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Pd-Catalyzed allylic alkylation of secondary nitroalkanes

Keisuke Maki, Motomu Kanai* and Masakatsu Shibasaki*

Graduate School of Pharmaceutical Sciences, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

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Abstract—A Pd-catalyzed allylic alkylation of secondary nitroalkanes, using a catalytic amount of external base, was developed. Simple allyl carbonate and monosubstituted allyl carbonates were used as electrophiles, and bulky secondary nitroalkanes were used as nucleophiles. This is the first catalytic allylic alkylation of bulky secondary nitroalkanes, such as 2-nitroheptane. The use of the strong base DBU in the aprotic polar solvent DMSO is a key in realizing the high reactivity. In an attempt to develop an asymmetric reaction, 2-aryloxazoline ligand PHOX **L1** gave excellent results for inducing chirality at the π-allyl moiety. As for asymmetric induction at the α-position of the NO_2 functionality, the free OH-group containing 2-aryloxazoline ligand **L4** showed moderate selectivity.

1. Introduction

Nitroalkanes are valuable prenucleophiles in synthetic organic chemistry, because the nitro group is easily transformed into a wide variety of functional groups, such as amines, carboxyl groups, hydroxylamines, imines, and oximes.[1–3] Nitroalkanes, however, are much less frequently applied to Pd-catalyzed allylic alkylation,[4] an effective synthetic methodology for the formation of carbon–carbon bonds, but are often used as prenucleophiles in 1,2- and 1,4-additions to carbonyl compounds.[5] Although allylic alkylation of nitroalkanes has been reported,[6,7] there are three major problems in those reactions.

(1) Applicable prenucleophiles are limited to nitromethane, primary nitroalkanes, and 2-nitropropane because bulky secondary nitroalkanes are hardly reactive; e.g., 2-nitrobutane and 2-nitropentane are far less reactive than 2-nitropropane.[6e]
(2) A stoichiometric amount of external base is often utilized. Although reactions without external base[6b,h,7a] and with a catalytic base[6e] are reported, a large amount of Pd catalyst and/or high temperature are usually required, perhaps because the reactivity is not satisfactory in these reactions.
(3) Enantioinduction at the α-position of the NO_2 group is difficult. There is only one study in which this type of enantioinduction was realized.[7b] Several primary nitroalkanes are applicable prenucleophiles in this reaction, whereas 3-pentene-2-ol-derived methyl carbonate is the only applicable π-allyl source. Therefore, there remains much room for improvement in α-asymmetric induction.

In this article, we report our effort to solve these problems.

2. Results and discussion

2.1. Solvent and external base effect

First, the solvent and external base effects were examined using cinnamyl alcohol derivative **1a** as an electrophile, 2-nitroheptane (**2a**) as a nucleophile, and Pd-tol-BINAP complex as a catalyst (Table 1). In entries 1–7, 10 mol % of DABCO was used as a base, and various solvents were evaluated. The more polar the solvent, the higher the obtained yield. In the case of DMSO, product **3aa** was generated in 50% yield (entry 5). In protic solvents, the reaction hardly proceeded (entries 6 and 7). Next, several catalytic bases were screened using DMSO as the solvent (entries 8–13). As the basicity increased, the yield improved. DBU was the optimum base, and a maximum yield of 86% was obtained (entry 13). In all entries, significant levels of enantioinduction were not observed, although the chiral ligand (*S*)-tol-BINAP was used (ee<5%).

2.2. Substrate generality

Substrate generality was investigated under the optimized conditions described above. Based on examinations of the Pd sources and ligands, $Pd(PPh_3)_4$ (catalyst A) was used for electrophile **1e**, and $Pd_2(dba)_3 \cdot CHCl_3$ and *rac*-BINAP (catalyst B) were used for other electrophiles. Yields exceeded 70% in most cases (Table 2). 3-Penten-2-ol

* Corresponding authors. Fax: +81 3 5684 5206; e-mail: mshibasa@mol.f.u-tokyo.ac.jp

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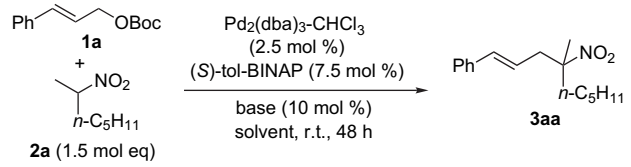
Table 1. Solvent and external base effect



Entry	Base	Solvent	Yield[a] (%)
1	DABCO	Toluene	6
2	DABCO	CH_2Cl_2	4
3	DABCO	THF	8
4	DABCO	DMF	35
5	DABCO	DMSO	50
6	DABCO	*t*-BuOH	0
7	DABCO	MeOH/CH_2Cl_2 (1:1)	0
8	None	DMSO	8
9	La (O*i*-Pr)$_3$	DMSO/THF (1:1)	14
10	*i*-Pr$_2$NEt	DMSO	15
11	TMG[b]	DMSO	75
12	TBD[c]	DMSO	71
13	DBU	DMSO	86

[a] NMR analysis.
[b] 1,1,3,3-Tetramethylguanidine.
[c] 1,5,7-Triazabicyclo[4.4.0]dec-5-ene.

derivative **1f**, however, was totally unreactive (entry 12), and only 41% of the target molecule was obtained, even when 5 mol % of the Pd catalyst and a stoichiometric amount of DBU were used (entry 13). Other acceptors, such as simple allyl carbonate **1b**, monosubstituted **1a**, **1c**, and **1d**, and 1,3-diphenylprop-2-en-1-ol derivative **1e**, gave satisfactory results. As for the nucleophile, all those tested reacted smoothly. In the case of 1-nitrohexane (**2e**), however, diallylated product **4** was generated in 15% yield (entry 10). Secondary nitroalkanes, 2-nitropropane (**2b**), bulky 2-nitroheptane (**2a**), and nitrocyclohexane (**2c**) showed good reactivity.

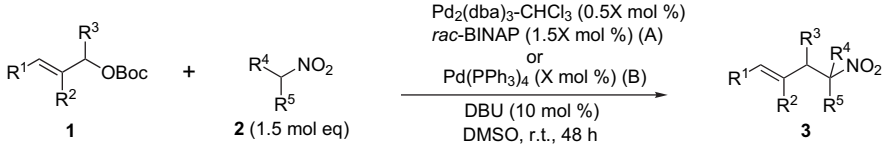
2.3. Mechanistic consideration

The proposed catalytic cycle of Pd and DBU in this reaction is depicted in Figure 1. π-Allyl–Pd complex **III**, generated from Pd catalyst and starting allyl carbonate **I** via the formation of Pd–olefin complex **II** and subsequent decarboxylation, reacted with nitronate **VII**, which was produced from starting nitroalkane **VI** and DBU, to give another Pd–olefin complex, **IV**. Dissociation of product **V** from **IV** regenerated the Pd catalyst. Protonated DBU in **VII** should be neutralized by the *tert*-butoxide anion in π-allyl–Pd complex **III**. The roles of DMSO and DBU are proposed to be as follows.

