Tetrahedron 67 (2011) 7686–7691

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Iridium-catalyzed allylic alkylation of monosubstituted allylic acetates with azlactone, and separation of diastereoisomers by sequential aza-Cope rearrangement

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ARTICLE INFO

Article history:
Received 28 June 2011
Received in revised form 5 August 2011
Accepted 5 August 2011
Available online 12 August 2011

ABSTRACT

The iridium-catalyzed allylic alkylation with azlactone and sequential aza-Cope rearrangement was demonstrated. The sequential reaction was effective in separating of diastereoisomers and afforded a diastereomerically pure azlactone derivative and oxazolinone derivative.

1. Introduction

Azlactones are useful compounds because they can be used to construct peptides or amino acid derivatives, and α,α-disubstituted azlactones can potentially be used to convert quaternary amino acid derivatives.[1] While several types of transition metal-catalyzed carbon–carbon bond formation reactions have been developed, there are still only limited examples of the transition metal-catalyzed construction of α,α-disubstituted azlactones.[2,3] For example, Trost reported the palladium or molybdenum-catalyzed regio- and/or enantioselective allylic alkylation of allylic esters with azlactones.[2] However, the transition metal-catalyzed allylic alkylation of monosubstituted allylic esters with an α-substituted azlactone usually gives a mixture of regio- and diastereoisomers. According to the pioneering work by Trost and Dogra, they discovered the $C_7H_8Mo(CO)_3$/ligand catalyst produces a branch-type product with a high diastereoselectivity,[2a] but the result of their molybdenum catalyst system is an exceptional case, and usually two types of diastereomeric isomers will be obtained simultaneously. We also confirmed that an allylic alkylation of monosubstituted allylic acetates with azlactones using several transition metal catalysts showed no diastereoselectivity. In addition, the separation of two diastereoisomers required careful silica gel column chromatography. In further investigation, we found that the one of the diastereoisomers, which was obtained from an iridium-catalyzed allylic alkylation[4,5] with azlactone, was selectively rearranged into oxazolinone derivatives. We now report the iridium-catalyzed allylic alkylation with azlactones, and accomplishment of the easy separation of diastereoisomers using the sequential aza-Cope rearrangement.

2. Results and discussion

Several iridium catalysts were evaluated for the allylic alkylation of racemic allylic acetate *rac*-**1a** with azlactone **2**. The screening of iridium catalysts revealed that the $[IrCl(cod)]_2$ exhibited a catalyst activity for the desired alkylation reaction.[6] Based on this initial result, we started our investigation of the iridium-catalyzed regio- and diastereo-selective allylic alkylation of monosubstituted allylic acetates **1a** with **2**. As shown in Table 1, the reaction by $[IrCl(cod)]_2$ gave a branch-type product as a mixture of two diastereomers, **3a-B1**[7] and **3a-B2**, with high regioselectivity, but low diastereoselectivity (Table 1, entry 1). Although we examined the reaction with the addition of several ligands, the diastereoselectivity did not increase (entries 2–5). However, when the reaction was conducted at 60 °C, we confirmed that decreasing the amount of **3a-B2** caused the formation of a new product (*E*)-**5a** (entry 6). The structure of (*E*)-**5a** was determined to be an oxazolinone derivative based on its NMR spectra and X-ray crystallographic analysis.[8] Again, the addition of ligands did not have any influence on the ratio of the products (entries 7–10). We next conducted the reaction at 80 °C with dioxane or toluene as the solvent, and confirmed that toluene inhibited the formation of linear-type product **4a** (entry 13), and the reaction in the dioxane solvent gave the branch-type product **3a-B1** as a single diastereoisomer (entry 14). However, we found no significant differences in the ratio of **3a-B1** and (*E*)-**5a** between results obtained from the dioxane or toluene solvent system.[9] On the other hand, the separation of **3a-B1** and **3a-B2** was very difficult, while **3a-B1** and (*E*)-**5a** were easily separated by silica gel column chromatography.

Concerning the formation of the oxazolinone derivative (*E*)-**5a**, we assumed that the one diastereoisomer **3a-B2** might selectively rearrange to (*E*)-**5a**, because the aza-Cope rearrangement[10] of **3a-B2** easily occurred through a chair-like transition state **T2**

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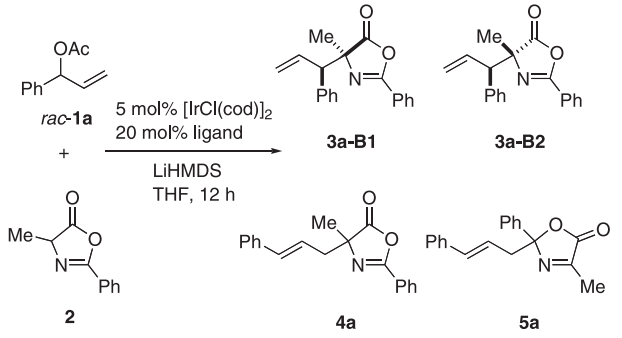
doi:10.1016/j.tet.2011.08.016

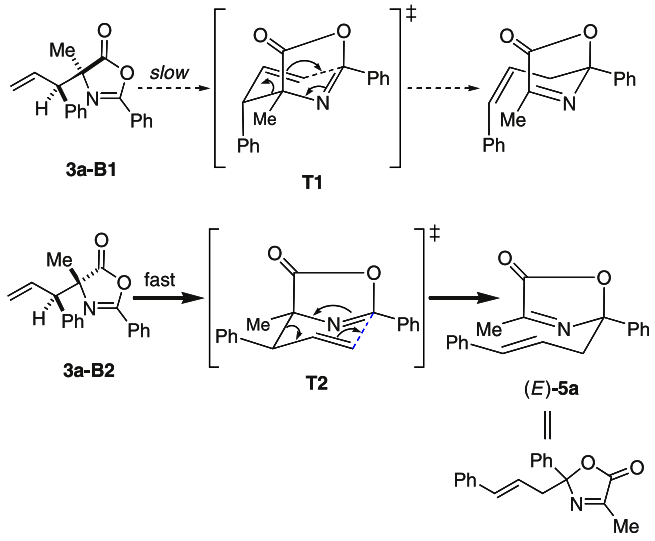
Table 1
Reaction conditions and product ratios for the Ir-catalyzed allylic alkylation of **2** with **1a**[a,b]



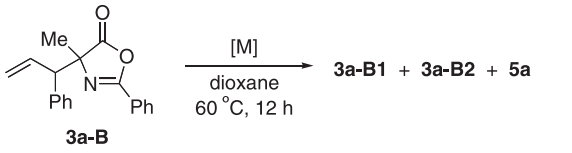
Entry	Ligand	Temp (°C)	3a-B1[c]	3a-B2	4a	5a[c]
1	—	rt	62	38	<1	<1
2	PPh_3	rt	33	31	<1	<1
3	P^tBu_3	rt	69	31	<1	<1
4	$P(OPh)_3$	rt	63	37	<1	<1
5	DPPE[d]	rt	47	42	<1	<1
6	—	60	57	8	2	33
7	PPh_3	60	57	8	<1	34
8	P^tBu_3	60	59	7	<1	34
9	$P(OPh)_3$	60	56	13	<1	29
10	DPPE[d]	60	44	11	<1	36
11[e]	—	60	50	10	2	37
12[f]	—	60	53 (57)	8	2	37 (32)
13[e]	—	80	42 (35)	3	<1	45 (43)
14[f]	—	80	38 (33)	<1	3	53 (50)

