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Diastereoselective Synthesis of Tetrahydrofurans by Lewis Acid Catalyzed Intermolecular Carbenoid–Carbonyl Reaction–Cycloaddition Sequences: Unusual Diastereoselectivity of Lewis Acid Catalyzed Cycloadditions

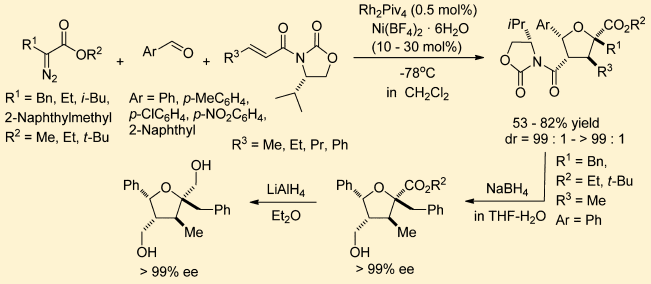
Yuta Hashimoto,[†] Kennosuke Itoh,[†] Akikazu Kakehi,[†] Motoo Shiro,[‡] and Hiroyuki Suga*[,†]

[†]Department of Chemistry and Material Engineering, Faculty of Engineering, Shinshu University, Wakasato, Nagano 380-8553, Japan and

[‡]Rigaku Corporation, 3-9-12 Matsubaracho, Akishima, Tokyo 196-8666, Japan

Supporting Information

ABSTRACT: The effects of including metal salts for three-component reactions involving α-alkyl-α-diazo esters, aromatic aldehydes, and 3-(2-alkenoyl)-2-oxazolidinones are described, in terms of yields and diastereoselectivities. Metal tetrafluoroborates (10−30 mol %) such as $Co(BF_4)_2·6H_2O$, $Ni(BF_4)_2·6H_2O$, and $AgBF_4$ were effective in delivering high yields and diastereoselectivities (93:7 to 99:1) of the corresponding tetrahydrofuran derivatives while suppressing the competitive formation of 1,3-dioxolane. Using (*S*)-3-(2-alkenoyl)-4-isopropyl-2-oxazolidinones as the dipolarophiles in the three-component reactions, in the presence of $Ni(BF_4)_2·6H_2O$ or $Co(ClO_4)_2·6H_2O$ (10−30 mol %), optically active tetrahydrofurans that possess four successive asymmetric centers were synthesized in high diastereoselectivities (99:1). On the basis of the configuration of the cycloadduct using the X-ray analysis, the high diastereoselectivity could be explained by the unusual *Re*-face approach to the dipolarophile in the presence of the Lewis acid, proceeding through the *s-cis* conformer of the 3-(2-alkenoyl)-2-oxazolidinone with the two carbonyls in opposing directions (dipole−dipole interaction).



INTRODUCTION

Recently we have reported that high levels of asymmetric induction could be achieved by employing catalytic amounts of chiral Lewis acids in the cycloaddition reactions of both electron-deficient and -rich dipolarophiles with cyclic carbonyl ylides that are generated from diazo carbonyl compounds via intramolecular carbenoid−carbonyl cyclization reactions.[1] Using this methodology, chiral epoxy-bridged bicyclic compounds containing several asymmetric centers were effectively constructed via a single cycloaddition step. Intramolecular carbenoid−carbonyl cyclization reactions are regarded as one of the most efficient scheme for the generation of carbonyl ylides, favored in terms of entropy, and are applicable over a wide range of dipolarophiles.[2] In contrast, intermolecular carbenoid−carbonyl reactions are limited to dipolarophiles possessing the same carbonyl components used for the carbonyl ylide formation or highly reactive dipolarophiles.[3] Although it is well-known that precursor Rh carbenoid complexes undergo undesirable β-hydride elimination,[4] a recent breakthrough by Fox describes the effective Rh-catalyzed three-component reactions of aldehydes, α-alkyl-α-diazo esters, and dipolarophiles to afford highly functionalized dihydro- and tetrahydrofuran products with high regio- and diastereoselectivities.[5] The problematic β-hydride elimination of the Rh carbenoid complexes was suppressed by employing dirhodium tetrapivalate (Rh_2Piv_4) as the catalyst at −78 °C. Furthermore, the scope of the dipolarophiles was expanded to include reactive olefinic and acetylenic dipolarophiles, albeit limited to terminal olefins and acetylenes, cyclic olefins, and dipolarophiles substituted with two electron-deficient groups. Consequently, we decided to investigate the use of metal salts as the catalytic Lewis acids for the purposes of (i) expanding the range of usable olefinic dipolarophiles, especially for nonterminal olefins of 2-alkenoic acid derivatives, (ii) eliminating the formation of competing dioxolanes, and (iii) improving the stereoselectivities of the reactions. Herein, we report on the three-component reactions of aromatic aldehydes, α-alkyl-α-diazo esters, and 2-alkenoic acid derivatives in the presence of metal salts $Ni(BF_4)_2·6H_2O$ and $Co(BF_4)_2·6H_2O$, which not only selectively promoted the cycloadditions with the olefinic dipolarophiles but also effectively improved the diastereoselectivities. Surprisingly, for the three-component reactions involving (*S*)-3-(2-alkenoyl)-4-isopropyl-2-oxazolidinones as the dipolarophile in the synthesis of chiral tetrahydrofuran derivatives, the use of these salts resulted in an unusual

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Scheme 1. Three-Component Reactions of Ethyl 2-Diazohydrocinnamate (1), Benzaldehyde (2), and Crotonoic Acid Derivatives 3a–d

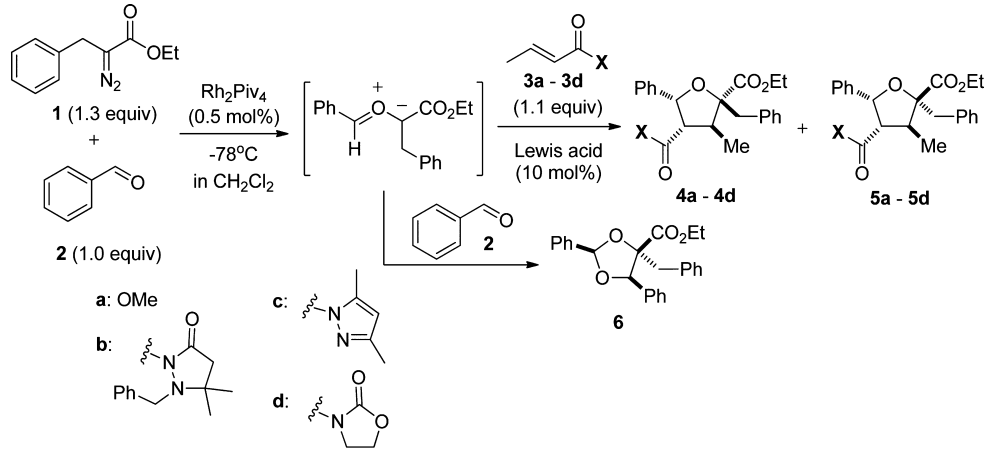

Table 1. Three-Component Reactions of Ethyl 2-Diazohydrocinnamate (1), Benzaldehyde (2), and Crotonoic Acid Derivatives 3a–d[a]

entry	dipolarophile **3**	Lewis acid	yield of **4** + **5** (%)	dr[b] (**4**:**5**)[c]	yield of **6** (%)
1	**3a**	none	5 (**4a** + **5a**)	92:8	20
2	**3a**	$Co(ClO_4)_2·6H_2O$	9 (**4a** + **5a**)	99:1	21
3	**3b**	none	3 (**4b** + **5b**)	44:56	40
4	**3b**	$Co(ClO_4)_2·6H_2O$	8 (**4b** + **5b**)	95:5	40
5	**3c**	none	52 (**4c** + **5c**)	81:19	18
6	**3c**	$Co(ClO_4)_2·6H_2O$	62 (**4c** + **5c**)	81:19	7
7	**3d**	none	79 (**4d** + **5d**)	88:12	4
8	**3d**	$Co(ClO_4)_2·6H_2O$	76 (**4d** + **5d**)	>99:1	2
9	**3d**	$Fe(ClO_4)_2·6H_2O$	69 (**4d** + **5d**)	>99:1	4
10	**3d**	$Ni(ClO_4)_2·6H_2O$	76 (**4d** + **5d**)	96:4	5
11	**3d**	$Zn(ClO_4)_2·6H_2O$	74 (**4d** + **5d**)	99:1	7
12	**3d**	$Cu(ClO_4)_2·6H_2O$	59 (**4d** + **5d**)	99:1	10
13	**3d**	$Co(BF_4)_2·6H_2O$	81 (**4d** + **5d**)	>99:1	2
14	**3d**	$Ni(BF_4)_2·6H_2O$	82 (**4d** + **5d**)	99:1	1
15	**3d**	$AgBF_4$	89 (**4d** + **5d**)	86:4	trace
16	**3d**	$Mg(OTf)_2$	78 (**4d** + **5d**)	74:26	9
17	**3d**	$Cu(OTf)_2$	61 (**4d** + **5d**)	99:1	5
18	**3d**	$Sc(OTf)_3$	57 (**4d** + **5d**)	>99:1	10
19	**3d**	$In(OTf)_3$	67 (**4d** + **5d**)	>99:1	4
20	**3d**	$Gd(OTf)_3$	63 (**4d** + **5d**)	>99:1	10