DMSO: Ionized states of π-allyl–Pd complex **III** and nitronate **VII** should be stable due to the high polarity of DMSO. As a result, the electrophilicity of the π-allyl–Pd cation and the nucleophilicity of the nitronate would be enhanced. These two factors should facilitate the nucleophilic attack of nitronate **VII** to π-allyl–Pd species **III**, which is generally thought to be the rate-determining step in catalytic allylic alkylations.

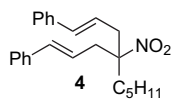
DBU: Nitroalkane is smoothly deprotonated by DBU. Deprotonation by *tert*-butoxide in **III** might be slow (Table 1, entry 8), probably due to steric factors derived from both nitroalkane and **III**. In the case of 2-nitropropane, the reaction proceeded rapidly even in the absence of external base.[8] This finding supports the assumption that the bulkiness of nitroalkane hinders the reactivity. A *tert*-butoxide **III** can be considered as a bulky base, because it consists of *tert*-butyl moiety and a sterically demanding counter cation, including

Table 2. Substrate generality



Entry	Electrophile				Nucleophile			Catalyst (A or B)	*X*	Temp (°C)	Yield[a] (%)
	R^1	R^2	R^3		R^4	R^5					
1	H	H	H	**1b**	Me	*n*-C_5H_{11}	**2a**	A	1	rt	96
2	H	Me	H	**1c**	Me	*n*-C_5H_{11}	**2a**	A	2	50	100
3	Me	H	H	**1d**	Me	*n*-C_5H_{11}	**2a**	A	2	50	82
4	Ph	H	H	**1a**	Me	*n*-C_5H_{11}	**2a**	A	1	50	72
5	Ph	H	Ph	**1e**	Me	*n*-C_5H_{11}	**2a**	B	2	rt	71[b]
6	Ph	H	Ph	**1e**	Me	Me	**2b**	B	1	rt	100
7	Ph	H	H	**1a**		*c*-Hexyl	**2c**	A	1	50	79
8	Ph	H	Ph	**1e**		*c*-Hexyl	**2c**	B	2	50	82
9	Ph	H	Ph	**1e**		*c*-Pentyl	**2d**	B	1	rt	100
10	Ph	H	H	**1a**	H	*n*-C_5H_{11}	**2e**	A	1	50	51[c]
11	Ph	H	Ph	**1e**	H	*n*-C_5H_{11}	**2e**	B	2	50	80[b]
12	Me	H	Me	**1f**	Me	Me	**2b**	A	2	50	Trace
13[d]	Me	H	Me	**1f**	Me	Me	**2b**	A	5	50	41

[a] NMR analysis.
[b] dr=1.1:1.
[c] 15% of diallylation product **4** was obtained.
[d] 100 mol % of DBU was used, *X*=5.



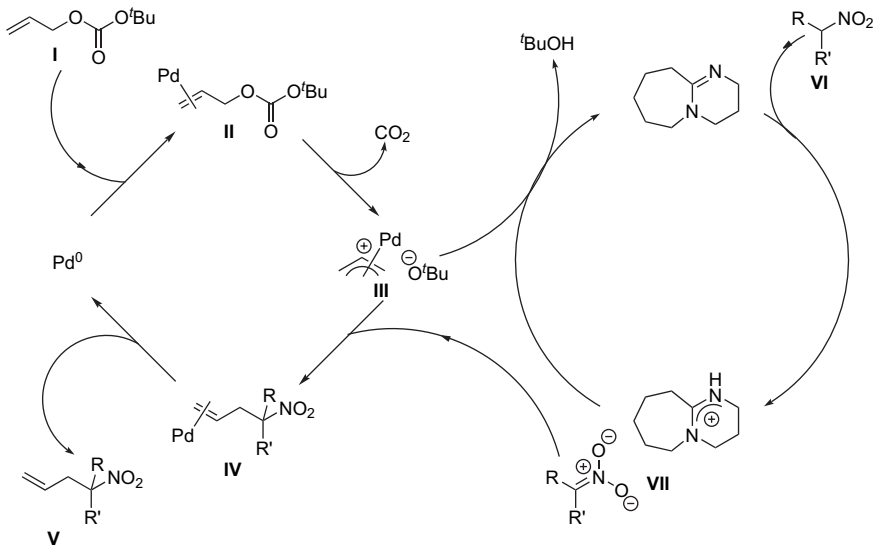


Figure 1. Catalytic cycle of Pd and DBU.

a phosphine ligand and π-allyl moiety. A strong base such as DBU is necessary to fully deprotonate the bulky nitroalkane. A high concentration of nitronate should be crucial for promoting this allylic substitution.

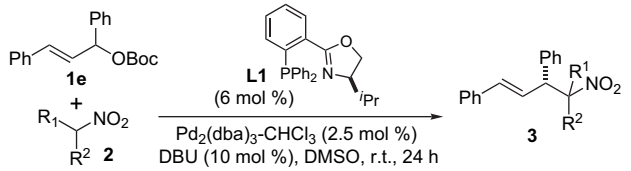
The low reactivity of the 3-penten-2-ol derivative **1f** is attributed to the character of **III**, generated from **1f**. Two methyl substituents of this π-allyl moiety would make **III** less cationic and sterically more hindered.

2.4. Catalytic asymmetric reaction using 1e as an electrophile

The asymmetric reaction was performed using **1e** as an acceptor. In initial investigations of the reaction conditions, PHOX ligand **L1**[9] showed high enantioselectivity. Using this ligand, the generality of the nucleophile was examined (Table 3). 2-Nitropropane (**2b**) gave the product **3eb** in quantitative yield and 94% ee (entry 1). The absolute configuration of **3eb** was assigned as *R* by comparing the sign of its optical rotation with data reported in the literature.[10]

The product derived from nitrocyclohexane (**2c**) was obtained in 78% yield and 82% ee (entry 2). In the case of nitrocyclopentane (**2d**), the product was obtained quantitatively, but the enantioselectivity was very low (entry 3). In entries 4 and 5, using ethyl 2-nitropropionate (**2f**) and 2-nitro-1-phenylpropane (**2g**) as donors, the ees were high, but the diastereomeric ratios were very low.

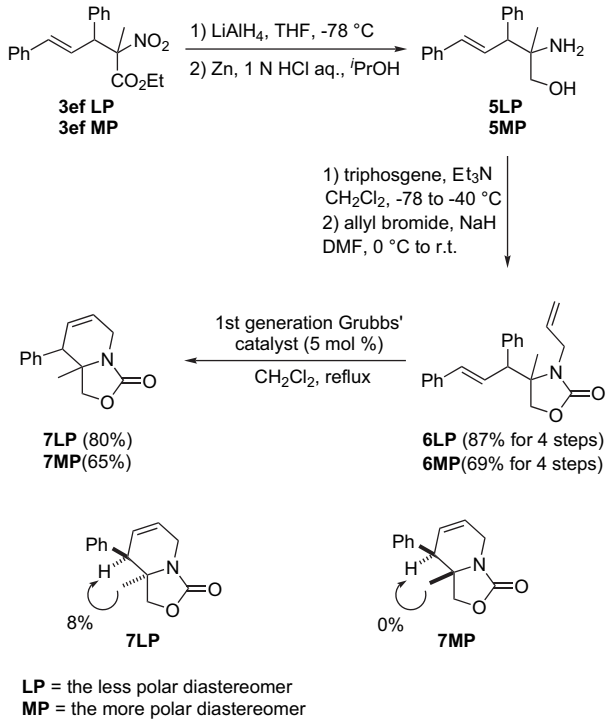
Table 3. Nucleophile generality of catalytic asymmetric allylation using **1e**



Entry	R^1	R^2	Yield[a] (%)		dr	ee[b] (%)
1	Me	Me	**2b**	100	—	94 (*R*)
2	*c*-Hexyl		**2c**	78	—	82
3	*c*-Pentyl		**2d**	100	—	5
4	Me	CO_2Et	**2f**	83	1.6:1	93:94
5	Me	Bn	**2g**	100	1.1:1	93:94

[a] NMR analysis.
[b] Chiral HPLC analysis.