[a] Reaction conditions: azlactone **2** (0.42 mmol), allylic acetate *rac*-**1a** (0.28 mmol), LiHMDS (0.4 mmol, 1.0 M in THF), 5 mol % of $[IrCl(cod)]_2$ and 20 mol % ligand in solvent (0.5 mL).
[b] Product ratios were determined by ^1H NMR using an internal standard (trioxane).
[c] Isolated yield is in parentheses.
[d] With 10 mol % of DPPE.
[e] Toluene was used as the solvent.
[f] Dioxane was used as the solvent.

(Scheme 1). To prove this expectation, we demonstrated the rearrangement reaction with **3a** (Scheme 2). When **3a-B1**, which is a mixture of two diastereoisomers, was treated at 60 °C in dioxane, we observed the disappearance of **3a-B2** and formation of (*E*)-**5a**. We also examined the role of the iridium catalyst in the



Scheme 1. Aza-Cope rearrangement.



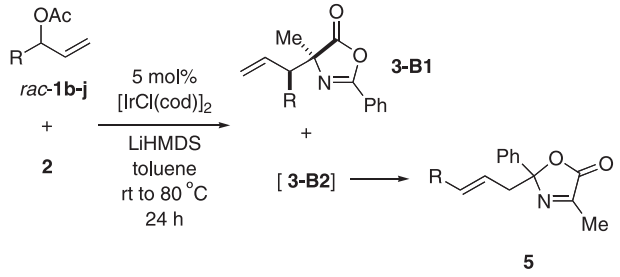
		NMR yield (%)		
3a-B	[M]	**3a-B1**	**3a-B2**	**5a**
B1/**B2** = 58/42	$[IrCl(cod)]_2$	50	2	37
B1/**B2** = 58/42	—	43	8	24

Scheme 2. Separation of branch type azlactone derivative **3a-B** via aza-Cope rearrangement.

rearrangement step. Although the rearrangement smoothly proceeded even without $[IrCl(cod)]_2$, the NMR yield of **3a-B1** and (*E*)-**5a** was slightly increased when the reaction was conducted in the presence the iridium catalyst. Based on the results, we concluded that the rearrangement might have been occurred as a result of a thermal effect, and that the contribution of the iridium catalyst was low.

We next demonstrated the iridium-catalyzed allylic alkylation with azlactone and the sequential aza-Cope rearrangement using several allylic acetates. As shown in Table 2, most of the aryl group substituted allylic acetates **1b**–**i** gave the expected results (entries 1–9). In all the reactions, the expected diastereomerically pure azlactone derivatives and rearranged oxazolinone derivatives were obtained. For example, the allylic acetate **1b**, which contained an electron-donating group at the *para*-position on the aromatic ring, gave a 39% of **3b-B1** and 58% of (*E*)-**5b**, respectively (entry 1). Reactions of **1c**–**e**, which have an electron-withdrawing group at the *para*-position on the aromatic ring, also gave two types of products with a reasonably good yield (entries 2, 4, and 5). The reaction proceeded without any change in the yield and ratio even with 0.5 mol % $[IrCl(cod)]_2$ (entry 3). The reactions of **1f** and **1g**, bearing an *ortho*-substituted aromatic group, also gave the desired products

Table 2
Ir-catalyzed alkylation of **1**, and sequential aza-Cope rearrangement[a]



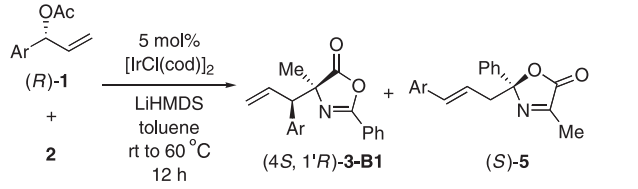
Entry	R	Yield (%) of **3-B1**	Yield (%) of **5**
1	4-$MeOC_6H_4$ (**1b**)	39	58
2	4-$CF_3C_6H_4$ (**1c**)	46	34
3[b]	4-$CF_3C_6H_4$ (**1c**)	46	34
4	4-ClC_6H_4 (**1d**)	45	41
5	4-BrC_6H_4 (**1e**)	46	38
6	2-$MeOC_6H_4$ (**1f**)	54	41
7	2-ClC_6H_4 (**1g**)	48	23
8	1-Naphthyl (**1h**)	47	40
9	2-Naphthyl (**1i**)	39	37
10[c]	$PhCH_2CH_2$ (**1j**)	22	<1

[a] Reaction conditions: **2** (0.42 mmol), **1b**–**j** (0.28 mmol), LiHMDS (0.4 mmol, 1.0 M in THF), and 5 mol % of $[IrCl(cod)]_2$ in toluene (0.5 mL) at room temperature for 12 h, then heated to 80 °C for 12 h.
[b] $[IrCl(cod)]_2$ (0.5 mol %) was used.
[c] Allylated product **3j-B2** (29% yield) was obtained.

(entries 6 and 7). Unfortunately, the alkyl group substituted allylic acetate **1j** did not produce the rearranged product **5j**, while it gave the alkylated products as an unseparable mixture of **3j**-**B1** and **3j**-**B2** (entry 10). This result suggested that azlactone derivative, which was formed from the reaction of alkyl group substituted allyl ester, is not appropriate for the aza-Cope rearrangements.

We further examined the reaction of the chiral allylic acetate to obtain both the chiral azlactone and chiral rearranged oxazolinone derivatives. Our preliminary results revealed that the reaction at 80 °C decreased the chirality of the products. However, we found that the reaction retained the chirality when carried out at room temperature for the allylic alkylation, then the temperature was raised to 60 °C for the aza-Cope rearrangement. The reaction of (*R*)-**1a** (99% ee) gave (4*S*,1′*R*)-**3a**-**B1** and (*S*)-**5a**,[11] but the enantiomeric excess of the products dropped slightly to 86% ee and 79% ee, respectively (Table 3, entry 1). The chirality of both products in the reaction with (*R*)-**1b** was significantly lower (entry 2), but we

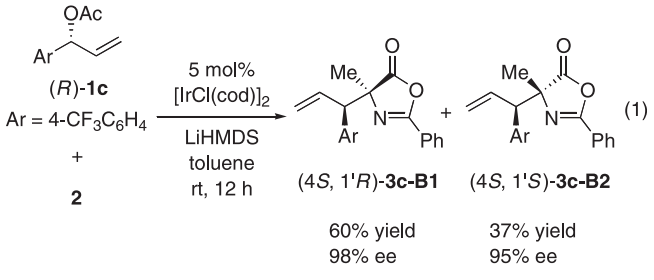
Table 3
Allylic alkylation of **2** with (*R*)-**1a**–**c**,**k**