[a]The reaction was carried out by adding a solution of ethyl 2-diazohydrocinnamate (**1**; 1.3 equiv) and benzaldehyde (**2**; 1.0 equiv) to a solution of Rh_2Piv_4 (0.5 mol %), crotonoic acid derivatives **3a–d** (1.1 equiv), and Lewis acids (10 mol %) in CH_2Cl_2 over a period of 1 h. [b]Diastereomer ratio. [c]Determined by ^1H NMR.

diastereoselective asymmetric induction that was not expected for such Lewis acid catalyzed cycloadditions with bidentate-type dipolarophiles.

RESULTS AND DISCUSSION

Initially, the three-component reactions of ethyl 2-diazohydrocinnamate (**1**), benzaldehyde (**2**), and the four crotonoic acid derivatives **3a–d** were carried out in CH_2Cl_2 at −78 °C in the presence of Rh_2Piv_4 (0.5 mol %) and in the absence of a Lewis acid. In general, a solution of **1** (1.3 equiv) and **2** (1.0 equiv) was added to a solution of olefins **3** (1.1 equiv) and Rh_2Piv_4 over a period of 1 h (Scheme 1 and Table 1, entries 1, 3, 5, and 7). Reactions were also carried out under similar conditions using $Co(ClO_4)_2·6H_2O$ (10 mol %) as the additive (entries 2, 4, 6, and 8). In the cases of methyl crotonate (**3a**) and 2-crotonoyl-3-pyrazolidinone (**3b**), the corresponding tetrahydofurans were obtained in low yields (3–9%) in which 1,3-dioxolane **6** was the main product (yields of 20–40%), either in the presence or absence of $Co(ClO_4)_2·6H_2O$: however, the diastereoselectivities of the tetrahydrofurans were improved by addition of $Co(ClO_4)_2·6H_2O$ (entries 1–4). The reactivities of 1-crotonoyl-3,5-dimethylpyrazole (**3c**) (entries 5 and 6) were higher than those of **3a**,**b**: moreover, the addition of $Co(ClO_4)_2·6H_2O$ suppressed the formation of 1,3-dioxolane **6**, thus increasing the yield of the tetrahydrofuran to 62% while maintaining comparable diastereoselectivity (entry 6). In the case of 3-crotonoyl-2-oxazolidinone (**3d**), the reaction readily afforded the product with a yield of 79% (diastereoselectivity 88:12) without the aid of any Lewis acids (entry 7). In the presence of $Co(ClO_4)_2·6H_2O$, the diastereoselectivity was improved to 99:1[6] (entry 8), albeit without improved yields. To improve both yields and

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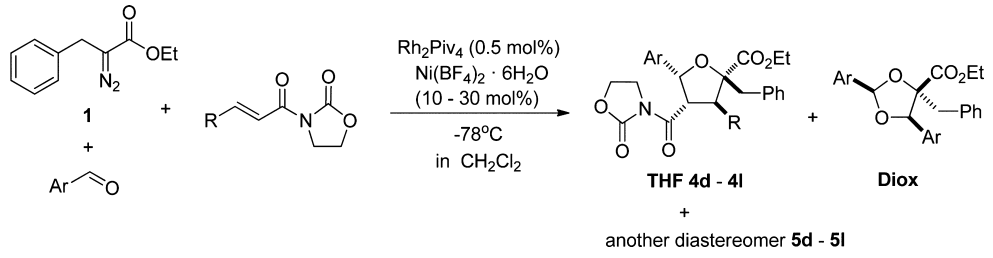
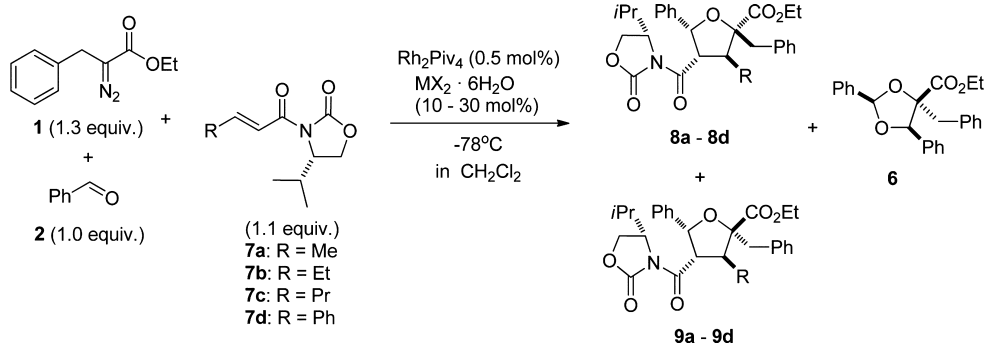
Table 2. Three-Component Reactions of Ethyl 2-Diazohydrocinnamate (1), Aldehydes, and 3-(2-Alkenoyl)-2-oxazolidinones[a]



entry	aldehyde (Ar)	dipolarophile (R)	amt (mol %)	yield of THF (%)	dr[b]	yield of Diox (%)
1	Ph	Me	none	79 (**4d** + **5d**)	88:12	4
2	Ph	Me	10	82 (**4d** + **5d**)	99:1	1
3	Ph	Et	none	53 (**4e** + **5e**)	86:14	4
4	Ph	Et	10	80 (**4e** + **5e**)	99:1	2
5	Ph	Pr	none	58 (**4f** + **5f**)	85:15	6
6	Ph	Pr	20	78 (**4f** + **5f**)	99:1	3
7	Ph	*i*-Pr	none	16 (**4g** + **5g**)	88:12	32
8	Ph	*i*-Pr	30	39 (**4g** + **5g**)	99:1	19
9	Ph	Ph	none	64 (**4h** + **5h**)	67:33	5
10	Ph	Ph	20	62 (**4h** + **5h**)	>99:1	4
11	*p*-MeC_6H_4	Me	none	59 (**4i** + **5i**)	81:19	6
12	*p*-MeC_6H_4	Me	20	84 (**4i** + **5i**)	99:1	3
13	*p*-ClC_6H_4	Me	none	60 (**4j** + **5j**)	88:12	6
14	*p*-ClC_6H_4	Me	10	67 (**4j** + **5j**)	99:1	3
15	*p*-$NO_2C_6H_4$	Me	none	63 (**4k** + **5k**)	74:26	8
16	*p*-$NO_2C_6H_4$	Me	10	65 (**4k** + **5k**)	93:7	6
17	2-naphthyl	Me	none	57 (**4l** + **5l**)	83:17	6
18	2-naphthyl	Me	10[c]	71 (**4l** + **5l**)	99:1	1

[a]The reaction was carried out by adding a solution of ethyl 2-diazohydrocinnamate (**1**; 1.3 equiv) and aldehyde (1.0 equiv) to a solution of Rh_2Piv_4 (0.5 mol %), 3-(2-alkenoyl)-2-oxazolidinone (1.1 equiv), and a Lewis acid (0−10 mol %) in CH_2Cl_2 over a period of 1 h. [b]Diastereomer ratio of THF derivatives determined by ^1H NMR. [c]$Co(ClO_4)_2·6H_2O$ was used.