The relative stereochemistry of **3ef** was determined by NOE analysis of **7**, which was synthesized from **3ef** in five steps (Scheme 1).[7d] At first, the ester moiety and nitro group of **3ef** (two diastereomers, **3efLP** and **3efMP**, separated by silica gel column chromatography; **3efLP** and **3efMP** stand for the less polar and the more polar diastereomers of **3ef**, respectively) were reduced with $LiAlH_4$ and Zn, respectively. One-step reduction of these two functionalities using



Scheme 1. Conversion of **3ef** and determination of stereochemistry.

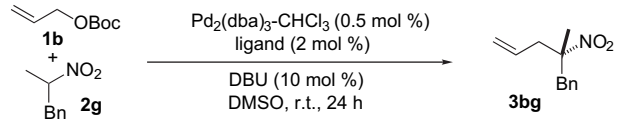
$LiAlH_4$ was unsuccessful. The obtained aminoalcohol **5** was converted to **6** via cyclic carbamate formation and N-allylation. The yields of **6LP** and **6MP** from **3ef** were 87% and 69%, respectively. Ring-closing metathesis of **6** using first-generation Grubbs' catalyst gave **7** in good yield. NOE analysis of **7** demonstrated that **3efLP** was a *syn* diastereomer (minor), and **3efMP** was an *anti* product (major).

2.5. Asymmetric induction at the α-position of NO_2 group

Next, we attempted asymmetric induction at the α-position of the NO_2 group. The product should be a precursor of chiral α-tertiary amines, which are not easily accessible using the current catalytic methods.[11] Results of the preliminary investigation are listed in Table 4. Allyl carbonate **1b** and nitroalkane **2g** were chosen as the substrates. Some chiral ligands were first examined, but none of them gave satisfactory results (entries 1–4), probably because the chiral ligand exists very far from the prochiral donor nitroalkane **2g** in the enantioinduction step.

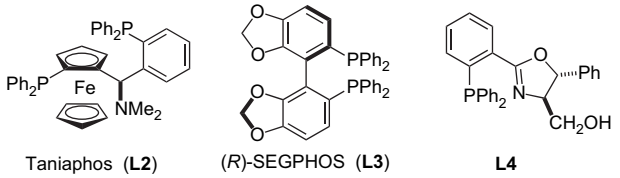
Therefore, **L4** was used based on the assumption that the nitronate derived from **2g** could interact with **L4** through hydrogen bonding with its free OH functionality.[12] This interaction should position **2g** closer to the chiral environment created by Pd and **L4**.[13] In DMSO, however, almost no chiral induction was observed (entry 5). Perhaps the polar solvent weakened the expected interaction between the ligand and the nitronate. To make the interaction more effective, less polar solvents were tested (entries 6–9). As expected, enantioselectivity was higher when a less polar solvent was utilized, although the yield was lower. In toluene, the yield and the ee were 56% and 42%, respectively (entry 9). A nearly quantitative yield of the target molecule was produced when the amount of **L4** was reduced to 1.3 mol % (1.3 equiv of Pd; entry 10). When **L1** was used, the same ee values were obtained both in DMSO and toluene (entries 2 and 11). Therefore it is likely that the expected interaction between the nitronate and the OH group of **L4** did work effectively. The ee was further improved to 49% by using TBD as an external base (entry 12). Although enantioselectivity was moderate, this is the first example of a catalytic asymmetric allylic alkylation of secondary nitroalkane that induces chirality at the α-position of an NO_2 group.

Table 4. Attempts toward α-asymmetric induction

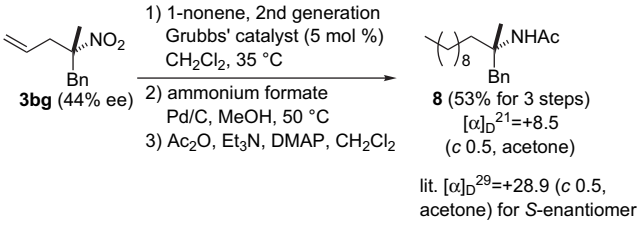


Entry	Ligand	Solvent	Yield[a] (%)	ee[b] (%)
1	(*S*)-tol-BINAP	DMSO	78	3
2[c]	**L1**	DMSO	100	18
3	Taniaphos (**L2**)	DMSO	63	2
4	(*R*)-SEGPHOS (**L3**)	DMSO	86	1
5	**L4**	DMSO	94	4
6	**L4**	DMF	41	17
7	**L4**	THF	63	36
8	**L4**	CH_2Cl_2	59	23
9	**L4**	Toluene	56	42
10[c]	**L4**	Toluene	95	44
11[c]	**L1**	Toluene	96	18
12[c,d]	**L4**	Toluene	94	49

[a] NMR analysis.
[b] Chiral HPLC analysis.
[c] 1.3 mol % of **L1** (entries 2 and 12) or **L4** (entries 10 and 11) was used.
[d] TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene) was used as external base.



The absolute configuration of **3bg** was determined as follows (Scheme 2). Cross metathesis between **3bg** and 1-nonene in the presence of second-generation Grubbs' catalyst, hydrogenation of the product, and subsequent N-acetylation gave known compound **8**[14] in 53% yield in three steps. Comparison of the sign of its optical rotation with the reported value indicated that the stereochemistry of **8** was *S*. When molecular hydrogen was used instead of ammonium formate in the hydrogenation of the cross metathesis product, the reaction was sluggish, and the yield was only ca. 20%, even under high pressure (ca. 50 atm). Adams' catalyst and Pearlman's catalyst gave the product in only trace amounts.



Scheme 2. Conversion of **3bg** and determination of its absolute configuration.

3. Conclusions

We developed a Pd-catalyzed allylic alkylation of secondary nitroalkanes using a catalytic amount of external base. Monosubstituted allyl carbonates and bulky secondary nitroalkanes can be used as electrophiles and nucleophiles, respectively. Bulky nitroalkanes such as 2-nitroheptane have not before been used in the Pd-catalyzed allylic alkylation. The strong base DBU and the aprotic polar solvent DMSO have important roles in realizing the high reactivity. In the asymmetric reaction using **1e** as an electrophile, the 2-aryloxazoline ligand PHOX **L1** gave excellent results for inducing chirality at the π-allyl moiety. As for asymmetric induction at the α-position of the NO_2 functionality, the free OH group-containing 2-aryloxazoline ligand **L4** produced moderate enantioselectivity. Chiral tertiary amines can be synthesized by this method. Further investigation of the effect of chiral ligands containing OH functionality could improve the enantioselectivity.