Entry	(*R*)-**1**	**B1**[a]	**5**[a]
1	Ar=Ph (**1a**)	70% Yield[b]	25% Yield
	(99% ee)	86% ee	79% ee
2	Ar=4-MeOC$_6$H$_4$ (**1b**)	47% Yield	39% Yield
	(98% ee)	44% ee	38% ee
3	Ar=4-FC$_6$H$_4$ (**1k**)	50% Yield	27% Yield
	(99% ee)	93% ee	88% ee
4	Ar=4-CF$_3$C$_6$H$_4$ (**1c**)	57% Yield	32% Yield
	(99% ee)	98% ee	93% ee

[a] Enatiomeric excess was determined by the chiral HPLC analysis.
[b] Mixture of **B1** (65%) and **B2** (5%).

confirmed that the enantiomeric excess of the allylic acetates, which possess an electron-withdrawing group on the phenyl group, was effectively transferred to the azlactone derivative and oxazolinone derivatives. When (*R*)-**1k** was used as a substrate, we could obtain the chiral azlactone derivative (4*S*,1′*R*)-**3k**-**B1** and (*S*)-**5k** with 93% ee and 88% ee, respectively. The best result was obtained in the reaction of (*R*)-**1c** (99% ee), and provided (4*S*,1′*R*)-**3c**-**B1** and (*S*)-**5c** with 98% ee and 93% ee, respectively (entry 4). Unfortunately, the chirality transfer is not perfect and the detailed mechanism of loosing the chirality has not yet been clarified. From these results and the allylic alkylation at room temperature (Eq. 1), it seems that chirality might be lost during both the alkylation and rearrangement steps.[12] However, it should be emphasized that we did succeed in obtaining diastereomerically pure chiral azlactone derivatives together with chiral oxazolinone derivatives.



3. Conclusion

We demonstrated the iridium-catalyzed allylic alkylation of monosubstituted allylic acetates with azlactone, and sequential aza-Cope rearrangement. This consecutive reaction protocol made it possible to obtain the diastereomerically pure alkylated azlactone derivatives and oxazolinone derivatives. We also succeeded in obtaining both the alkylated and rearranged products with 98% ee and 93% ee, respectively.

4. Experimental section

4.1. General

All manipulations were carried out under a nitrogen atmosphere. NMR spectra were recorded on a 600 MHz (for ^{1}H), 151 MHz (for ^{13}C) and 565 MHz (for ^{19}F) NMR spectrometer. Chemical shifts are reported in δ parts per million referenced to an internal $SiMe_4$ standard for ^{1}H NMR, and internal C_6F_6 standard for ^{19}F NMR. Residual chloroform (δ 77.0 for ^{13}C) was used as internal reference for ^{13}C NMR. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 25 °C unless otherwise noted. [IrCl(cod)]$_2$, PPh_3, $P(OPh)_3$, DPPE, and other reagents and solvents were purchased from common commercial sources and were used without further purification. Allylic acetates[13–17] and azlactone **2**[18] were prepared according to the literature.

4.2. General procedure for the iridium-catalyzed allylic alkylation of allylic acetates with azlactones, and sequential aza-Cope rearrangement

A typical procedure is given for the reaction of *rac*-**1b** with **2** (Table 2, entry 1). To a solution of [IrCl(cod)]$_2$ (9.4 mg, 0.014 mmol) and azlactone **2** (74 mg, 0.42 mmol) in anhydrous dioxane (0.5 mL) was added *rac*-**1b** (50 mg, 0.28 mmol). LiHMDS (0.39 mmol, 0.39 mL of 1M in THF) was slowly added at 0 °C, and stirred at room temperature for 12 h. After complete conversion of allylic acetate **1b**, as indicated by TLC, the reaction mixture was heated to 80 °C and stirred for 12 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$, and extracted with ethyl acetate (3×2 mL). The combined organic layers were dried over $MgSO_4$ and evaporated. The residue was chromatographed on silica gel (hexane/diethyl ether=4/1) to give 34.8 mg (39%) of **3b**-**B1** and 52.4 mg (58%) of **5b**.

4.2.1. (S)-4-Methyl-2-phenyl-4-((R*)-1-phenylallyl)oxazol-5(4H)-one (**3a**-**B1**).* Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.35 (s, 3H), 3.69 (d, *J*=9.5 Hz, 1H), 5.09 (dd, *J*=1.3, 10.1 Hz, 1H), 5.19 (d, *J*=16.9 Hz, 1H), 6.01 (ddd, *J*=9.5, 10.1, 16.9 Hz, 1H), 7.26 (d, *J*=14.7 Hz, 1H), 7.33 (t, *J*=7.7 Hz, 2H), 7.45–7.50 (m, 4H), 7.57 (t, *J*=7.7 Hz, 1H), 8.01 (dd, *J*=1.4, 8.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 22.5, 57.6, 73.6, 118.9, 125.9, 127.4, 128.0, 128.5, 128.8, 129.2, 132.7, 135.6, 138.4, 159.9, 180.7. IR (neat) 3405, 2980, 1815, 1739, 1653, 1581, 1493, 1241, 1003, 927, 703. HRMS (ESI): *m*/*z*: calcd for $C_{19}H_{18}NO_2^+$ $[M+H]^+$ 292.1338, found 292.1328. The alkylated product **3a**-**B1** was solvolyzed by K_2CO_3/MeOH, and the relative configuration was determined by the comparison with the reported ^{1}H NMR data.

*4.2.2. (S)-4-Methyl-2-phenyl-4-((R)-1-phenylallyl)oxazol-5(4H)-one ((4S,1′R)-**3a**-**B1**).* Colorless oil. $[\alpha]_D^{26}$ −39.6 (*c* 3.5, $CHCl_3$) (86% ee). Enantiomer ratio was determined by HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol=25/1, flow: 1.0 mL/min, 254 nm, 35 °C, t_R 19.1 min (minor); t_R 23.7 min (major)).

4.2.3. (R)-4-Methyl-2-phenyl-4-((R*)-1-phenylallyl)oxazol-5(4H)-one (**3a**-**B2**).* Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.58 (s, 3H), 3.71 (d, *J*=6.6 Hz, 1H), 5.30 (d, *J*=16.8 Hz, 1H), 5.32 (dd, *J*=1.2, 9.6 Hz, 1H), 6.38 (ddd, *J*=6.6, 9.6, 16.8 Hz, 1H), 7.11–7.19 (m, 5H), 7.44 (t,

J=8.4 Hz, 2H), 7.52–7.87 (m, 1H), 7.88 (d, J=8.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 22.6, 57.5, 72.9, 119.4, 125.8, 127.5, 127.9, 128.3, 128.7, 128.7, 132.6, 135.3, 138.1, 160.2, 180.1. IR (neat) 3064, 2979, 1822, 1652, 1452, 1295, 1004, 707. HRMS (ESI): m/z: calcd for $C_{19}H_{18}NO_2^+$ $[M+H]^+$ 292.1338, found 292.1327.

