.8$ Hz, 2H), 7.84 (d, $J = 8.8$ Hz, 2H), 7.58 – 7.55 (m, 4H), 7.51 (d, $J = 8.2$ Hz, 2H), 7.46 (t, $J = 7.6$ Hz, 2H), 7.38 (t, $J = 7.4$ Hz, 1H), 6.26 (s, 1H), 5.84 – 5.77 (m, 1H), 5.36 (d, $J = 16.9$ Hz, 1H), 5.26 (d, $J = 10.2$ Hz, 1H), 4.50 (td, $J = 7.6, 5.3$ Hz, 1H), 4.12 (dd, $J = 9.1, 7.0$ Hz, 1H), 3.85 (dd, $J = 9.2, 5.1$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 150.2, 144.6, 142.5, 140.4, 135.6, 135.4, 129.0, 128.9, 128.0, 127.8, 127.3, 127.2, 124.2, 119.4, 92.3, 71.2, 62.0. IR (CH_2Cl_2): ν_{max} (cm^{-1}) = 3109, 3064, 2993, 2911, 2815, 2235, 1712, 1635, 1509, 1356, 1234, 1163, 888, 788, 654, 616. HRMS (ESI⁺) calcd for $\text{C}_{23}\text{H}_{20}\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 459.0985, Found: 459.0990.

(2*S*,4*R*)-2-([1,1'-biphenyl]-4-yl)-3-((4-nitrophenyl)sulfonyl)-4-vinyloxazolidine (3d')

White solid; **m.p.**: 140 - 143 °C; 23% yield (20.0mg); HPLC *ee*: 80% [Daicel CHIRALPAK AD-H (0.46 cm × 25cm); *n*-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; $t_{\text{R}} = 23.81$ (minor), 26.79 (major) min]. $[\alpha]_{\text{D}}^{20} = -8.9$ (c 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 8.11 (d, $J = 8.8$ Hz, 2H), 7.59 – 7.51 (m, 4H), 7.50 – 7.43 (m, 4H), 7.39 (t, $J = 7.2$ Hz, 1H), 7.35 (d, $J = 8.2$ Hz, 2H), 6.21 (s, 1H), 5.97 – 5.87 (m, 1H), 5.44 (d, $J = 17.1$ Hz, 1H), 5.33 (d, $J = 10.1$ Hz, 1H), 4.49 (dt, $J = 8.6, 5.7$ Hz, 1H), 4.33 (dd, $J = 8.7, 6.1$ Hz, 1H), 3.89 (dd, $J = 8.8, 5.4$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 149.8, 146.2, 142.9, 140.2, 135.6, 134.4, 129.1, 128.6, 128.5, 128.0, 127.2, 127.0, 123.8, 119.4, 92.2, 71.8, 62.7. IR (CH_2Cl_2): ν_{max} (cm^{-1}) = 3109, 3060, 2999, 2910, 2819, 2232, 1721, 1633, 1505, 1353, 1234, 1161, 881, 785, 659, 610. HRMS (ESI⁺) calcd for $\text{C}_{23}\text{H}_{20}\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 459.0985, Found: 459.0990.

(2*R*,4*R*)-2-(naphthalen-1-yl)-3-((4-nitrophenyl)sulfonyl)-4-vinyloxazolidine (3e)

White solid; **m.p.**: 127 - 129 °C; 28% yield (22.9 mg); HPLC *ee*: 97% [Daicel CHIRALPAK IC-H (0.46 cm × 25cm); *n*-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; $t_{\text{R}} = 32.07$ (major), 37.52 (minor) min]. $[\alpha]_{\text{D}}^{20} = +28.1$ (c 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 8.23 (t, $J = 9.0$ Hz, 3H), 7.93 – 7.79 (m, 4H), 7.67 (d, $J = 7.1$ Hz, 1H), 7.58 – 7.47 (m, 2H), 7.42 (t, $J = 7.7$

Hz, 1H), 6.88 (s, 1H), 6.06 (ddd, $J = 17.0, 10.2, 8.1$ Hz, 1H), 5.49 (d, $J = 17.1$ Hz, 1H), 5.40 (d, $J = 10.2$ Hz, 1H), 4.56 (q, $J = 7.1$ Hz, 1H), 4.15 (dd, $J = 9.2, 7.0$ Hz, 1H), 3.76 (dd, $J = 9.2, 6.5$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 150.5, 143.9, 138.1, 134.8, 133.9, 132.4, 129.0, 127.6, 126.1, 125.2, 124.5, 124.0, 119.7, 91.0, 71.1, 62.0. **IR** (CH_2Cl_2): ν_{max} (cm^{-1}) = 3111, 3054, 2983, 2922, 2831, 2286, 1729, 1611, 1519, 1346, 1269, 1183, 877, 793, 691, 613. **HRMS** (ESI^+) calcd for $\text{C}_{21}\text{H}_{18}\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 433.0829, Found: 433.0835.