4. Experimental

4.1. General

Infrared (IR) spectra were recorded on a JASCO FTIR 410 Fourier transform infrared spectrophotometer. NMR spectra

were recorded on a JEOL JNM-LA500, ECX500 or ECA500 spectrometer, operating at 500 MHz for ^{1}H NMR and 125.65 MHz for ^{13}C NMR. Chemical shifts were reported in parts per million on the scale relative to residual $CHCl_3$ (δ=7.24 for ^{1}H NMR and δ=77.0 for ^{13}C NMR) as an internal reference. ESI mass spectra were measured on Waters-ZQ4000. EI mass spectra were measured on a JEOL JMS-BU20 GCmate or a JEOL JMS-700V. Optical rotations were measured on a JASCO P-1010 polarimeter. Column chromatography was performed with silica gel Merck 60 (230–400 mesh ASTM). The ee was determined by HPLC analysis. HPLC was performed on JASCO HPLC systems consisting of the flowing: pump, 880-PU or PU-980; detector, 875-UV or UV-970, measured at 254 nm. Reactions were carried out in dry solvents under an argon atmosphere, unless otherwise stated.

4.2. General procedure for Pd-catalyzed allylic alkylation of secondary nitroalkane

To a stirred solution of Pd complex ($Pd_2(dba)_3\cdot CHCl_3$ and phosphine ligand, or $Pd(PPh_3)_4$), and external base (0.02 mmol) in the solvent indicated (200 μL), allyl carbonate (0.2 mmol) and nitroalkane (0.3 mmol) were successively added at room temperature. After the time indicated, the reaction mixture was passed through a plug of silica gel (5 g) eluting with AcOEt (40 mL). After evaporation of the solvent, yield and dr were determined by ^{1}H NMR using DMF as internal standard. ee was determined by chiral HPLC analysis after PTLC purification.

4.2.1. 4-Methyl-4-nitronon-1-ene (3ba). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.81 (br t, J=6.1 Hz, 3H), 1.06–1.16 (m, 1H), 1.16–1.28 (m, 5H), 1.67–1.73 (m, 1H), 1.85–1.94 (m, 1H), 2.46 (dd, J=7.4, 14.3 Hz, 1H), 2.66 (dd, J=6.9, 14.3 Hz, 1H), 5.05–5.11 (m, 2H), 5.58 (dddd, J=6.9, 7.4, 10.3, 17.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 13.9, 21.9, 22.3, 23.4, 31.6, 39.3, 43.8, 91.1, 120.3, 131.2; IR (neat, cm^{-1}): 1092, 1539, 2957; MS (EI) m/z 139 (M^+-NO_2); HRMS (EI) calcd for $C_{10}H_{19}$ (M^+-NO_2): 139.1487, found: 139.1485.

4.2.2. 2,4-Dimethyl-4-nitronon-1-ene (3ca). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.81 (br t, J=7.2 Hz, 3H), 1.02–1.12 (m, 1H), 1.16–1.32 (m, 5H), 1.45 (s, 3H), 1.61 (br s, 3H), 1.58–1.67 (m, 1H), 1.90–2.01 (m, 1H), 2.38 (d, J=14.3 Hz, 1H), 2.78 (d, J=14.3 Hz, 1H), 4.65 (br s, 1H), 4.84 (br s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 13.9, 21.3, 22.3, 23.4, 23.5, 31.6, 40.5, 47.8, 91.1, 116.5, 139.6; IR (neat, cm^{-1}): 1092, 1539, 2957; MS (EI) m/z 153 (M^+-NO_2); HRMS (EI) calcd for $C_{11}H_{21}$ (M^+-NO_2): 153.1643, found: 153.1647.

4.2.3. (2*E*)-5-Methyl-5-nitrodec-2-ene (3da). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.86 (br t, J=7.2 Hz, 3H), 1.10–1.19 (m, 1H), 1.21–1.33 (m, 5H), 1.47 (s, 3H), 1.64 (dd, J=1.2, 6.9 Hz, 3H), 1.67–1.76 (m, 1H), 1.90–2.00 (m, 1H), 2.42 (dd, J=8.0, 14.3 Hz, 1H), 2.62 (dd, J=7.4, 14.3 Hz, 1H), 5.25 (qddd, J=1.2, 7.4, 8.0, 16.2 Hz, 1H), 5.53 (qd, J=6.9, 16.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 13.9, 18.0, 21.7, 22.3, 23.4, 31.7, 39.3, 42.9, 91.5, 123.5, 131.1; IR (neat, cm^{-1}): 1092, 1539, 2928; MS (EI) m/z 153 (M^+-NO_2); HRMS (EI) calcd for $C_{11}H_{21}$ (M^+-NO_2): 153.1643, found: 153.1639.

4.2.4. (1*E*)-4-Methyl-4-nitro-1-phenynon-1-ene (3aa). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.81 (br t, J=6.8 Hz, 3H), 1.10–1.31 (m, 6H), 1.69–1.78 (m, 1H), 1.90–1.99 (m, 1H), 2.60 (dd, J=8.0, 14.3 Hz, 1H), 2.82 (dd, J=7.5, 14.3 Hz, 1H), 5.95 (ddd, J=7.5, 8.0, 16.1 Hz, 1H), 6.40 (d, J=16.1 Hz, 1H), 7.13–7.18 (m, 1H), 7.20–7.28 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 13.9, 22.0, 22.3, 23.4, 31.6, 39.5, 43.1, 91.4, 122.4, 126.3, 127.7, 128.5, 135.1, 136.7; IR (neat, cm^{-1}): 969, 1091, 1389, 1537, 2955; MS (EI) m/z 215 (M^+-NO_2); HRMS (EI) calcd for $C_{16}H_{23}$ (M^+-NO_2): 215.1800, found: 215.1802.

4.2.5. (1*E*)-4-Methyl-4-nitro-1,3-diphenylnon-1-ene (diastereomixture) (3ea). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.76 (br t, J=6.9 Hz, 3H for minor), 0.78 (br t, J=6.9 Hz, 3H for major), 0.93–1.08 (m, 1H), 1.08–1.30 (m, 5H), 1.32–1.40 (m, 1H for minor), 1.48 (s, 3H for major), 1.51 (s, 3H for minor), 1.64–1.73 (m, 1H for major), 2.07–2.18 (m, 1H), 3.97 (d, J=9.2 Hz, 1H for minor), 4.05 (d, J=9.8 Hz, 1H for major), 6.42–6.34 (m, 1H), 6.48 (dd, J=9.2, 16.0 Hz, 1H for minor), 6.52 (d, J=15.6 Hz, 1H for major), 7.10–7.33 (m, 10H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 13.9, 13.9, 17.9, 18.0, 22.4, 22.4, 23.4, 23.5, 31.6, 31.7, 38.7, 38.9, 58.4, 58.6, 95.0, 95.6, 125.7, 126.4, 126.5, 127.6, 127.7, 127.7, 127.9, 128.5, 128.5, 128.6, 128.9, 129.3, 134.2, 134.6, 136.6, 136.7, 138.1, 138.3; IR (neat, cm^{-1}): 967, 1389, 1454, 1537, 2955; MS (EI) m/z 291 (M^+-NO_2); HRMS (EI) calcd for $C_{22}H_{27}$ (M^+-NO_2): 291.2113, found: 291.2108.