*4.2.4. 2-(3-Phenyl-2-propenyl)-4-methyl-2-phenyloxazol-5(2H)-one (**5a**).* Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.27 (s, 3H), 2.99 (ddd, J=1.1, 7.5, 14.2 Hz, 1H), 3.05 (ddd, J=1.1, 7.5, 14.2 Hz, 1H), 5.90 (dt, J=7.5, 15.8 Hz, 1H), 6.39 (d, J=15.8 Hz, 1H), 7.22–7.29 (m, 5H), 7.36–7.41 (m, 3H), 7.58 (d, J=6.9 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 44.8, 107.2, 120.5, 125.9, 126.3, 127.8, 128.6, 128.6, 128.9, 136.4, 136.8, 138.5, 160.4, 165.2. IR (neat) 3060, 3030, 1784, 1654, 1449, 1308, 1148, 967, 747, 695. HRMS (ESI): m/z: calcd for $C_{19}H_{18}NO_2^+$ $[M+H]^+$ 292.1338, foundx292.1329.

*4.2.5. (S)-2-(3-Phenyl-2-propenyl)-4-methyl-2-phenyloxazol-5(2H)-one ((S)-**5a**).* Colorless oil. $[\alpha]_D^{26}$ −5.6 (c 2.3, $CHCl_3$) (79% ee). Enantiomer ratio was determined by HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol=25/1, flow: 1.0 mL/min, 254 nm, 35 °C, t_R 26.3 min (minor); t_R 34.4 min (major)).

4.2.6. (S)-4-((R*)-1-(4-Methoxyphenyl)allyl)-4-methyl-2-phenyloxazol-5(4H)-one (**3b**-**B1**).* Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.35 (s, 3H), 3.65 (d, J=9.4 Hz, 1H), 3.79 (s, 3H), 5.07 (d, J=10.1 Hz, 1H), 5.17 (d, J=16.9 Hz, 1H), 5.98 (ddd, J=9.4, 10.1, 16.9 Hz, 1H), 6.87 (d, J=8.6 Hz, 2H), 7.37 (d, J=8.6 Hz, 2H), 7.49 (dd, J=7.4, 7.4 Hz, 2H), 7.57 (dd, J=7.4, 7.4 Hz, 1H), 8.01 (d, J=7.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 22.5, 55.2, 56.7, 73.6, 113.9, 118.6, 125.9, 128.0, 128.8, 130.2, 130.5, 132.7, 135.8, 158.9, 159.8, 180.8. IR (neat) 3072, 2933, 2836, 1814, 1736, 1611, 1512, 1451, 1247, 1004, 925, 704. HRMS (ESI): m/z: calcd for $C_{20}H_{20}NO_3^+$ $[M+H]^+$ 322.1443, found 322.1433.

*4.2.7. (S)-4-((R)-1-(4-Methoxyphenyl)allyl)-4-methyl-2-phenyloxazol-5(4H)-one ((4S,1′R)-**3b**-**B1**).* Colorless oil. $[\alpha]_D^{27}$ −26.2 (c 4.3, $CHCl_3$) (44% ee). Enantiomer ratio was determined by HPLC using a Daicel CHIRALPAK AD-H (hexane/2-propanol=99/1, flow: 1.0 mL/min, 254 nm, 35 °C, t_R 8.5 min (major); t_R 10.2 min (minor)).

*4.2.8. (E)-2-(3-(4-Methoxyphenyl)allyl)-4-methyl-2-phenyloxazol-5(2H)-one (**5b**).* White solid. Mp 115–117 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.27 (s, 3H), 2.97 (ddd, J=1.0, 7.5, 14.2 Hz, 1H), 3.04 (ddd, J=1.0, 7.5, 14.2 Hz, 1H), 3.79 (s, 3H), 5.74 (dt, J=7.5, 15.8 Hz, 1H), 6.33 (d, J=15.8 Hz, 1H), 6.82 (d, J=8.8 Hz, 2H), 7.2 (d, J=8.8 Hz, 2H), 7.35–7.4 (m, 3H), 7.58 (d, J=7.1, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 44.8, 55.3, 107.3, 114.1, 118.2, 125.9, 127.5, 128.6, 128.9, 129.6, 135.9, 138.6, 159.4, 160.4, 165.2. IR (neat) 3037, 2903, 2840, 1784, 1654, 1609, 1515, 1443, 1296, 1242, 978, 758. HRMS (ESI): m/z: calcd for $C_{20}H_{20}NO_3^+$ $[M+H]^+$ 322.1443, found 322.1446.

*4.2.9. (S,E)-2-(3-(4-Methoxyphenyl)allyl)-4-methyl-2-phenyloxazol-5(2H)-one ((S)-**5b**).* White solid. $[\alpha]_D^{27}$ −4.2 (c 3.2, $CHCl_3$) (38% ee). Enantiomer ratio was determined by HPLC using a Daicel CHIRALPAK AD-H (hexane/2-propanol=19/1, flow: 1.0 mL/min, 254 nm, 35 °C, t_R 9.5 min (minor); t_R 11.1 min (major)).

4.2.10. (S)-4-Methyl-2-phenyl-4-((R*)-1-(4-(trifluoromethyl)phenyl)allyl)oxazol-5(4H)-one (**3c**-**B1**).* Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.34 (s, 3H), 3.77 (d, J=9.6 Hz, 1H), 5.13 (dd, J=0.9, 10.1 Hz, 1H), 5.21 (d, J=16.8 Hz, 1H), 5.95 (ddd, J=9.6, 10.1, 16.8 Hz, 1H), 7.50 (t, J=7.6 Hz, 2H), 7.60–7.61 (m, 5H), 8.03 (d, J=11.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 22.4, 57.2, 73.2, 119.7, 124.2 (q, J_{C-F}=272.0 Hz), 125.5 (q, J_{C-F}=4.0 Hz), 125.7, 128.0, 128.9, 129.7, 129.7 (q, J_{C-F}=32.5 Hz), 132.9, 134.8, 142.6, 160.2, 180.2. ^{19}F NMR (565 MHz, $CDCl_3$) δ 99.2. IR (neat) 3071, 2982, 1818, 1734, 1652, 1494, 1452, 1326, 1167, 1006, 929, 708. HRMS (ESI): m/z: calcd for $C_{20}H_{17}F_3NO_2^+$ $[M+H]^+$ 360.1211, found 360.1200.

*4.2.11. (S)-4-Methyl-2-phenyl-4-((R)-1-(4-(trifluoromethyl)phenyl)allyl)oxazol-5(4H)-one ((4S,1′R)-**3c**-**B1**).* Colorless oil. $[\alpha]_D^{25}$ −43.3 (c 3.6, $CHCl_3$) (98% ee). Enantiomer ratio was determined by HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol=250/1, flow: 0.5 mL/min, 254 nm, 35 °C, t_R 42.1 min (major); t_R 49.6 min (minor)).