Scheme 2. Three-Component Reactions of Ethyl 2-Diazohydrocinnamate (1), Benzaldehyde (2), and (*S*)-3-(2-Alkenoyl)-4-isopropyl-2-oxazolidinones 7a−d



diastereoselectivities, several Lewis acids such as perchlorates, tetrafluoroborates, and triflates were evaluated (entries 9−20). The use of the tetrafluoroborates $Co(BF_4)_2·6H_2O$, $Ni(BF_4)_2·6H_2O$, and $AgBF_4$ resulted in yields of 81−89% (entries 13−15). With the exceptions of $AgBF_4$ and $Mg(OTf)_2$, the Lewis acids improved the diasteroselectivities (96:4−99:1). On the basis of these results, the reaction conditions featuring $Ni(BF_4)_2·6H_2O$ (entry 14) as the Lewis acid were chosen for the next step of our investigations.

To investigate the scope of our methodology in terms of aldehydes and olefinic dipolarophiles, the three-component reactions were carried out using several aromatic aldehydes and 3-(2-alkenoyl)-2-oxazolidinones. The yields and diastereoselectivities of the reactions, with or without $Ni(BF_4)_2·6H_2O$, for 3-(2-alkenoyl)-2-oxazolidinones having Et, Pr, *i*-Pr, or Ph as the R substituent are given in Table 2 (entries 3−10). In most cases, the addition of $Ni(BF_4)_2·6H_2O$ (10−30 mol %) improved both the yields and diastereoselectivities of the corresponding tetrahydrofuran cycloadducts (entries 4, 6, 8, and 10), with the sole exception of the modest yield afforded by 3-(4-methyl-2-pentenoyl)-2-oxazolidinone (entry 8). Of note, the addition of $Ni(BF_4)_2·6H_2O$ dramatically improved the diastereoselectivity for the reaction of 3-cinnamoyl-2-oxazoridinone (from 67:33 to >99:1) (entry 9 vs 10). Next, the three-component reaction was carried out, with or without $Ni(BF_4)_2·6H_2O$, using ethyl 2-diazohydrocinnamate (**1**), 3-crotonoyl-2-oxazolidinone (**3d**), and several aromatic aldehydes that possess electron-withdrawing or -releasing groups at the *para* position on the

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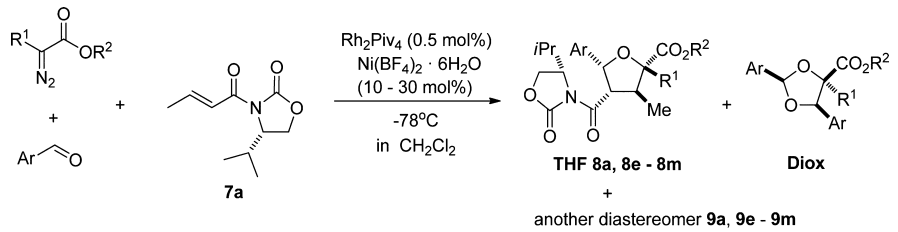
Table 3. Three-Component Reactions of Ethyl 2-Diazohydrocinnamate (1), Benzaldehyde (2), and (*S*)-3-(2-Alkenoyl)-4-isopropyl-2-oxazolidinones 7a–d[a]

entry	dipolarophile 7 (R)	Lewis acid (mol %)	yield of 8 + 9 (%)	dr[b] (8:9)[c]	yield of 6 (%)
1	7a (Me)	none	58 (8a + 9a)	65:35	20
2	7a (Me)	$Co(ClO_4)_2·6H_2O$ (10)	50 (8a + 9a)	>99:1	20
3	7a (Me)	$Co(BF_4)_2·6H_2O$ (10)	51 (8a + 9a)	>99:1	11
4	7a (Me)	$Ni(BF_4)_2·6H_2O$ (10)	80 (8a + 9a)	99:1	3
5	7b (Et)	none	32 (8b + 9b)	86:14	25
6	7b (Et)	$Ni(BF_4)_2·6H_2O$ (30)	61 (8b + 9b)	99:1	6
7	7c (Pr)	none	27 (8c + 9c)	83:17	19
8	7c (Pr)	$Ni(BF_4)_2·6H_2O$ (30)	59 (8c + 9c)	>99:1	6
9	7d (Ph)	none	39 (8d + 9d)	67:33	18
10	7d (Ph)	$Ni(BF_4)_2·6H_2O$ (30)	53 (8d + 9d)	>99:1	7

[a]The reaction was carried out by adding a solution of ethyl 2-diazohydrocinnamate (1; 1.3 equiv) and benzaldehyde (2; 1.0 equiv) to a solution of Rh_2Piv_4 (0.5 mol %), 3-(2-alkenoyl)-4-isopropyl-2-oxazolidinones 7a–d (1.1 equiv), and Lewis acids (0–30 mol %) in CH_2Cl_2 over a period of 1 h. [b]Diastereomer ratio. [c]Determined by ^1H NMR.

Table 4. Three-Component Reactions of α-Diazo Esters, Aldehydes, and (*S*)-3-Crotonoyl-4-isopropyl-2-oxazolidinone (7a)[a]



entry	diazo ester (R^1, R^2)	aldehyde (Ar)	amt (mol %)	yield of THF (%)	dr[b]	yield of Diox (%)
1	Bn, Et	Ph	none	58 (8a + 9a)	65:35	20
2	Bn, Et	Ph	10	80 (8a + 9a)	99:1	3
3	Et, Et	Ph	none	60 (8e + 9e)	68:32	10
4	Et, Et	Ph	10	75 (8e + 9e)	99:1	1
5	*i*-Bu, Et	Ph	none	62 (8f + 9f)	72:28	12
6	*i*-Bu, Et	Ph	10	82 (8f + 9f)	>99:1	1
7	1-NAPCH$_2$,[c] Et	Ph	none	52 (8g + 9g)	69:31	13
8	1-NAPCH$_2$,[c] Et	Ph	10	79 (8g + 9g)	>99:1	1
9	Bn, Et	*p*-MeC_6H_4	none	41 (8h + 9h)	79:21	17
10	Bn, Et	*p*-MeC_6H_4	30	70 (8h + 9h)	99:1	2
11	Bn, Et	*p*-ClC_6H_4	none	42 (8i + 9i)	78:22	18
12	Bn, Et	*p*-ClC_6H_4	30	67 (8i + 9i)	99:1	1
13	Bn, Et	*p*-$NO_2C_6H_4$	none	39 (8j + 9j)	80:20	15
14	Bn, Et	*p*-$NO_2C_6H_4$	30	68 (8j + 9j)	99:1	1
15	Bn, Et	2-naphthyl	none	48 (8k + 9k)	84:16	6
16	Bn, Et	2-naphthyl	20[d]	71 (8k + 9k)	>99:1	2
17	Bn, Me	Ph	none	60 (8l + 9l)	63:27	15
18	Bn, Me	Ph	10	78 (8l + 9l)	99:1	2
19	Bn, *t*-Bu	Ph	none	45 (8m + 9m)	>99:1	24
20	Bn, *t*-Bu	Ph	10	73 (8m + 9m)	>99:1	9

[a]The reaction was carried out by adding a solution of α-diazo ester (1.3 equiv) and aldehyde (1.0 equiv) to a solution of Rh_2Piv_4 (0.5 mol %), 3-crotonoyl-2-oxazolidinone (1.1 equiv), and a Lewis acid (0–30 mol %) in CH_2Cl_2 over a period of 1 h. [b]Diastereomer ratio of THF derivatives determined by ^1H NMR. [c]1-Naphthylmethyl. [d]$Co(ClO_4)_2·6H_2O$ was used.

benzene ring (entries 11–18). Similarly, in all cases, the addition of $Ni(BF_4)_2·6H_2O$ (10–20 mol %) resulted in higher yields and diastereoselectivities ((93:7)–(99:1)) (entries 12, 14, 16, and 18).