4.2.6. (2′*E*)-1-Nitro-1-(3′-phenylprop-2′-enyl)cyclohexane (3ac). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.20–1.29 (m, 1H), 1.31–1.42 (m, 2H), 1.46–1.64 (m, 5H), 2.32–2.40 (m, 2H), 2.61 (br d, J=7.5 Hz, 2H), 5.94 (dt, J=7.5, 16.0 Hz, 1H), 6.34 (d, J=16.0 Hz, 1H), 7.11–7.18 (m, 1H), 7.19–7.27 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 22.2, 24.7, 33.8, 43.9, 91.6, 121.8, 126.3, 126.3, 127.6, 128.5, 134.9, 136.6; IR (neat, cm^{-1}): 1074, 1343, 1448, 1525, 2936; MS (EI) m/z 245 (M^+); HRMS (EI) calcd for $C_{15}H_{19}NO_2$ (M^+): 245.1416, found: 245.1421.

4.2.7. (2′*E*)-1-Nitro-1-(1′,3′-diphenylprop-2′-enyl)cyclohexane (3ec). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.09–1.10 (m, 1H), 1.13–1.31 (m, 2H), 1.41–1.50 (m, 1H), 1.50–1.64 (m, 4H), 2.41–2.53 (m, 2H), 3.71 (d, J=9.8 Hz, 1H), 6.41 (d, J=15.5 Hz, 1H), 6.48 (dd, J=9.8, 15.5 Hz, 1H), 7.10–7.13 (m, 2H), 7.13–7.21 (m, 2H), 7.21–7.27 (m, 4H), 7.27–7.31 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 22.2, 24.5, 31.9, 32.4, 32.4, 59.1, 95.3, 125.7, 126.5, 127.7, 127.8, 128.5, 128.5, 128.9, 134.2, 136.7, 138.0; IR (neat, cm^{-1}): 974, 1431, 1532, 2940; MS (EI) m/z 275 (M^+-NO_2); HRMS (EI) calcd for $C_{21}H_{23}$ (M^+-NO_2): 275.1800, found: 275.1801.; $[\alpha]_D^{21}$ −47.4 (c 1.27, CH_2Cl_2, 82% ee); HPLC (DAICEL CHIRALCEL OJ-H, 2-propanol/hexane 1:99, flow 1.0 mL/min) t_R 9.4 min (minor) and 16.3 min (major).

4.2.8. (2′*E*)-1-Nitro-1-(1′,3′-diphenylprop-2′-enyl)cyclopentane (3ed). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.48–1.65 (m, 4H), 1.81–1.91 (m, 1H), 1.93–2.03 (m, 1H), 2.46–2.55 (m, 2H), 4.13 (dd, J=3.4, 5.2 Hz, 1H), 6.41–6.45 (m, 2H), 7.11–7.19 (m, 4H), 7.19–7.25 (m, 4H), 7.25–7.30 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 23.1, 23.3, 34.1, 34.5,

55.8, 104.5, 126.3, 126.4, 127.6, 127.8, 128.5, 128.6, 128.6, 134.1, 136.6, 138.6; IR (neat, cm^{-1}): 967, 1355, 1453, 1537, 2962; MS (EI) *m/z* 261 (M^+-NO_2); HRMS (EI) calcd for $C_{20}H_{21}$ (M^+-NO_2): 261.1643, found: 261.1639; $[\alpha]_D^{20}$ −23.4 (*c* 4.92, CH_2Cl_2, 5% ee); HPLC (DAICEL CHIRALCEL OD-H, 2-propanol/hexane 1:199, flow 1.0 mL/min) t_R 9.9 min (major) and 11.5 min (minor).

4.2.9. (1*E*)-4-Nitro-1-phenylnon-1-ene (3ae). ^1H NMR (500 MHz, $CDCl_3$) δ: 0.81 (br t, *J*=7.0 Hz, 3H), 1.14–1.35 (m, 6H), 1.64–1.73 (m, 1H), 1.89–1.98 (m, 1H), 2.57 (ddd, *J*=6.9, 8.0, 14.9 Hz, 1H), 2.75 (ddd, *J*=7.5, 8.5, 14.9 Hz, 1H), 5.94–6.02 (m, 1H), 5.98 (ddd, *J*=6.9, 7.5, 16.0 Hz, 1H), 6.40 (d, *J*=16.0 Hz, 1H), 7.13–7.18 (m, 1H), 7.20–7.27 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 13.8, 22.3, 25.4, 31.1, 33.3, 37.3, 88.4, 122.7, 126.3, 126.3, 127.7, 128.5, 128.5, 134.3, 136.5; IR (neat, cm^{-1}): 966, 1074, 1377, 1550, 2928; MS (EI) *m/z* 201 (M^+-NO_2); HRMS (EI) calcd for $C_{15}H_{21}$ (M^+-NO_2): 201.1643, found: 201.1644.

4.2.10. (1*E*)-4-Nitro-1,3-diphenylnon-1-ene (less polar) (3eeLP). ^1H NMR (500 MHz, $CDCl_3$) δ: 0.75 (br t, *J*=7.5 Hz, 3H), 1.05–1.20 (m, 6H), 1.32–1.39 (m, 1H), 1.77–1.86 (m, 1H), 3.78 (dd, *J*=9.2, 10.9 Hz, 1H), 4.75 (ddd, *J*=2.9, 10.9, 10.9 Hz, 1H), 6.23 (dd, *J*=9.2, 16.0 Hz, 1H), 6.37 (d, *J*=16.0 Hz, 1H), 7.11–7.16 (m, 1H), 7.16–7.25 (m, 7H), 7.25–7.32 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 13.8, 22.4, 25.5, 30.9, 31.9, 53.8, 93.2, 126.5, 127.2, 127.7, 127.8, 127.9, 128.4, 129.3, 133.0, 136.4, 138.7; IR (neat, cm^{-1}): 967, 1095, 1455, 1550, 2927; MS (EI) *m/z* 277 (M^+-NO_2); HRMS (EI) calcd for $C_{21}H_{25}$ (M^+-NO_2): 277.1956, found: 277.1951.

4.2.11. (1*E*)-4-Nitro-1,3-diphenylnon-1-ene (more polar) (3eeMP). ^1H NMR (500 MHz, $CDCl_3$) δ: 0.84 (br t, *J*=6.9 Hz, 3H), 1.24–1.32 (m, 6H), 3.93 (dd, *J*=9.7, 10.3 Hz, 1H), 4.85 (ddd, *J*=3.4, 10.3, 10.9 Hz, 1H), 6.20 (dd, *J*=9.7, 16.1 Hz, 1H), 6.54 (d, *J*=16.1 Hz, 1H), 7.21–7.25 (m, 4H), 7.27–7.34 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 13.9, 22.3, 25.6, 31.1, 32.4, 54.0, 92.5, 126.4, 126.8, 127.5, 127.6, 128.0, 128.6, 129.0, 133.6, 136.3, 139.0; IR (neat, cm^{-1}): 967, 1095, 1455, 1550, 2927; MS (EI) *m/z* 277 (M^+-NO_2); HRMS (EI) calcd for $C_{21}H_{25}$ (M^+-NO_2): 277.1956, found: 277.1950.