*4.2.12. (R)-4-Methyl-2-phenyl-4-((R)-1-(4-(trifluoromethyl)phenyl)allyl)oxazol-5(4H)-one ((4R,1′R)-**3c**-**B2**).* Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.59 (s, 3H), 3.78 (d, J=9.6 Hz, 1H), 5.32 (d, J=16.8 Hz, 1H), 5.36 (dd, J=0.9, 10.1 Hz, 1H), 6.36 (ddd, J=9.6, 10.1, 16.8 Hz, 1H), 7.31 (d, J=8.2 Hz, 2H), 7.42 (d, J=8.2 Hz, 2H), 7.46 (t, J=7.5 Hz, 2H), 7.57 (t, J=7.5 Hz, 1H), 7.88 (d, J=7.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 22.7, 57.0, 72.6, 120.2, 124.0 (q, J_{C-F}=272.1 Hz), 125.2 (q, J_{C-F}=3.3 Hz), 125.5, 127.8, 128.8, 129.1, 129.6 (q, J_{C-F}=32.4 Hz), 130.1, 132.9, 134.5, 142.3, 160.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ 99.1. IR (neat) 3063, 2938, 1819, 1654, 1329, 1160, 1127, 1069, 1006, 905, 708. HRMS (ESI): m/z: calcd for $C_{20}H_{17}F_3NO_2^+$ $[M+H]^+$ 360.1211, found 360.1202. $[\alpha]_D^{25}$ −69.5 (c 0.6, $CHCl_3$) (95% ee). Enantiomer ratio was determined by HPLC using a Daicel CHIRALCEL OD-H (hexane/2-propanol=500/1, flow: 0.2 mL/min, 254 nm, 35 °C, t_R 44.6 min (major); t_R 49.8 min (minor)).

*4.2.13. (E)-4-Methyl-2-phenyl-2-(3-(4-(trifluoromethyl)phenyl)allyl)oxazol-5(2H)-one ((**5c**)).* White solid. Mp 124–126. ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.28 (s, 3H), 3.00 (ddd, J=0.9, 7.5, 14.2 Hz, 1H), 3.09 (ddd, J=0.9, 7.5, 14.2 Hz, 1H), 6.01 (dt, J=7.5, 15.9 Hz, 1H), 6.42 (d, J=15.9 Hz, 1H), 7.34–7.42 (m, 5H), 7.53 (d, J=8.2 Hz, 2H), 7.57 (d, J=6.9 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 13.9, 44.7, 107.0, 123.5, 124.2 (q, J_{C-F}=272.0 Hz), 125.6 (q, J_{C-F}=3.9 Hz), 125.9, 126.5, 128.6, 129.0, 129.5 (q, J_{C-F}=32.2 Hz), 135.0, 138.2, 140.1, 160.5, 165.1. ^{19}F NMR (565 MHz, $CDCl_3$) δ 99.3. IR (neat) 3062, 3043, 2905, 1793, 1655, 1616, 1451, 1415, 1337, 1122, 981, 764, 700. HRMS (ESI): m/z: calcd for $C_{20}H_{17}F_3NO_2^+$ $[M+H]^+$ 360.1211, found 360.1216.

*4.2.14. (S,E)-4-Methyl-2-phenyl-2-(3-(4-(trifluoromethyl)phenyl)allyl)oxazol-5(2H)-one ((S)-**5c**).* Colorless oil. $[\alpha]_D^{24}$ −2.8 (c 2.6, $CHCl_3$) (93% ee). Enantiomer ratio was determined by HPLC using a Daicel CHIRALPAK AD-H (hexane/2-propanol=99/1, flow: 1.0 mL/min, 254 nm, 35 °C, t_R 14.6 min (major); t_R 20.8 min (minor)).

4.2.15. (S)-4-((R*)-1-(4-Chlorophenyl)allyl)-4-methyl-2-phenyloxazol-5(4H)-one (**3d**-**B1**).* White solid. Mp 106–114 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.34 (s, 3H), 3.67 (d, J=9.3 Hz, 1H), 5.1 (dd, J=1.0, 10.1 Hz, 1H), 5.18 (d, 16.9 Hz, 1H), 5.94 (ddd, J=9.3, 10.1, 16,9 Hz, 1H), 7.31 (d, J=8.5 Hz, 2H), 7.4 (d, J=8.5 Hz, 2H), 7.5 (t, J=7.5 Hz, 2H), 7.59 (t, J=7.5 Hz, 1H), 8.01 (d, J=7.1 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 22.5, 56.8, 73.3, 119.3, 125.8, 128.1, 128.7, 128.8, 130.6, 132.8, 133.3, 135.2, 137.0, 160.1, 180.4. IR (neat) 3064, 1810, 1654, 1493, 1452, 1287, 1004, 919, 848. HRMS (ESI): m/z: calcd for $C_{19}H_{17}ClNO_2^+$ $[M+H]^+$ 326.0948, found 326.0945.

*4.2.16. (E)-2-(3-(4-Chlorophenyl)allyl)-4-methyl-2-phenyloxazol-5(2H)-one (**5d**).* White solid. Mp 158–163 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.27 (s, 3H), 2.97 (ddd, J=1.1, 7.5, 14.2 Hz, 1H), 3.05 (ddd, J=1.1, 7.5, 14.2 Hz, 1H), 5.88 (dt, J=7.5, 15.8 Hz, 1H), 6.34 (d, J=15.8 Hz, 1H), 7.19 (d, J=8.5 Hz, 2H), 7.25 (d, J=8.5 Hz, 2H), 7.34–7.41 (m, 3H), 7.57 (d, J=6.9 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 44.7, 107.1, 121.3, 125.9, 127.5, 128.6, 128.8, 129.0, 133.4, 135.1, 135.2, 138.3, 160.4, 165.1. IR (neat) 3064, 1784, 1488, 1148, 978, 758. HRMS (ESI): m/z: calcd for $C_{19}H_{17}ClNO_2^+$ $[M+H]^+$ 326.0948, found 326.0946.

4.2.17. (S)-4-((R*)-1-(4-Bromophenyl)allyl)-4-methyl-2-phenyloxazol-5(4H)-one (**3e**-**B1**).* White solid. Mp 116–122 °C. ^{1}H

NMR (600 MHz, $CDCl_3$) δ 1.55 (s, 3H), 3.66 (d, J=9.4 Hz, 1H), 5.1 (dd, J=1.0, 10.1 Hz, 1H), 5.18 (d, J=16.9 Hz, 1H), 5.92 (ddd, J=9.4, 10.1, 16.9 Hz, 1H), 7.35 (d, J=8.5 Hz, 2H), 7.46–7.51 (m, 4H), 7.59 (t, J=7.4 Hz, 1H), 8.01 (d, J=7.9 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 22.5, 56.8, 73.2, 119.4, 121.5, 125.8, 128.0, 128.8, 131.0, 131.7, 132.9, 135.1, 137.5, 160.1, 180.4. IR (neat) 2984, 1810, 1649, 1488, 1322, 1287, 1038, 1009, 933, 803, 691. HRMS (ESI): m/z: calcd for $C_{19}H_{17}BrNO_2^+$ $[M+H]^+$ 370.0443, found 370.0445.