Encouraged by the dramatic effects of the metal tetrafluorobarates on the three-component reactions, we next turned our attention to the synthesis of optically active teterahydrofuran derivatives using the diastereoselective synthesis starting with chiral oxazolidinones. First, as shown in Scheme 2, a three-component reaction involving ethyl 2-diazohydrocinnamate (1), benzaldehyde (2), and (*S*)-3-crotonoyl-4-isopropyl-2-oxazolidinone (7a) was carried out in the absence of a Lewis acid (Table 3, entry 1), under conditions similar to those previously described for 3-crotonoyl-2-oxazolidinone (3d). Although there are eight possible diastereomers of the corresponding tetrahydrofuran, the reaction afforded only two diastereomers (with a ratio of 65:35 and a combined yield of 58%), along with 1,3-dioxolane 6 (20% yield). Next, the effect of additives on this three-component reaction was investigated using three metal salts (10 mol %). Again, the addition of

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$Ni(BF_4)_2·6H_2O$ was favorable, in terms of both diastereoselectivity (99:1) and yield (80%), by suppressing the formation of 1,3-dioxolane **6** (3% yield) (entry 4). In contrast, the addition of $Co(ClO_4)_2·6H_2O$ or $Co(BF_4)_2·6H_2O$ resulted in lower yields, albeit with higher diastereoselectivities (>99:1) (entries 2 and 3).

Consequently, the reactions of (*S*)-3-(2-alkenoyl)-4-isopropyl-2-oxazolidinones **7b–d** (R = Et, Pr, Ph) were investigated using $Ni(BF_4)_2·6H_2O$ as the catalyst (entries 5–10). Although the reactions required a greater amount of $Ni(BF_4)_2·6H_2O$ (30 mol %) to afford moderate yields (53–61%), the presence of the metal salt significantly improved the diastereoselectivities ((99:1)–(>99:1)) (entries 6, 8, and 10). It is important to note that optically active tetrahydrofuran derivatives that possess four successive asymmetric centers can be readily and selectively prepared via this one-pot reaction.

We next investigated the applicability of our procedure to aldehydes and diazo substrates that correspond to the Ar and R^1 substituents on the tetrahydrofuran ring (Table 4). Several ethyl α-alkyl-α-diazo esters readily underwent the three-component reaction involving benzaldehyde (**2**) and (*S*)-3-crotonoyl-4-isopropyl-2-oxazolidinone (**7a**), in the presence of $Ni(BF_4)_2·6H_2O$ (10 mol %), to give the products in good yields (75–82%) and high diastereoselectivities ((99:1)–(>99:1)) (entries 4, 6, and 8). Several aromatic aldehydes were also effective in affording high diastereoselectivities ((99:1)–(>99:1)) for the reactions of 2-diazohydrocinnamate (**1**) and (*S*)-3-crotonoyl-4-isopropyl-2-oxazolidinone (**7a**): the reactions, however, required somewhat higher catalyst loadings (20–30 mol %) of $Ni(BF_4)_2·6H_2O$ or $Co(ClO_4)_2·6H_2O$ to afford moderate yields (67–71%) (entries 10, 12, 14, and 16). For the 2-diazohydrocinnamates, our results indicate that large R^2 substituents such as *t*-Bu can afford high diastereoselectivities, even in the absence of Lewis acids (entry 19). Nonetheless, the inclusion of $Ni(BF_4)_2·6H_2O$ (10 mol %) was rather effective in affording a good yield (73%).

In the case of the three-component reaction involving *tert*-butyl 2-diazohydrocinnamate, benzaldehyde (**2**), and (*S*)-3-crotonoyl-4-isopropyl-2-oxazolidinone (**7a**), the absolute stereochemistry of the major diastereomer product (recystallized from hexane) was determined using X-ray crystal analysis (see the Supporting Information). As shown in Figure 1, cyclo-

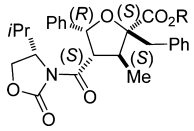
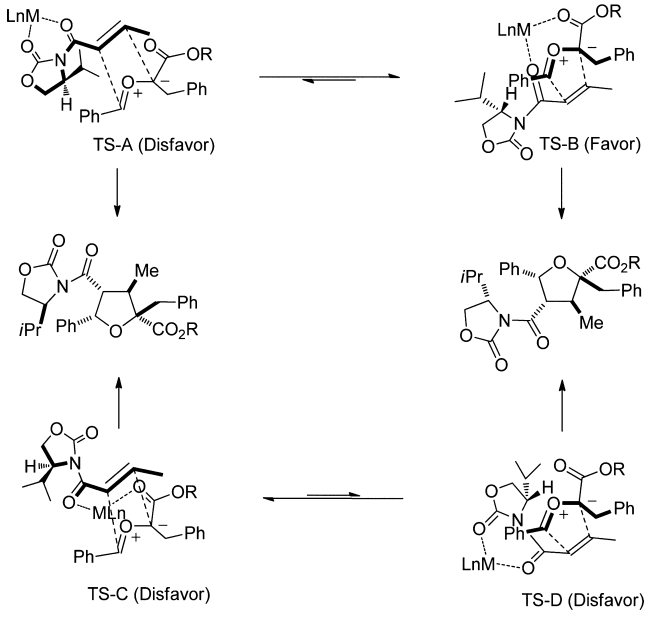


Figure 1. Absolute configuration of cycloadduct **8m**.

adduct **8m** possesses a 2*S*,3*S*,4*S*,5*R* configuration on its tetrahydrofuran ring. Similarly, the diol derivative of cycloadduct **8a**, which is the major product for the reaction involving ethyl 2-diazohydrocinnamate (**1**), was also shown to possess the same configuration (Scheme 6). Although the high diastereoselectivities of these reactions are typically attributed to the chelate complex of the *s-cis* conformer of 2-oxazolidinone **7a** with $Ni(BF_4)_2$ allowing the *Si*-face approach of the carbonyl ylide to the dipolarophile with *endo* orientation via strong LUMO activation[7] (Scheme 3, TS-A), the above absolute configuration of the cycloadducts did not allow this explanation. The stereochemistry of the tetrahydrofuran ring of minor cycloadduct **9a** (Table 4, entry 1; in the absence of

Scheme 3. Proposed Mechanism for High Diastereoselectivity



Lewis acid) was determined as having the 2*R*,3*S*,4*S*,5*R* configuration using differential NOE spectra (Figure 2) of the

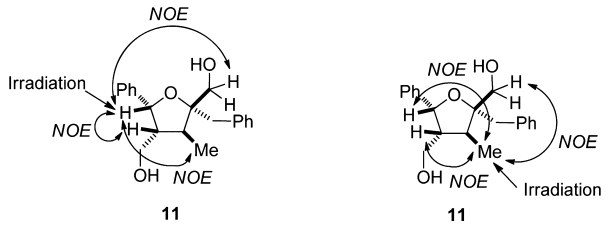


Figure 2. NOEs observed by differential NOE spectra.

corresponding isolable diol **11** that was obtained via $LiAlH_4$ reduction (Scheme 4). This configuration suggests that the addition of $Ni(BF_4)_2·6H_2O$ favors the formation of conformer A between the two carbonyl ylide conformers proposed by Fox[5] (Scheme 5). To clarify the relative configuration of four possible cycloadducts obtained from either conformer A or B by *endo* or *exo* approaches, the expected transition states are shown in Scheme 5. From the stereochemistry determined for cycloadducts **8a** and **9a**, it is suggested that the continuous *Re*-face selection of (*S*)-crotonoyl-4-isopropyl-2-oxazolidinone by the *endo* approach exclusively occurred both with and without $Ni(BF_4)_2·6H_2O$ after formation of the conformer A. Selective formation of the conformer A and activation of the reaction by $Ni(BF_4)_2·6H_2O$ seems to favor the reaction through TS-B in the transition state (Scheme 3). Similar transition states were proposed for *N*-metalated azomethine ylides in the diastereoselective and enantioselective cycloaddition reactions with electron-deficient olefinic dipolarophiles.[8] Furthermore, recently the similar highly diastereoselective *Re*-face selection of the *s-cis* conformer for (*S*)-(2-alkenoyl)-4-phenyl-2-oxazolidinones by dipole–dipole interactions in the cycloaddition reactions of nitrile ylides in the absence of a Lewis acid were reported by Sibi,[9] although there have been only a few scattered examples of moderate to good selectivity using the chiral oxazolidinone auxiliaries without Lewis acids. Although **8a**,**m**