4.2.12. Ethyl (4*E*)-2-methyl-2-nitro-3,5-diphenyl-4-pentenoate (less polar diastereomer) (3efLP). ^1H NMR (500 MHz, $CDCl_3$) δ: 1.19 (t, *J*=7.5 Hz, 3H), 1.75 (s, 3H), 4.18 (qd, *J*=7.5, 7.5 Hz, 1H), 4.19 (qd, *J*=7.5, 7.5 Hz, 1H), 4.54 (dd, *J*=1.2, 6.9 Hz, 1H), 6.44–6.53 (m, 2H), 7.14–7.18 (m, 1H), 7.20–7.30 (m, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 13.8, 20.2, 54.6, 62.9, 96.2, 125.5, 126.5, 127.9, 128.0, 128.5, 128.7, 129.5, 134.6, 136.6, 136.9, 166.6; IR (neat, cm^{-1}): 1095, 1246, 1553, 1747, 2928; MS (EI) *m/z* 293 (M^+-NO_2); HRMS (EI) calcd for $C_{20}H_{21}O_2$ (M^+-NO_2): 293.1542, found: 293.1546; $[\alpha]_D^{22}$ −52.7 (*c* 0.56, CH_2Cl_2, 94% ee); HPLC (DAICEL CHIRALCEL OJ-H, methanol/hexane 1:19, flow 1.0 mL/min) t_R 11.7 min (major) and 49.6 min (minor).

4.2.13. Ethyl (4*E*)-2-methyl-2-nitro-3,5-diphenyl-4-pentenoate (more polar diastereomer) (3efMP). ^1H NMR (500 MHz, $CDCl_3$) δ: 1.12 (t, *J*=7.1 Hz, 3H), 1.75 (s, 3H), 4.08 (q, *J*=7.1 Hz, 2H), 4.56 (d, *J*=8.6 Hz, 1H), 6.45 (d, *J*=16.0 Hz, 1H), 6.58 (dd, *J*=8.6, 16.0 Hz, 1H), 7.12–7.30 (m, 10H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 13.7, 20.3, 54.5, 62.9, 96.3, 125.7, 126.5, 127.8, 128.0, 128.5, 128.7, 129.5, 134.54, 136.6, 136.7, 166.6; IR (neat, cm^{-1}): 1104, 1254, 1550, 1745, 2923; MS (EI) *m/z* 293 (M^+-NO_2); HRMS (EI) calcd for $C_{20}H_{21}O_2$ (M^+-NO_2): 293.1542, found: 293.1546; $[\alpha]_D^{22}$ −70.2 (*c* 0.785, CH_2Cl_2, 93% ee); HPLC (DAICEL CHIRALCEL OJ-H, methanol/hexane 1:19, flow 1.0 mL/min) t_R 10.7 min (major) and 44.0 min (minor).

4.2.14. (1*E*)-4-Methyl-4-nitro-1,3,5-triphenylpent-1-ene (diastereomixture) (3eg). ^1H NMR (500 MHz, $CDCl_3$) δ: 1.38 (s, 3H for minor), 1.39 (s, 3H for major), 2.55 (d, *J*=14.3 Hz, 1H for major), 2.97 (d, *J*=14.4 Hz, 1H for minor), 3.54–3.60 (m, 1H), 4.14 (d, *J*=9.2 Hz, 1H for major), 4.25 (d, *J*=10.3 Hz, 1H for minor), 6.42 (d, *J*=16.1 Hz, 1H for major), 6.45–6.55 (m, 1H), 6.64 (d, *J*=16.1 Hz, 1H for minor), 6.85–6.92 (m, 1H), 6.94–7.00 (m, 1H), 7.10–7.38 (m, 13H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 17.1, 17.6, 44.8, 44.9, 58.4, 58.6, 95.4, 95.9, 125.4, 125.5, 126.5, 126.6, 127.4, 127.4, 127.8, 127.8, 127.9, 128.1, 128.5, 128.5, 128.6, 128.7, 128.8, 128.9, 129.5, 130.1, 130.2, 134.3, 134.5, 134.5, 135.3, 136.5, 136.6, 137.8, 138.1; IR (neat, cm^{-1}): 909, 1495, 1539, 2250, 3029; MS (EI) *m/z* 311 (M^+-NO_2); HRMS (EI) calcd for $C_{24}H_{23}$ (M^+-NO_2): 311.1800, found: 311.1801; $[\alpha]_D^{23}$ −62.3 (*c* 1.86, CH_2Cl_2, 1.1:1 diastereomixture (93%–94% ee)); HPLC (DAICEL CHIRALCEL OD-H, 2-propanol/hexane 1:99, flow 1.0 mL/min) t_R 12.7 min (major A), 14.1 min (minor A), 19.6 min (major B), and 25.3 min (minor B).

4.2.15. (4*E*)-2-Methyl-2-nitro-1-phenylpent-4-ene (3bg). ^1H NMR (500 MHz, $CDCl_3$) δ: 1.40 (s, 3H), 2.44 (dd, *J*=8.0, 14.3 Hz, 1H), 2.79 (dd, *J*=7.4, 14.3 Hz, 1H), 2.98 (d, *J*=13.8 Hz, 1H), 3.29 (d, *J*=13.8 Hz, 1H), 5.08–5.15 (m, 2H), 5.63 (dddd, *J*=7.4, 8.0, 9.7, 14.7 Hz, 1H), 7.00–7.05 (m, 2H), 7.17–7.25 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 21.3, 43.8, 45.6, 91.5, 120.8, 127.5, 128.5, 130.1, 130.8, 134.6; IR (neat, cm^{-1}): 1092, 1388, 1540, 2926; MS (EI) *m/z* 159 (M^+-NO_2); HRMS (EI) calcd for $C_{21}H_{25}$ (M^+-NO_2): 159.1174, found: 159.1178; $[\alpha]_D^{20}$ +17.0 (*c* 0.1, CH_2Cl_2, 49% ee); HPLC (DAICEL CHIRALCEL OJ-H, 2-propanol/hexane 1:19, flow 1.0 mL/min) t_R 9.8 min (minor) and 10.9 min (major).