*4.2.18. (E)-2-(3-(4-Bromophenyl)allyl)-4-methyl-2-phenyloxazol-5(2H)-one ((**5e**)).* White solid. Mp 158–162 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.27 (s, 3H), 2.96 (ddd, J=1.1, 7.4, 14.2 Hz, 1H), 3.05 (ddd, J=1.1, 7.4, 14.2 Hz, 1H), 5.89 (dt, J=7.4, 15.8 Hz, 1H), 6.32 (d, J=15.8 Hz, 1H), 7.12 (d, J=8.4 Hz, 2H), 7.36–7.41 (m, 5H), 7.57 (d, J=7.0 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 44.7, 107.1, 121.5, 121.6, 125.9, 127.8, 128.6, 129.0, 131.7, 135.2, 135.7, 138.3, 160.4, 165.1. IR (neat) 3063, 2939, 1787, 1655, 1488, 1451, 1307, 1224, 1071, 804, 611. HRMS (ESI): m/z: calcd for $C_{19}H_{17}BrNO_2^+$ $[M+H]^+$ 370.0443, found 370.0445.

4.2.19. (S)-4-((R*)-1-(2-Methoxyphenyl)allyl)-4-methyl-2-phenyloxazol-5(4H)-one (**3f**-**B1**).* White solid. Mp 116–118 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.35 (s, 3H), 3.85 (s, 3H), 4.48 (d, J=9.6 Hz, 1H), 5.05 (dd, J=1.8, 10.2 Hz, 1H), 5.20 (ddd, J=1.8, 16.8 Hz, 1H), 5.91 (ddd, J=16.8, 9.6, 10.2 Hz, 1H), 6.88 (ddd, J=9.6, 10.2, 16.8 Hz, 1H), 7.00 (ddd, J=1.0, 7.6, 7.6 Hz, 1H), 7.24 (dd, J=1.0, 7.6, 7.6 Hz, 1H), 7.49 (t, J=7.4 Hz, 2H), 7.57 (t, J=7.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.9, 50.0, 55.5, 73.8, 110.7, 118.9, 120.8, 126.1, 126.8, 128.0, 128.2, 128.8, 129.7, 132.6, 135.6, 157.3, 159.6, 180.9. IR (neat) 3033, 3006, 2836, 1806, 1640, 1461, 1300, 1242, 1099, 1076, 919, 879, 749, 678. HRMS (ESI): m/z: calcd for $C_{20}H_{20}NO_3^+$ $[M+H]^+$ 322.1443, found 322.1434.

*4.2.20. (E)-2-(3-(2-Methoxyphenyl)allyl)-4-methyl-2-phenyloxazol-5(2H)-one (**5f**).* Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.27 (s, 3H), 3.01 (dd, J=7.4, 14.2 Hz, 1H), 3.08 (dd, J=7.4, 14.2 Hz, 1H), 3.80 (s, 3H), 5.89 (dt, J=7.4, 16.0 Hz, 1H), 6.69 (d, J=16.0 Hz, 1H), 6.83 (d, J=8.2 Hz, 1H), 6.88 (t, J=7.5 Hz, 1H), 7.2 (t, J=7.5 Hz, 1H), 7.26 (d, J=7.5 Hz, 1H), 7.35–7.41 (m, 3H), 7.59 (d, J=7.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 13.9, 45.1, 55.4, 77.4, 107.3, 110.9, 120.7, 121.2, 125.9, 127.0, 128.6, 128.8, 128.9, 131.5, 138.6, 156.7, 160.3, 165.3. IR (neat) 3031, 2938, 2837, 1780, 1598, 1580, 1489, 1148, 974, 753, 700. HRMS (ESI): m/z: calcd for $C_{20}H_{20}NO_3^+$ $[M+H]^+$ 322.1443, found 322.1433.

4.2.21. (S)-4-((R*)-1-(2-Chlorophenyl)allyl)-4-methyl-2-phenyloxazol-5(4H)-one (**3g**-**B1**).* Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.37 (s, 3H), 4.53 (d, J=9.0 Hz, 1H), 5.09 (d, J=10.2 Hz, 1H), 5.24 (d, J=16.8 Hz, 1H), 5.81 (ddd, J=9.0, 10.2, 16.8 Hz, 1H), 7.20 (t, J=7.6 Hz, 1H), 7.32 (t, J=7.6, 1H), 7.39 (d, J=8.0 Hz, 1H), 7.49 (t, J=7.8 Hz, 2H), 7.58 (t, J=7.8 Hz, 1H), 7.90 (d, J=7.6 Hz, 1H), 8.04 (d, J=7.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.8, 51.8, 73.8, 119.9, 125.9, 127.1, 128.1, 128.5, 128.8, 129.7, 130.3, 132.8, 134.7, 134.8, 136.1, 160.0, 180.4. IR (neat) 3069, 1817, 1651, 1580, 1451, 1293, 1159, 1005, 929, 877, 700. HRMS (ESI): m/z: calcd for $C_{19}H_{17}ClNO_2^+$ $[M+H]^+$ 326.0948, found 326.0938.

*4.2.22. (E)-2-(3-(2-Chlorophenyl)allyl)-4-methyl-2-phenyloxazol-5(2H)-one ((**5g**)).* Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.29 (s, 3H), 3.04 (ddd, J=1.2, 7.2, 14.4 Hz, 1H), 3.11 (ddd, J=1.2, 7.2, 14.4 Hz, 1H), 5.89 (dt, J=7.2, 15.6 Hz, 1H) 6.75 (d, J=15.6 Hz, 1H), 7.17 (m, 2H), 7.30–7.42 (m, 5H), 7.59 (d, J=7.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 44.7, 107.0, 123.6, 125.9, 126.9, 127.0, 128.6, 128.8, 129.0, 129.7, 132.8, 132.9, 135.0, 138.3, 160.4, 165.1. IR (neat) 3062, 1783, 1655, 1470, 1449, 1308, 1149, 967, 752, 699. HRMS (ESI): m/z: calcd for $C_{19}H_{17}ClNO_2^+$ $[M+H]^+$ 326.0948, found 326.0938.