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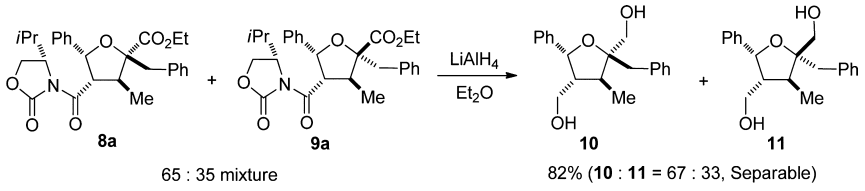
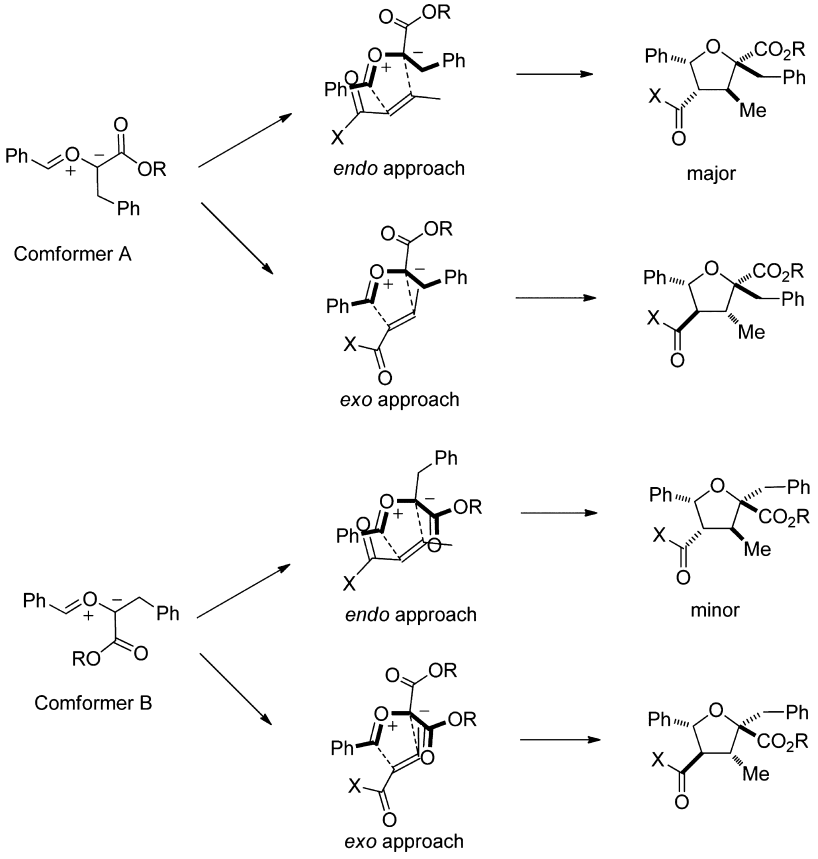
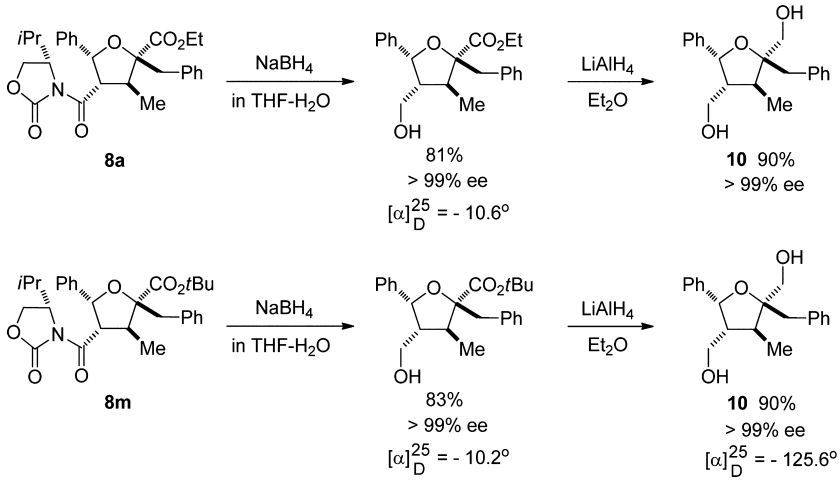
Scheme 4. Reduction of Tetrahydrofurans with $LiAlH_4$



Scheme 5. Proposed Transition States for Conformers A and B



Scheme 6. Selective Reduction of Chiral Tetrahydrofuran Derivatives



could be produced by *Re*-face selection of the *s-trans* conformation of (*S*)-crotonoyl-4-isopropyl-2-oxazolidinone chelated with $Ni(BF_4)_2$ as shown in TS-D (Scheme 3), it is not likely to occur because of a steric interaction between the olefin and the chiral substituent of the auxiliary. In the NMR studies of (*S*)-crotonoyl-4-isopropyl-2-oxazolidinone in the

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presence of Et_2AlCl, chelated and nonchelated conformers both having an *s-cis* conformation similar to TS-A and TS-B (Scheme 3), respectively, were observed, and the preferred conformer depended on the amount of the Lewis acid.[10] Therefore, the configuration of **8a** can be explained as the *Re*-face approach to the dipolarophile, which proceeds through an *s-cis* conformer of oxazolidinone **7a**, with the two carbonyls in directions opposite to each other (dipole−dipole interaction). Accordingly, the high diastereoselectivity of the three-component reaction can be attributed to the coordination of the Lewis acid to both the ester carbonyl of the ylide and the carbonyl of an alkenoyl group in the dipolarophile (Scheme 3, TS-B).

To expand the applicability of these chiral tetrahydrofurans within organic syntheses, selective conversions of several functional groups were undertaken (Scheme 6). Chiral tetrahydrofuran **8a** and its *t*-Bu ester analogue **8m** were readily converted to the monoalcohols by the selective reduction of the oxazolidinone moiety using $NaBH_4$ in $THF-H_2O$ in high yields. Subsequent and successive reductions of the ester moieties of the monoalcohols were achieved using $LiAlH_4$ in high yield to give the enantiomerically pure diol **10** (>99% ee, confirmed using chiral HPLC analysis).

CONCLUSIONS

Our investigations of the three-component reactions of ethyl 2-diazohydrocinnamate (**1**), aromatic aldehydes, and 3-(2-alkenoyl)-2-oxazolidinones have demonstrated that the addition of metal tetrafluoroborates such as $Co(BF_4)_2{\cdot}6H_2O$, $Ni(BF_4)_2{\cdot}6H_2O$, and $AgBF_4$ was highly effective in improving the yields of the desired tetrahydrofuran derivatives while suppressing the competitive formation of 1,3-dioxolane. Remarkably, the addition of $Ni(BF_4)_2{\cdot}6H_2O$ resulted in high diastereoselectivities ((93:7)−(>99:1)). For the three-component reactions of α-alkyl-α-diazo esters, aromatic aldehydes, and (*S*)-3-crotonoyl-4-isopropyl-2-oxazolidinone (**7a**) with $Ni(BF_4)_2{\cdot}6H_2O$ or $Co(ClO_4)_2{\cdot}6H_2O$ as a catalyst, several chiral terahydrofurans that possess four successive asymmetric centers along with the corresponding chiral oxazolidinone auxiliaries were successfully synthesized, with extremely high diastereoselectivities ((99:1)−(>99:1)). For the three-component reactions of *tert*-butyl 2-diazohydrocinnamate, benzaldehyde (**2**), and (*S*)-3-crotonoyl-4-isopropyl-2-oxazolidinone (**7a**), X-ray crystal analysis of the product revealed unexpected configurations, suggesting highly diastereoselective asymmetric induction behavior of the metal salts. The mechanism for the high diastereoselectivity can be attributed to the *Re*-face approach to the dipolarophile proceeding through an *s-cis* conformer of oxazolidinone **7a** with the two carbonyls in opposing directions (dipole−dipole interaction). Moreover, the coordination of $Ni(BF_4)_2$ to both the ester carbonyl of the carbonyl ylide and the carbonyl of an alkenoyl group in the dipolarophile during the transition state (TS-B) would favor the selective formation of a stable conformer of the carbonyl ylide.

EXPERIMENTAL SECTION

General Methods. Melting points were determined on a melting point apparatus and are uncorrected. IR spectra were taken with a FT/IR spectrophotometer. ^1H NMR spectra were recorded on 300, 400, and 500 MHz spectrometers. Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded on 75, 100, and 125 MHz spectrometers using broad-band proton decoupling. Chemical shifts are expressed in parts per million using the middle resonance of $CDCl_3$ (77.0 ppm) as an internal standard. Hydrogen multiplicity (C, CH, CH_2, CH_3) information was obtained from carbon DEPT spectra. For preparative column chromatography, Wakogel C-300HG was employed. All reactions were carried out under an argon atmosphere in dried glassware.