4.3. Conversion of 3ef and determination of its stereochemistry

4.3.1. (1″*R*,4*R*,2″*E*)-4-(1″,3″-Diphenylprop-2″-enyl)-3-(2′-propenyl)-4-methyl-oxazolidin-2-one (6LP). To a suspension of $LiAlH_4$ (10.5 mg, 0.28 mmol) in THF (0.5 mL), a solution of **3efLP** (62.7 mg, 0.185 mmol) in THF (0.5 mL) was slowly added at −78 °C. After 15 min, 1 N aq HCl (1.0 mL) was slowly added to the mixture at 0 °C. The product was extracted with CH_2Cl_2. The combined organic layer was washed with brine and dried over Na_2SO_4. After filtration and evaporation, the residue was dissolved in 2-propanol (4.0 mL). To the solution, 1 N HCl (2.0 mL) and Zn powder (0.240 g, 3.7 mmol) were added, and the whole was stirred for 15 min at room temperature. To the

mixture, satd $NaHCO_3$ was added, and the whole was stirred for 30 min. After filtration, the product was extracted with CH_2Cl_2, and the combined organic layer was dried over Na_2SO_4. After filtration and evaporation, the residue was dissolved in CH_2Cl_2 (1.0 mL). To the solution, Et_3N (69.7 μL, 0.50 mmol) and triphosgene (59.3 mg, 0.20 mmol) were added at −78 °C. The mixture was gradually warmed to −40 °C, and stirred for 15 min. 1 N HCl was slowly added to the mixture, and the product was extracted with CH_2Cl_2. The combined organic layer was washed with satd $NaHCO_3$ and brine, and dried over Na_2SO_4. After filtration and evaporation, the residue was dissolved in DMF (1.0 mL). To the solution, NaH (24 mg, 0.60 mmol) was added at 0 °C, and the whole was stirred for 15 min at the same temperature. To the mixture, allyl bromide (51.7 μL, 0.60 mmol) was added, and the whole was stirred for 2 h at room temperature. After satd NH_4Cl was added to the mixture, the product was extracted with AcOEt. The combined organic layer was washed with brine, and dried over Na_2SO_4. After filtration and evaporation, the residue was purified through silica gel column chromatography (AcOEt/hexane 2:8–3:7). The target molecule **6LP** was obtained as colorless solid (53.6 mg, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.22 (s, 3H), 3.42 (dd, J=6.9, 16.6 Hz, 1H), 3.66 (d, J=8.0 Hz, 1H), 3.76 (d, J=8.8 Hz, 1H), 3.88 (dd, J=5.7, 16.6 Hz, 1H), 4.57 (d, J=8.8 Hz, 1H), 5.09 (d, J=17.2 Hz, 1H), 5.15 (d, J=17.2 Hz, 1H), 5.80 (dddd, J=5.7, 6.9, 10.3, 17.2 Hz, 1H), 6.36 (d, J=16.0 Hz, 1H), 6.45 (dd, J=8.0, 16.0 Hz, 1H), 7.15–7.31 (m, 10H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 23.7, 43.8, 55.5, 64.1, 71.0, 117.2, 126.4, 126.5, 127.6, 127.8, 128.6, 128.8, 128.9, 129.0, 134.1, 134.6, 136.6, 139.0, 157.7; IR (KBr, cm^{-1}) 1054, 1400, 1743, 2922, 3470; MS (EI) m/z 140 (M^+−PhCHCHCHPh); HRMS calcd for $C_7H_{10}NO_2$ (M^+−PhCHCHCHPh): 140.0775, found: 140.0779; $[\alpha]_D^{19}$ +80.5 (c 0.19, $CHCl_3$).

4.3.2. (1″*R*,4*S*,2″*E*)-4-(1″,3″-Diphenylprop-2″-enyl)-3-(2′-propenyl)-4-methyl-oxazolidin-2-one (6MP). Following the procedure for **6LP**, **6MP** was obtained as colorless oil in 69% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.22 (s, 3H), 3.54 (dd, J=6.9, 16.6 Hz, 1H), 3.59 (d, J=8.0 Hz, 1H), 3.78 (d, J=8.8 Hz, 1H), 3.95 (dd, J=5.2, 16.6 Hz, 1H), 4.48 (d, J=8.8 Hz, 1H), 5.08 (d, J=10.3 Hz, 1H), 5.13 (d, J=17.2 Hz, 1H), 5.68–5.79 (dddd, J=5.2, 6.9, 10.3, 17.2 Hz, 1H), 6.41–6.50 (m, 2H), 7.15–7.31 (m, 10H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 24.1, 44.3, 56.2, 63.9, 71.1, 117.0, 126.2, 126.3, 127.7, 127.9, 128.5, 128.7, 128.7, 134.0, 134.2, 136.5, 138.7, 157.5; IR (neat, cm^{-1}): 1056, 1402, 1746, 3027, 3469; MS (EI) m/z 140 (M^+−PhCHCHCHPh); HRMS calcd for $C_7H_{10}NO_2$ (M^+−PhCHCHCHPh): 140.0775, found: 140.0774; $[\alpha]_D^{19}$ −60.9 (c 0.33, $CHCl_3$).

4.3.3. (8*R*,8a*R*)-8a-Methyl-8-phenyl-1,5,8,8a-tetrahydrooxazolo[3,4-*a*]pyridin-3-one (7LP). To a solution of **6LP** (13.3 mg, 0.040 mmol) in CH_2Cl_2 (4.0 mL), first-generation Grubbs' catalyst (1.8 mg, 0.020 mmol) was added. The mixture was refluxed for 1 h. After cooling to room temperature, the solvent was evaporated, and the residue was chromatographed on silica gel (AcOEt/hexane 2:8–3:7). The product was obtained as pale yellow solid (7.3 mg, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.46 (s, 3H), 3.20 (br s, 1H), 3.71 (br d, J=18.9 Hz, 1H), 3.77 (d, J=7.9 Hz, 1H), 3.79 (d, J=7.9 Hz, 1H), 4.31 (br d, J=18.9 Hz, 1H), 5.83–5.91 (m, 2H), 7.00–7.04 (m, 2H), 7.20–7.23 (m, 1H), 7.23–7.28 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 25.4, 39.0, 49.4, 58.3, 71.6, 122.0, 127.2, 127.8, 128.8, 129.1, 138.2, 156.8; IR (KBr, cm^{-1}) 1072, 1416, 1737, 2918, 3450; MS (EI) m/z 229 (M^+); HRMS calcd for $C_{14}H_{15}NO_2$ (M^+): 229.1098, found: 229.1096; $[\alpha]_D^{19}$ −730 (c 0.1, $CHCl_3$). The absolute configuration at C8 position is considered as *R* by analogy with **3eb**.

4.3.4. (8*R*,8a*S*)-8a-Methyl-8-phenyl-1,5,8,8a-tetrahydrooxazolo[3,4-*a*]pyridin-3-one (7MP). Following the procedure for **7LP**, **7MP** was obtained as pale yellow oil in 65% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.05 (s, 3H), 3.69 (m, 1H), 3.64–3.71 (m, 1H), 3.83 (d, J=8.9 Hz, 1H), 4.21–4.29 (m, 1H), 4.40 (d, J=8.9 Hz, 1H), 5.83–5.92 (m, 2H), 7.14–7.18 (m, 2H), 7.27–7.36 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 18.4, 39.1, 47.9, 58.5, 73.0, 123.8, 127.6, 128.3, 128.6, 129.0, 139.1, 157.0; IR (neat, cm^{-1}): 1066, 1409, 1757, 2920, 3400; MS (EI) m/z 229 (M^+); HRMS calcd for $C_{14}H_{15}NO_2$ (M^+): 229.1098, found: 229.1100; $[\alpha]_D^{19}$ +22 (c 0.15, $CHCl_3$). The absolute configuration at C8 position is considered as *R* by analogy with **3eb**.