4.2.23. (S)-4-Methyl-4-((R*)-1-(naphthalen-1-yl)allyl)-2-phenyloxazol-5(4H)-one (**3h**-**B1**).* White solid. Mp 112–119 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.37 (s, 3H), 4.73 (d, J=8.4 Hz, 1H), 5.09 (d, J=10.2 Hz, 1H), 5.27 (d, J=16.8 Hz, 1H), 6.05 (ddd, J=8.4, 10.2, 16.8 Hz, 1H), 7.46–7.51 (m, 3H), 7.53–7.60 (m, 3H), 7.79 (d, J=8.2 Hz, 1H), 7.86 (d, J=8.2 Hz, 1H), 7.99 (d, J=7.8 Hz, 2H), 8.07 (d, J=5.7 Hz, 1H), 8.28 (d, J=8.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 22.3, 50.5, 74.4, 119.1, 123.1, 125.6, 125.6, 125.9, 126.3, 126.5, 127.9, 128.1, 128.8, 129.2, 132.3, 132.8, 134.0, 134.6, 136.0, 159.9, 181.1. IR (neat) 3061, 2931, 1814, 1655, 1451, 1291, 1155, 1005, 927, 878, 782, 692. HRMS (ESI): m/z: calcd for $C_{23}H_{20}NO_2^+$ $[M+H]^+$ 342.1494, found 342.1484.

*4.2.24. (E)-4-Methyl-2-(3-(naphthalen-1-yl)allyl)-2-phenyloxazol-5(2H)-one (**5h**).* Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.29 (s, 3H), 3.11 (dd, J=7.2, 14.4 Hz, 1H), 3.18 (dd, J=7.2, 14.4 Hz, 1H), 5.92 (dt, J=7.2, 15.6 Hz, 1H), 7.11 (d, J=15.6 Hz, 1H), 7.37–7.43 (m, 5H), 7.48 (t, J=3.8 Hz, 2H), 7.63 (d, J=7.6 Hz, 2H), 7.76 (t, J=4.7 Hz, 1H), 7.83 (d, J=9.4 Hz, 1H), 7.91 (d, J=9.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.1, 45.0, 107.3, 123.9, 123.9, 124.0, 125.7, 125.9, 126.0, 126.1, 128.1, 128.5, 128.7, 129.0, 131.1, 133.5, 134.3, 134.7, 138.5, 160.5, 165.3. IR (neat) 3060, 1781, 1736, 1655, 1449, 1325, 1148, 967, 778, 701. HRMS (ESI): m/z: calcd for $C_{23}H_{20}NO_2^+$ $[M+H]^+$ 342.1494, found 342.1488.

4.2.25. (S)-4-Methyl-4-((R*)-1-(naphthalen-2-yl)allyl)-2-phenyloxazol-5(4H)-one (**3i**-**B1**).* White solid. Mp 150–153 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.37 (s, 3H), 3.88 (d, J=9.0 Hz, 1H), 5.11 (d, J=10.2 Hz, 1H), 5.23 (d, J=16.8 Hz, 1H), 6.08 (ddd, J=9.0, 10.2, 16.8 Hz, 1H), 7.44–7.51 (m, 4H), 7.58 (t, J=7.4 Hz, 1H), 7.68 (d, J=8.5 Hz, 1H), 7.83 (q, J=8.7 Hz, 3H), 7.88 (s, 1H), 8.04 (d, J=7.9 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 22.7, 57.7, 73.7, 77.4, 119.1, 126.0, 126.2, 127.2, 127.7, 128.0, 128.1, 128.3, 128.3, 128.9, 132.8, 132.8, 133.5, 135.7, 136.1, 160.0, 180.8. IR (neat) 3064, 2979, 1810, 1649, 1448, 1287, 1152, 996, 919, 745, 713. HRMS (ESI): m/z: calcd for $C_{23}H_{20}NO_2^+$ $[M+H]^+$ 342.1494, found 342.1487.

*4.2.26. (E)-4-Methyl-2-(3-(naphthalen-2-yl)allyl)-2-phenyloxazol-5(2H)-one (**5i**).* White solid. Mp 176–179 °C (decomp.). ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.28 (s, 3H), 3.06 (dd, J=1.2, 7.4 Hz, 1H), 3.11 (dd, J=1.2, 7.4 Hz, 1H), 6.04 (dt, J=7.4, 15.8 Hz, 1H), 6.55 (d, J=15.8 Hz, 1H), 7.36–7.48 (m, 6H), 7.60 (d, J=7.1 Hz, 2H), 7.63 (s, 1H), 7.75 (d, J=8.6 Hz, 1H), 7.78 (d, J=6.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 44.9, 107.2, 120.8, 123.4, 125.9, 126.0, 126.3, 126.3, 127.7, 128.0, 128.3, 128.6, 128.9, 133.0, 133.5, 134.1, 136.5, 138.4, 160.4, 165.2. IR (neat) 3057, 2915, 1781, 1655, 1141, 1077, 988, 819, 745, 699. HRMS (ESI): m/z: calcd for $C_{23}H_{20}NO_2^+$ $[M+H]^+$ 342.1494, found 342.1484.

4.2.27. (S)-4-Methyl-2-phenyl-4-((S*)-5-phenylpent-1-en-3-yl)oxazol-5(4H)-one (**3j**-**B1**).* Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.45 (s, 3H), 1.54–1.60 (m, 2H), 2.41–2.49 (m, 2H), 2.67 (ddd, J=5.3, 10.1, 14.4 Hz, 1H), 5.23 (d, J=17.0 Hz, 1H), 5.36 (d, J=10.1 Hz, 1H), 5.78 (ddd, J=10.1, 17.0 Hz, 1H), 7.10 (d, J=7.6 Hz, 2H), 7.15 (t, J=7.4 Hz, 1H), 7.24 (t, J=7.4 Hz, 2H), 7.47 (t, J=7.7 Hz, 2H), 7.56 (t, J=7.7 Hz, 1H), 7.98 (d, J=7.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 22.8, 31.0, 33.5, 51.2, 72.1, 120.3, 125.9, 125.9, 128.0, 128.4, 128.5, 128.8, 132.7, 135.9, 141.5, 160.0, 181.0. IR (neat) 2931, 1818, 1655, 1496, 1452, 1321, 1291, 1164, 999, 861, 694. HRMS (ESI): m/z: calcd for $C_{21}H_{22}NO_2^+$ $[M+H]^+$ 320.1651, found 320.1640.

4.2.28. (R)-4-Methyl-2-phenyl-4-((S*)-5-phenylpent-1-en-3-yl)oxazol-5(4H)-one (**3j**-**B2**).* Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.48 (s, 3H) 1.67 (m, 1H), 1.92–1.97 (m, 1H), 2.40–2.49 (m, 2H), 2.72 (ddd, J=4.2, 10.2, 14.4 Hz, 1H), 5.20 (dd, J=1.1, 17.0 Hz, 1H), 5.25 (dd, J=1.5, 10.2 Hz, 1H), 5.67 (ddd, J=10.2, 17.0 Hz, 1H), 7.15 (d, J=9.5 Hz,

2H), 7.18 (t, J=7.4 Hz, 1H), 7.26 (t, J=7.4 Hz, 2H), 7.48 (t, J=7.4 Hz, 2H), 7.57 (t, J=7.4 Hz, 1H), 7.99 (d, J=7.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 25.6, 33.1, 36.6, 54.0, 75.5, 123.4, 129.1, 129.2, 131.2, 131.6, 131.7, 132.0, 135.9, 138.8, 144.9, 163.3, 183.4. IR (neat) 2933, 1820, 1653, 1496, 1451, 1321, 1292, 1159, 1003, 926, 879, 694. HRMS (ESI): m/z: calcd for $C_{21}H_{22}NO_2^+$ $[M+H]^+$ 320.1651, found 320.1642.