Materials. Methyl crotonate (**3a**) and aromatic aldehydes are commercially available and were used without further purification. 3-Crotonoyl-2-oxazolidinone (**3b**),[11] 1-crotonoyl-3,5-dimethylpyrazole (**3c**),[12] 1-benzyl-2-crotonoyl-5,5-dimethyl-3-pyrazolidinone (**3d**),[13] 3-[(*E*)-2-pentenoyl]-2-oxazolidinone,[14] 3-[(*E*)-2-hexenoyl]-2-oxazolidinone,[11] 3-[(*E*)-4-methyl-2-pentenoyl]-2-oxazolidinone,[11] 3-cinnamoyl-2-oxazolidinone,[15] (*S*)-3-crotonoyl-4-isopropyl-2-oxazolidinone (**7a**),[16] (*S*)-4-isopropyl-3-[(*E*)-2-pentenoyl]-2-oxazolidinone (**7b**),[17] and (*S*)-3-cinnamoyl-4-isopropyl-2-oxazolidinone (**7d**)[16] were prepared by the procedure reported in the literature. Dirhodium tetrapivalate (Rh_2Piv_4) was prepared by the method reported in the literature.[18] Ethyl 2-diazohydrocinnamate (**1**), ethyl 2-diazopropanoate, ethyl 2-diazobutanoate, ethyl 2-diazo-4-methylpentanoate, and ethyl 2-diazo-3-(1-naphthyl)propanoate were prepared from the corresponding β-keto esters according to literature protocols.[19,4a−d,5] Powdered 4 Å molecular sieves (MS 4 Å) are commercially available (Aldrich) and were dried in vacuo at 200 °C for 12 h before use. $Ni(ClO_4)_2{\cdot}6H_2O$, $Ni(BF_4)_2{\cdot}6H_2O$, $Co(ClO_4)_2{\cdot}6H_2O$, $Co(BF_4)_2{\cdot}6H_2O$ and other metal salts are commercially available and were used without further purification. CH_2Cl_2 was purified by distillation first from $CaCl_2$ and then CaH_2 under argon before use.

General Procedure for the Ni(II)-Catalyzed Reaction Exemplified by the Reaction of Ethyl 2-Diazohydrocinnamate (1), Benzaldehyde (2), and 3-Crotonoyl-2-oxazolidinone (3d). To a solution of 3-crotonoyl-2-oxazolidinone (68.3 mg, 0.44 mmol), Rh_2Piv_4 (1.2 mg, 2.6×10^{-4} mmol), $Ni(BF_4)_2{\cdot}6H_2O$ (13.6 mg, 0.040 mmol), and MS 4 Å (500 mg) in CH_2Cl_2 (4 mL) at −78 °C (dry ice/acetone bath) was added a solution of ethyl 2-diazohydrocinnamate (106.2 mg, 0.52 mmol) and benzaldehyde (41 μL, 0.40 mmol) in CH_2Cl_2 (5 mL) over a period of 1 h using a syringe pump. The syringe was washed with CH_2Cl_2 (1 mL), and then the stirring was continued for 10 min at −78 °C. After the mixture was warmed to room temperature, it was filtered through Celite (1 cm) and a plug of silica gel (3 cm) with AcOEt/hexane (1/1, 80 mL) as an eluent. The solvent was removed in vacuo, and the residue was purified by column chromatography ((9/10)−(8/2), hexane/AcOEt) to provide 143.5 mg (82%) of **4d** and **5d** along with 0.8 mg (1%) of 1,3-dioxolane **6**. The **4d**:**5d** ratio was determined to be 99:1 by ^1H NMR analysis (400 MHz). Cycloadduct **4d** (124.2 mg, 71%) could be separated from the mixture of **4d** and **5d** by careful column chromatography (95/5, hexane/AcOEt).

Cycloadducts **4e** and **5e** (144.5 mg, 80%, **4e**:**5e** = 99:1) were synthesized according to the general procedure. Cycloadduct **4e** (130.6 mg, 72%) could be separated from the mixture of **4e** and **5e** by careful column chromatography.

Cycloadducts **4f** and **5f** (145.2 mg, 78%, **4f**:**5f** = 99:1) were synthesized according to the general procedure. Cycloadduct **4f** (124.6 mg, 67%) could be separated from the mixture of **4f** and **5f** by careful column chromatography.

Cycloadducts **4g** and **5g** (72.6 mg, 39%, **4g**:**5g** = 99:1) were synthesized according to the general procedure. Cycloadduct **4g** (31.0 mg, 17%) could be separated from the mixture of **4g** and **5g** by careful column chromatography.

Cycloadduct **4h** (124.0 mg, 62%, **4h**:**5h** = >99:1) was synthesized according to the general procedure.

Cycloadducts **4i** and **5i** (151.6 mg, 84%, **4i**:**5i** = 99:1) were synthesized according to the general procedure. Cycloadduct **4i** (142.6 mg, 79%) could be separated from the mixture of **4i** and **5i** by careful column chromatography.

Cycloadducts **4j** and **5j** (126.6 mg, 67%, **4j**:**5j** = 99:1) were synthesized according to the general procedure. Cycloadduct **4j** (110.5 mg, 58%) could be separated from the mixture of **4j** and **5j** by careful column chromatography.

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Cycloadducts **4k** and **5k** (125.6 mg, 65%, **4k**:**5k** = 93: 7) were synthesized according to the general procedure. Cycloadduct **4k** (109.1 mg, 56%) could be separated from the mixture of **4k** and **5k** by careful column chromatography.

Cycloadducts **4l** and **5l** (138.7 mg, 71%, **4l**:**5l** = 99:1) were synthesized according to the general procedure. Cycloadduct **4l** (124.6 mg, 64%) could be separated from the mixture of **4l** and **5l** by careful column chromatography.

(2S,3S*,4S*,5R*)-Ethyl 2-benzyl-3-methyl-4-(2-oxo-3-oxazolidinylcarbonyl)-5-phenyltetrahydrofuran-2-carboxylate (**4d**):* colorless needles; mp 129−131 °C (benzene); IR (KBr) 2980, 2917, 1774, 1725, 1703, 1387, 1280, 1218, 746, 704 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.24 (3H, t, J = 7.1 Hz), 1.29 (3H, d, J = 6.8 Hz), 2.97 (1H, d, J = 13.9 Hz), 3.02 (1H, dq, J = 10.9, 6.8 Hz), 3.24−3.32 (2H, m), 3.70 (1H, ddd, J = 7.2, 9.4, 16.6 Hz), 3.94 (1H, dt, J = 7.2, 9.4 Hz), 4.14−4.25 (3H, m), 4.41 (1H, dd, J = 9.8, 10.9 Hz), 5.68 (1H, d, J = 9.8 Hz), 7.14−7.19 (1H, m), 7.21−7.29 (7H, m), 7.34−7.36 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5 (CH_3), 14.2 (CH_3), 36.9 (CH_2), 42.4 (CH_2), 43.0 (CH), 56.6 (CH), 61.2 (CH_2), 62.1 (CH_2), 79.6 (CH), 88.3 (C), 126.4 (CH), 127.1 (CH), 127.8 (CH), 128.0 (CH), 128.2 (CH), 130.0 (CH), 135.6 (C), 138.6(C), 153.0 (C), 169.4 (C), 171.7 (C); MS (EI) m/z 437 (M^+), 364, 346, 291, 273, 202, 184, 146, 131, 91, 77, 57, 43, 29; HRMS (EI) calcd for $C_{25}H_{27}NO_6$ (M^+) 437.1838, found 437.1811. Anal. Calcd for $C_{25}H_{27}NO_6$: C, 68.63; H, 6.22; N, 3.20. Found: C, 68.91; H, 6.0; N, 3.09.