4.4. Conversion of 3bg and determination of its absolute configuration

4.4.1. *N*-(1-Benzyl-1-methylundecyl)acetamide (8). To a mixture of **3bg** (101.7 mg, 0.496 mmol) and 1-nonene (430 mL, 2.48 mmol) in CH_2Cl_2 (2.5 mL), second generation Grubbs' catalyst (21.2 mg, 0.0248 mmol) was added. The mixture was stirred at 35 °C for 5 h. After cooling to room temperature, the solvent was evaporated, and the residue was passed through short pad silica gel (hexane only to AcOEt/hexane 1:19) to remove the catalyst and 1-nonene derivatives. After the solvent was evaporated, Pd/C (60.0 mg), ammonium formate (1.89 g, 30.0 mmol), and MeOH (5.0 mL) were added to the residue, and the mixture was stirred at 50 °C for 24 h. After filtration, the solvent was evaporated, and the residue was dissolved in CH_2Cl_2 (2.5 mL). To this solution, DMAP (60.5 mg, 0.0496 mmol), Et_3N (280 μL, 0.992 mmol), and Ac_2O (95.0 μL, 0.496 mmol) were added. The mixture was stirred at room temperature for 12 h. After the solvent was evaporated, the residue was purified through silica gel column chromatography (AcOEt/hexane 1:4). Product **8** was obtained in 53% yield (72.3 mg, 0.263 mmol). $[\alpha]_D^{21}$ +8.5 (c 0.5, acetone).

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References and notes

1. (a) Barrett, A. G. M.; Grabowski, G. G. *Chem. Rev.* **1986**, *86*, 751; (b) Ono, N. *The Nitro Group in Organic Synthesis*; Wiley-VCH: Weinheim, NY, 2001; (c) Berner, O. M.; Tedeschi, L.; Enders, D. *Eur. J. Org. Chem.* **2002**, 1877.
2. (a) Seebach, D.; Colvin, E. W.; Lehr, F.; Weller, T. *Helv. Chim. Acta* **1985**, *68*, 1592; (b) Brown, B. R. *The Organic Chemistry*

of Aliphatic Nitrogen Compounds; Oxford University: Oxford, 1994; pp 443–469; (c) Seebach, D.; Colvin, E. W.; Lehr, F.; Weller, T. *Chimia* **1979**, *33*, 1.

3. (a) *The Chemistry of Amino, Nitro and Related Groups*; Patai, S., Ed.; John Wiley & Sons: Chichester, 1996; (b) Rosini, G.; Ballini, R. *Synthesis* **1988**, 833; (c) Coombes, R. G. *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Sutherland, I. O., Eds.; Pergamon: Oxford, 1979; Vol. 2, pp 303–382.
4. (a) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921; (b) Acemoglu, L.; Williams, J. M. J. *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; 2002; Vol. 2, p 1945; (c) Belda, O.; Moberg, C. *Acc. Chem. Res.* **2004**, *37*, 2921; (d) Kazmaier, U. *Curr. Org. Chem.* **2003**, *7*, 317; (e) Trost, B. M. *Chem. Pharm. Bull.* **2002**, *50*, 1.
5. Reviews of catalytic asymmetric reactions: (a) Palomo, C.; Oiarbide, M.; Mielgo, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 5442; (b) Shibasaki, M.; Sasai, H.; Arai, T. *Angew. Chem., Int. Ed.* **1997**, *36*, 1236; (c) Ballini, R.; Bosica, G.; Fiorini, D.; Palmieri, A.; Petrini, M. *Chem. Rev.* **2005**, *105*, 933.
6. (a) Tsuji, J.; Yamakawa, T.; Mandai, T. *Tetrahedron Lett.* **1978**, *19*, 565; (b) Tsuji, J.; Shimizu, I.; Minami, I.; Ohashi, Y.; Sugiura, T.; Takahashi, K. *J. Org. Chem.* **1985**, *50*, 1523; (c) Aleksandrowicz, P.; Piotrowska, H.; Sas, W. *Pol. J. Chem.* **1981**, *55*, 1469; (d) Aleksandrowicz, P.; Piotrowska, H.; Sas, W. *Tetrahedron* **1982**, *38*, 1321; (e) Aleksandrowicz, P.; Piotrowska, H.; Sas, W. *Monatsh. Chem.* **1982**, *113*, 1221; (f) Wade, P. A.; Morrow, S. D.; Hardinger, S. A. *J. Org. Chem.* **1982**, *47*, 365; (g) Ganet, J. P.; Grisoni, S. *Tetrahedron Lett.* **1986**, *27*, 4165; (h) Deardorff, D. R.; Savin, K. A.; Justman, C. J.; Karanjawala, Z. E.; Sheppeck, J. E.; Harger, D. C.; Aydin, N. *J. Org. Chem.* **1996**, *61*, 3616.
7. (a) Rieck, H.; Helmchen, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2687; (b) Trost, B. M.; Surivet, J.-P. *J. Am. Chem. Soc.* **2000**, *122*, 6291; (c) Trost, B. M.; Surivet, J.-P. *Angew. Chem., Int. Ed.* **2000**, *39*, 3122; (d) Nemoto, T.; Jin, L.; Nakamura, H.; Hamada, Y. *Tetrahedron Lett.* **2006**, *47*, 6577.
8. In the absence of external base, the reaction between **1e** and 2-nitropropane (**2b**) using 2 mol % of $Pd(PPh_3)_4$ gave the product **3eb** in 87% yield.
9. (a) von Matt, P.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 566; (b) Sprinz, J.; Helmchen, G. *Tetrahedron Lett.* **1993**, *34*, 1769; (c) Dawson, G. J.; Frost, C. G.; Williams, J. M. J. *Tetrahedron Lett.* **1993**, *34*, 3149.
10. Seebach, D.; Devaquet, E.; Ernst, A.; Hatakawa, M.; Kuehnle, F. N. M.; Schweizer, W. B.; Weber, B. *Helv. Chim. Acta* **1995**, *78*, 1636.
11. (a) Wada, R.; Shibuguchi, T.; Makino, S.; Oisaki, K.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2006**, *128*, 7687; (b) Suto, Y.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2007**, *129*, 500.
12. (a) Hayashi, T.; Yamamoto, A.; Ito, Y.; Nishioka, E.; Miura, H.; Yanagi, K. *J. Am. Chem. Soc.* **1989**, *111*, 6301; (b) Hayashi, T.; Kanehira, K.; Hagihara, T.; Kumada, M. *J. Org. Chem.* **1988**, *53*, 113.
13. (a) Lloyd-Jones, G. C.; Butts, C. P. *Tetrahedron* **1998**, *54*, 901; (b) Froelander, A.; Lutsenko, S.; Privalov, T.; Moberg, C. *J. Org. Chem.* **2005**, *70*, 9882.
14. Satoh, T.; Fukuda, Y. *Tetrahedron* **2003**, *59*, 9803.