(2*S*,4*R*)-2-(naphthalen-1-yl)-3-((4-nitrophenyl)sulfonyl)-4-vinyloxazolidine (3e')

White solid; **m.p.**: 127 - 129 °C; 27% yield (22.1 mg); **HPLC ee**: 41% [Daicel CHIRALPAK IC-H (0.46 cm \times 25cm); *n*-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_{r} = 48.99 (minor), 52.06 (major) min]. $[\alpha]_{\text{D}}^{20} = -42.4$ (c 1.0, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.06 - 7.99 (m, 1H), 7.95 (d, $J = 8.6$ Hz, 2H), 7.86 (d, $J = 8.2$ Hz, 1H), 7.82 - 7.76 (m, 1H), 7.66 (d, $J = 7.1$ Hz, 1H), 7.55 (d, $J = 8.7$ Hz, 2H), 7.48 - 7.41 (m, 3H), 6.75 (s, 1H), 5.99 - 5.84 (m, 1H), 5.52 (d, $J = 17.0$ Hz, 1H), 5.34 (d, $J = 10.1$ Hz, 1H), 4.82 - 4.73 (m, 1H), 4.34 (dd, $J = 9.0, 6.3$ Hz, 1H), 3.92 (dd, $J = 9.0, 4.1$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 149.5, 145.5, 134.9, 133.9, 131.0, 130.7, 130.6, 128.8, 128.6, 127.7, 126.6, 126.0, 124.7, 123.6, 123.3, 119.5, 91.2, 71.1, 62.8. **IR** (CH_2Cl_2): ν_{max} (cm^{-1}) = 3108, 3052, 2988, 2929, 2830, 2288, 1722, 1610, 1522, 1349, 1266, 1190, 870, 791, 694, 615. **HRMS** (ESI^+) calcd for $\text{C}_{21}\text{H}_{18}\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 433.0829, Found: 433.0835.

(2*R*,4*R*)-2-(3-bromophenyl)-3-((4-nitrophenyl)sulfonyl)-4-vinyloxazolidine (3f)

Pale yellow solid; **m.p.**: 117 - 119 °C; 34% yield (29.7 mg); **HPLC ee**: 81% [Daicel CHIRALPAK AD-H (0.46 cm \times 25cm); *n*-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 254 nm; t_{r} = 21.37 (major), 24.18 (minor) min]. $[\alpha]_{\text{D}}^{20} = +24.1$ (c 1.0, CHCl_3). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.31 (d, $J = 8.6$ Hz, 2H), 7.86 (d, $J = 8.6$ Hz, 2H), 7.51 (s, 1H), 7.48 (d, $J = 8.0$ Hz, 1H), 7.42 (d, $J = 7.7$ Hz, 1H), 7.24 (t, $J = 7.8$ Hz, 1H), 6.16 (s, 1H), 5.78 - 5.69 (m, 1H), 5.35 (d, $J = 17.0$ Hz, 1H), 5.27 (d, $J = 10.2$ Hz, 1H), 4.46 (q, $J = 6.9$ Hz, 1H), 4.14 - 4.07 (m, 1H), 3.78 (dd, $J = 9.0, 5.4$ Hz, 1H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 150.3, 144.2, 139.1, 135.0, 132.6, 130.3, 130.2, 128.9, 126.3, 124.3, 122.7, 119.6, 91.5, 71.2, 62.0. **IR** (CH_2Cl_2): ν_{max} (cm^{-1}) = 3120, 3033, 2977, 2918, 2825, 2274, 1719, 1610, 1515, 1342, 1266, 1188, 870, 799, 684, 609. **HRMS** (ESI^+) calcd for $\text{C}_{17}\text{H}_{15}\text{BrN}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 460.9777, Found: 460.9787.

(2*S*,4*R*)-2-(3-bromophenyl)-3-((4-nitrophenyl)sulfonyl)-4-vinyloxazolidine (3f')

Pale yellow solid; **m.p.**: 117 - 119 °C; 29% yield (25.3 mg); **HPLC ee**: 75% [Daicel CHIRALPAK AD-H (0.46 cm \times 25cm); *n*-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 254 nm; t_{r} = 17.63 (major), 26.39 (minor) min]. $[\alpha]_{\text{D}}^{20} = -4.5$ (c 1.0, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.19 (d, $J = 8.3$ Hz, 2H), 7.56 (d, $J = 8.4$ Hz, 2H), 7.51 - 7.44 (m, 1H), 7.38 - 7.31 (m, 1H), 7.27 - 7.13 (m, 2H), 6.11 (s, 1H), 6.01 - 5.87 (m, 1H), 5.47 (d, $J = 17.0$ Hz, 1H), 5.36 (d, $J = 10.1$ Hz, 1H), 4.49 (dt, $J = 9.0, 5.5$ Hz, 1H), 4.31 (dd, $J = 8.9, 5.7$ Hz, 1H), 3.89 (dd, $J = 8.9, 5.3$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 149.9, 145.9, 138.8, 134.2, 132.8, 130.8, 130.0, 128.3, 127.3, 123.9, 122.5, 119.6, 91.4, 71.8, 62.7. **IR** (CH_2Cl_2): ν_{max} (cm^{-1}) = 3117, 3029, 2973, 2918, 2820, 2277, 1720, 1611, 1519, 1346, 1262, 1189, 871, 7990, 682, 610. **HRMS** (ESI^+) calcd for $\text{C}_{17}\text{H}_{15}\text{BrN}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 460.9777, Found: 460.9787.

4. Conclusions

In conclusion, we have utilized rhodium/tridentate sulfoxide-*N*-olefin hybrid Ligand catalyzed asymmetric allylic substitution to furnish a tandem reaction of VECs and various substituted *N*-nosylimines. Chiral oxazolidines diastereomers as (3 + 2) cycloadducts were synthesized in good to high yield with moderate to excellent enantioselectivity. The outcome for the low diastereoselectivity is discussed as well along with a proposed mechanism. More tandem reaction based on these results are undergoing in our lab.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org. Experimental details, NMR spectra, X-ray Crystallographic Information, HPLC Spectra, HRMS data for new products.

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