*4.2.29. (S)-4-((R)-1-(4-Fluorophenyl)allyl)-4-methyl-2-phenyloxazol-5(4H)-one ((4S,1′R)-**3k**-**B1**).* Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.34 (s, 3H), 3.69 (d, J=9.6 Hz, 1H), 5.11 (dd, J=1.1, 10.2 Hz, 1H), 5.18 (dd, J=1.1, 16.8 Hz, 1H), 5.96 (ddd, J=9.6, 10.2, 16.8 Hz, 1H), 7.03 (t, J=8.6 Hz, 2H), 7.42 (d, J=8.6 Hz, 1H), 7.43 (d, J=8.6 Hz, 1H), 7.49 (d, J=7.5 Hz, 1H), 7.50 (d, J=7.5 Hz, 1H), 7.59 (t, J=7.5 Hz, 1H), 8.01 (d, J=8.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 22.4, 56.7, 73.4, 115.4 (J_{C-F}=78.8 Hz), 119.1, 125.8, 128.0, 128.8, 130.7 (J_{C-F}=31.6 Hz), 132.8, 134.2, 135.4, 162.1 (J_{C-F}=245 Hz), 162.9, 180.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ 46.5 (sep, J=4.0 Hz). IR (neat) 2981, 1817, 1654, 1509, 1451, 1294, 1226, 1161, 927, 1004, 915, 702. HRMS (ESI): m/z: calcd for $C_{19}H_{17}FNO_2^+$ $[M+H]^+$ 310.1243, found 310.1234. $[\alpha]_D^{24}$ −29.0 (c 3.2, $CHCl_3$) (93% ee). Enantiomer ratio was determined by HPLC using a Daicel CHIRALPAK AD-H (hexane/2-propanol=200/1, flow: 0.2 mL/min, 254 nm, 35 °C, t_R 33.1 min (major); t_R 37.2 min (minor)).

*4.2.30. (S,E)-2-(3-(4-Fluorophenyl)allyl)-4-methyl-2-phenyloxazol-5(2H)-one ((S)-**5k**).* Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.28 (s, 3H), 2.97 (ddd, J=1.1, 7.5, 14.3 Hz, 1H), 3.05 (ddd, J=1.1, 7.5, 14.3 Hz, 1H), 5.81 (dt, J=7.5, 15.8 Hz, 1H), 6.35 (d, J=15.8 Hz, 1H), 6.97 (t, J=8.7 Hz, 2H), 7.23 (q, J=5.3 Hz, 2H), 7.35–7.42 (m, 3H), 7.58 (d, J=6.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 44.7, 107.1, 115.5 (J_{C-F}=22.7 Hz), 120.2, 125.9, 127.8 (J_{C-F}=52.7 Hz), 128.6, 129.0, 132.9 (J_{C-F}=3.3 Hz), 135.2, 138.3, 160.4, 162.4 (J_{C-F}=246 Hz), 165.2. ^{19}F NMR (565 MHz, $CDCl_3$) δ 47.5 (sep, J=4.5 Hz). IR (neat) 3064, 2943, 1779, 1662, 1600. 1519, 1425, 1318, 1228, 1143, 1013, 843, 704. HRMS (ESI): m/z: calcd for $C_{19}H_{17}FNO_2^+$ $[M+H]^+$ 310.1243, found 310.1234. $[\alpha]_D^{24}$ −5.8 (c 1.9, $CHCl_3$) (88% ee). Enantiomer ratio was determined by HPLC using a Daicel CHIRALPAK AD-H (hexane/2-propanol=99/1, flow: 1.0 mL/min, 254 nm, 35 °C, t_R 14.3 min (major); t_R 17.6 min (minor)).

*4.2.31. (S,E)-2-(3-(4-Bromophenyl)allyl)-2-(4-chlorophenyl)-4-methyloxazol-5(2H)-one ((S)-**5lb**).* White solid. Mp 214–216 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.28 (s, 3H), 2.92 (dd, J=7.2, 14.4 Hz, 1H), 3.00 (dd, J=7.2, 14.4 Hz, 1H), 5.88 (dt, J=7.2, 16.2 Hz, 1H), 6.31 (d, J=16.2 Hz, 1H), 7.13 (d, J=8.5 Hz, 2H), 7.37 (d, J=8.5 Hz, 2H), 7.41 (d, J=8.5 Hz, 2H), 7.50 (t, J=8.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 44.8, 106.5, 121.0, 121.7, 127.3, 127.8, 128.8, 131.7, 135.0, 135.4, 135.4, 136.7, 160.6, 164.8. IR (neat) 3036, 2923, 1773, 1657, 1488, 1401, 1150, 971, 806. HRMS (ESI): m/z: calcd for $C_{19}H_{10}BrClNO_2^+$ $[M+H]^+$ 404.0053, found 404.0045. $[\alpha]_D^{24}$ −2.0 (c 0.30, $CHCl_3$) (99% ee). Enantiomer ratio was determined by HPLC using a Daicel CHIRALPAK AD-H (hexane/2-propanol=19/1, flow: 0.5 mL/min, 254 nm, 35 °C, t_R 19.1 min (major); t_R 21.4 min (minor)). Recrystallization from dichloromethane/hexane at 5 °C gave a suitable colorless crystal for X-ray study (CCDC 820985).

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.08.016.

References and notes

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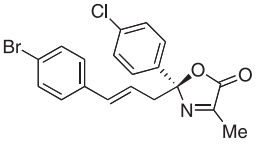
6. Reaction by $IrCl_3$, $Ir(acac)_3$, $Ir_4(CO)_{12}$, $Ir(cod)(acac)$ or $[IrCp^*Cl_2]_2$ resulted in no reaction.
7. Relative stereochemistry was determined by comparison with reported NMR data in Ref. 2a.
8. Olefin geometry was determined to be *E* by X-ray crystallographic analysis of **5lb**; see also Ref. 10.



5lb

9. The reaction using NaHMDS exhibited a lower yield, although the almost same product ratio was obtained.
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11. Absolute configuration of oxazolinone derivatives was determined by X-ray crystallographic analysis of (*S*)-**5lb**. Detailed X-ray crystallographic data are available from the CCDC, 12 Union Road, Cambridge CB2, 1EZ, UK (www.ccdc.cam.ac.uk) (CCDC 820985; see also Supplementary data).
12. The aza-Cope rearrangement of diastereomerically pure (*4S1′S*)-**3c**-**B2** (95% ee) in toluene at 60 °C gave a 93% ee of (*S*)-**5c**.
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