(2R,3S*,4S*,5R*)-Ethyl 2-benzyl-3-methyl-4-(2-oxo-3-oxazolidinylcarbonyl)-5-phenyltetrahydrofuran-2-carboxylate (**5d**):* although **5d** could not be separated by chromatography from a mixture with major **4d** and dipolarophile **3a**, it could be characterized by ^1H NMR; ^1H NMR (400 MHz, $CDCl_3$) δ 1.11 (3H, d, J = 6.8 Hz), 1.32 (3H, t, J = 7.1 Hz), 2.90 (1H, dq, J = 6.8, 11.1 Hz), 3.25 (1H, d, J = 14.2 Hz), 3.42 (1H, d, J = 14.2 Hz), 3.04 (1H, m), 3.63 (1H, ddd, J = 7.2, 9.4, 10.8 Hz), 3.86 (1H, dt, J = 7.2, 9.0 Hz), 4.12−4.33 (3H, m), 4.32 (1H, dd, J = 10.0, 11.1 Hz), 5.81 (1H, d, J = 10.0 Hz), 6.90−6.93 (2H, m), 7.13−7.37 (8H, m).

(2S,3S*,4S*,5R*)-Ethyl 2-benzyl-3-ethyl-4-(2-oxo-3-oxazolidinylcarbonyl)-5-phenyltetrahydrofuran-2-carboxylate (**4e**):* colorless needles; mp 155−157 °C (benzene); IR (KBr) 2972, 2933, 1767, 1726, 1703, 1387, 1274, 740, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.92 (3H, t, J = 7.4 Hz), 1.24 (3H, t, J = 7.1 Hz), 1.55 (1H, m), 2.02 (1H, m), 2.95 (1H, ddd, J = 6.6, 9.8, 10.9 Hz), 3.02 (1H, d, J = 13.9 Hz), 3.23 (1H, m), 3.28 (1H, d, J = 13.9 Hz), 3.67 (1H, ddd, J = 7.0, 9.4, 10.9 Hz), 3.87 (1H, m), 4.11−4.25 (3H, m), 4.58 (1H, t, J = 9.8 Hz), 5.63 (1H, d, J = 9.8 Hz), 7.13−7.36 (8H, m), 7.38−7.51 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.3 (CH_3), 14.2 (CH_3), 22.8 (CH_2), 36.7 (CH_2), 42.5 (CH_2), 50.1 (CH), 55.0 (CH), 61.2 (CH_2), 61.9 (CH_2), 80.0 (CH), 88.4 (C), 126.3 (CH), 127.3 (CH), 127.7 (CH), 127.9 (CH), 128.1 (CH), 130.1 (CH), 135.8 (C), 138.1 (C), 153.0 (C), 170.3 (C), 171.9 (C); MS (EI) m/z 451 (M^+), 379, 361, 291, 273, 264, 217, 199, 171, 131, 91, 77, 57, 43, 29, 15. Anal. Calcd for $C_{26}H_{29}NO_6$: C, 69.16; H, 6.47; N, 3.10. Found: C, 68.99; H, 6.37; N, 3.39.

(2R,3S*,4S*,5R*)-Ethyl 2-benzyl-3-ethyl-4-(2-oxo-3-oxazolidinylcarbonyl)-5-phenyltetrahydrofuran-2-carboxylate (**5e**):* although **5e** could not be separated by chromatography from a mixture with major **4e** and 3-(2-pentenoyl)-2-oxazolidinone, it could be characterized by ^1H NMR; ^1H NMR (400 MHz, $CDCl_3$) δ 0.95 (3H, t, J = 7.3 Hz), 1.30 (3H, t, J = 7.1 Hz), 1.55 (1H, m), 1.74 (1H, m), 2.85 (1H, ddd, J = 6.4, 9.8, 10.5 Hz), 3.04 (1H, m), 3.30 (1H, d, J = 14.4 Hz), 3.47 (1H, d, J = 14.4 Hz), 3.61 (1H, m), 3.80 (1H, m), 4.07−4.27 (3H, m), 4.50 (1H, t, J = 9.8 Hz), 5.81 (1H, d, J = 9.8 Hz), 7.01−7.04 (2H, m), 7.13−7.31 (8H, m).

(2S,3S*,4S*,5R*)-Ethyl 2-benzyl-4-(2-oxo-3-oxazolidinylcarbonyl)-5-phenyl-3-propyltetrahydrofuran-2-carboxylate (**4f**):* colorless needles; mp 162−164 °C (benzene); IR (KBr) 2929, 1771, 1721, 1702, 1384, 1219, 760, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.95 (3H, t, J = 7.3 Hz, Me), 1.24 (3H, t, J = 7.1 Hz), 1.15−1.35 (2H, m), 1.50 (1H, m),1.92 (1H, m), 2.94 (1H, ddd, J = 6.7, 9.7, 10.9 Hz), 3.02 (1H, d, J = 14.0 Hz), 3.29 (1H, d, J = 14.0 Hz), 3.31 (1H, m), 3.67 (1H, ddd, J = 7.0, 9.3, 10.9 Hz), 3.86 (1H, m), 4.11−4.25 (3H, m), 4.57 (1H, t, J = 9.7 Hz), 5.63 (1H, d, J = 9.7 Hz), 7.13−7.31 (8H, m), 7.37−7.40 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2 (CH_3), 14.4 (CH_3), 21.9 (CH_2), 32.1 (CH_2), 36.5 (CH_2), 42.4 (CH_2), 48.3 (CH), 55.3 (CH), 61.2 (CH_2), 61.9 (CH_2), 80.0 (CH), 88.4 (C), 126.3 (CH), 127.3 (CH), 127.7 (CH), 127.9 (CH), 128.1 (CH), 130.0 (CH), 135.7 (C), 138.0 (C), 153.0 (C), 170.3 (C), 171.8 (C); MS (EI) m/z 465 (M^+), 393, 374, 306, 287, 241, 213, 185, 157, 131, 105, 91, 77, 57, 43, 29, 15. Anal. Calcd for $C_{27}H_{31}NO_6$: C, 69.66; H, 6.71; N, 3.01. Found: C, 69.82; H, 6.83; N, 3.17.

(2R,3S*,4S*,5R*)-Ethyl 2-benzyl-4-(2-oxo-3-oxazolidinylcarbonyl)-5-phenyl-3-propyltetrahydrofuran-2-carboxylate (**5f**):* although **5f** could not be separated by chromatography from a mixture with major **4f** and 3-(2-hexenoyl)-2-oxazolidinone, it could be characterized by ^1H NMR; ^1H NMR (400 MHz, $CDCl_3$) δ 0.95 (3H, t, J = 7.3 Hz), 1.30 (3H, t, J = 7.1 Hz), 1.51 (1H, m), 1.63 (1H, m), 1.70 (1H, m), 1.92 (1H, m), 2.84 (1H, ddd, J = 6.6, 9.8, 10.5 Hz), 3.11 (1H, dt, J = 5.1, 9.5 Hz), 3.29 (1H, d, J = 14.2 Hz), 3.46 (1H, d, J = 14.2 Hz), 3.61 (1H, ddd, J = 7.1, 9.5, 11.0 Hz), 3.81 (1H, m), 4.10−4.27 (3H, m), 4.50 (1H, t, J = 9.8 Hz), 5.83 (1H, d, J = 9.8 Hz), 7.00−7.02 (2H, m), 7.13−7.36 (8H, m).

(2S,3S*,4S*,5R*)-Ethyl 2-benzyl-3-isopropyl-4-(2-oxo-3-oxazolidinylcarbonyl)-5-phenyltetrahydrofuran-2-carboxylate (**4g**):* colorless needles; mp 155−158 °C (benzene); IR (KBr) 2964, 2922, 1774, 1733, 1700, 1390, 1217, 748, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.91 (3H, d, J = 6.8 Hz), 1.09 (3H, d, J = 6.8 Hz), 1.28 (3H, t, J = 7.1 Hz), 2.10 (1H, m), 2.92 (1H, ddd, J = 6.9, 9.4, 10.9 Hz), 3.06 (1H, d, J = 14.2 Hz), 3.28 (1H, dd, J = 8.4, 9.8 Hz), 3.40 (1H, d, J = 14.2 Hz), 3.67 (1H, ddd, J = 6.9, 9.4, 10.9 Hz), 3.87 (1H, dt, J = 6.9, 9.4 Hz), 4.10−4.28 (3H, m), 4.77 (1H, t, J = 9.8 Hz), 5.58 (1H, d, J = 9.8 Hz), 7.15 (1H, m), 7.19−7.32 (7H, m), 7.42−7.44 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0 (CH_3), 22.36 (CH_3), 22.41 (CH_3), 36.0 (CH_2), 36.0 (CH_2), 42.5 (CH), 53.4 (CH), 55.6 (CH), 61.3 (CH_2), 61.9 (CH_2), 80.3 (CH), 88.5 (C), 126.4 (CH), 127.7 (CH), 127.9 (CH), 128.0 (CH), 128.3 (CH), 130.7 (CH), 136.2 (C), 138.5 (C), 153.3 (C), 171.1 (C), 172.6 (C); MS (EI) m/z 465 (M^+), 392, 374, 306, 287, 241, 213, 185, 171, 157, 131, 115, 91, 77, 71, 43, 29, 15; HRMS (EI) calcd for $C_{27}H_{31}NO_6$: 465.2151, found 465.2148.

(2R,3S*,4S*,5R*)-Ethyl 2-benzyl-3-isopropyl-4-(2-oxo-3-oxazolidinylcarbonyl)-5-phenyltetrahydrofuran-2-carboxylate (**5g**):* although **5g** could not be separated by chromatography from a mixture with major **4g** and 3-(4-methyl-2-pentenoyl)-2-oxazolidinone, it could be characterized by ^1H NMR; ^1H NMR (500 MHz, $CDCl_3$) δ 0.87 (3H, d, J = 7.0 Hz), 0.92 (3H, d, J = 7.0 Hz), 0.99 (3H, t, J = 7.1 Hz), 1.98 (1H, m), 2.99 (1H, ddd, J = 6.3, 9.4, 10.4 Hz), 3.10 (1H, dd, J = 8.0, 11.0 Hz), 3.32 (1H, d, J = 13.9 Hz), 3.48 (1H, d, J = 13.9 Hz), 3.63 (1H, m), 3.79 (1H, m), 4.11−4.30 (3H, m), 4.68 (1H, dd, J = 9.8, 11.0 Hz), 5.68 (1H, d, J = 9.8 Hz), 6.97−7.02 (2H, m), 7.15−7.31 (8H, m).

(2S,3S*,4S*,5R*)-Ethyl 2-benzyl-3,5-diphenyl-4-(2-oxo-3-oxazolidinylcarbonyl)tetrahydrofuran-2-carboxylate (**4h**):* colorless needles; mp 168−170 °C (benzene); IR (KBr) 2981, 1778, 1745, 1698, 1388, 1197, 743, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.20 (3H, t, J = 7.2 Hz), 2.81 (1H, d, J = 13.9 Hz), 2.96 (1H, ddd, J = 6.7, 9.3, 10.9 Hz), 3.10 (1H, d, J = 13.9 Hz), 3.58 (1H, ddd, J = 7.0, 9.3, 10.9 Hz), 3.87 (1H, m), 4.10−4.22 (3H, m), 4.52 (1H, d, J = 10.6 Hz), 5.36 (1H, dd, J = 9.8, 10.6 Hz), 5.91 (1H, d, J = 9.8 Hz), 7.10−7.17 (5H, m), 7.25−7.41 (8H, m), 7.49−7.51 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2 (CH_3), 38.2 (CH_2), 42.2 (CH_2), 54.3 (CH), 54.4 (CH), 61.2 (CH_2), 62.1 (CH_2), 79.9 (CH), 88.6 (C), 126.3 (CH), 127.1 (CH), 127.6 (CH), 127.8 (CH), 127.9 (CH), 128.2 (CH), 128.3 (CH), 129.3 (CH), 130.1 (CH), 135.2 (C), 135.5 (C), 138.2 (C), 153.0 (C), 169.0 (C), 171.1 (C); MS (EI) m/z 499 (M^+), 426, 408, 339, 321, 293, 219, 192, 131, 105, 91, 77, 65, 43, 29, 15. Anal. Calcd for $C_{30}H_{29}NO_6$: C, 72.23; H, 5.85; N, 2.80. Found: C, 72.10; H, 5.79; N, 2.89.

(2R,3S*,4S*,5R*)-Ethyl 2-benzyl-3,5-diphenyl-4-(2-oxo-3-oxazolidinylcarbonyl)tetrahydrofuran-2-carboxylate (**5h**):* although **5h** could not be separated by chromatography from a mixture with major **4h** and *trans*-3-cinnamoyl-2-oxazolidinone, it could be characterized by ^1H NMR; ^1H NMR (400 MHz, $CDCl_3$) δ 1.02

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(3H, t, J = 7.2 Hz), 2.90 (1H, ddd, J = 6.4, 9.3, 10.0 Hz), 3.33 (1H, d, J = 14.3 Hz), 3.46 (1H, d, J = 14.3 Hz), 3.54 (1H, ddd, J = 7.0, 9.3, 10.9 Hz), 3.74−3.84 (2H, m), 3.97−4.11 (2H, m), 4.28 (1H, d, J = 10.0 Hz), 5.26 (1H, t, J = 10.0 Hz), 6.14 (1H, d, J = 10.0 Hz), 7.15−7.18 (2H, m), 7.21−7.38 (13H, m).

(2S,3S*,4S*,5R*)-Ethyl 2-benzyl-3-methyl-4-(2-oxo-3-oxazolidinylcarbonyl)-5-(p-tolyl)tetrahydrofuran-2-carboxylate (**4i**):* colorless needles; mp 150−153 °C (benzene); IR (KBr) 2975, 1770, 1724, 1701, 1388, 1282, 1108, 706 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.23 (3H, t, J = 7.1 Hz), 1.28 (3H, d, J = 6.8 Hz), 2.28 (3H, s), 2.96 (1H, d, J = 13.9 Hz), 3.08 (1H, ddd, J = 6.6, 9.3, 10.9 Hz), 3.26 (1H, d, J = 13.9 Hz), 3.27 (1H, m), 3.73 (1H, ddd, J = 7.0, 9.3, 10.9 Hz), 3.99 (1H, m), 4.11−4.26 (3H, m), 4.34 (1H, dd, J = 9.9, 10.9 Hz), 5.66 (1H, d, J = 9.9 Hz), 7.06−7.08 (2H, m), 7.14−7.27 (7H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5 (CH_3), 14.2 (CH_3), 21.2 (CH_3), 36.9 (CH_2), 42.4 (CH_2), 42.9 (CH), 56.5 (CH), 61.1 (CH_2), 62.1 (CH_2), 79.5 (CH), 88.2 (C), 126.3 (CH), 126.9 (CH), 127.9 (CH), 128.4 (CH), 130.0 (CH), 135.6 (C), 135.7 (C), 137.7 (C), 152.9 (C), 169.5 (C), 171.8 (C); MS (EI) m/z 451 (M^+), 379, 361, 291, 273, 217, 199, 171, 146, 131, 105, 91, 77, 57, 43, 29, 15. Anal. Calcd for $C_{26}H_{29}NO_6$: C, 69.16; H, 6.47; N, 3.10. Found: C, 69.03; H, 6.34; N, 3.37.

(2R,3S*,4S*,5R*)-Ethyl 2-benzyl-3-methyl-4-(2-oxo-3-oxazolidinylcarbonyl)-5-(p-tolyl)tetrahydrofuran-2-carboxylate (**5i**):* although **5i** could not be separated by chromatography from a mixture with major **4i** and dipolarophile **3a**, it could be characterized by ^1H NMR; ^1H NMR (400 MHz, $CDCl_3$) δ 1.10 (3H, d, J = 6.8 Hz), 1.31 (3H, t, J = 7.1 Hz), 2.27 (3H, s), 2.96 (1H, dq, J = 11.0, 6.8 Hz), 3.00 (1H, m), 3.23 (1H, d, J = 14.0 Hz), 3.41 (1H, d, J = 14.0 Hz), 3.63 (1H, ddd, J = 7.1, 9.4, 10.9 Hz), 3.88 (1H, m), 4.12−4.24 (3H, m) 4.32 (1H, dd, J = 9.8, 11.0 Hz), 5.76 (1H, d, J = 9.8 Hz), 6.93−6.96 (2H, m), 7.30−7.38 (7H, m).

(2S,3S*,4S*,5R*)-Ethyl 2-benzyl-5-(4-chlorophenyl)-3-methyl-4-(2-oxo-3-oxazolidinylcarbonyl)tetrahydrofuran-2-carboxylate (**4j**):* colorless needles; mp 162−165 °C (benzene); IR (KBr) 2974, 1766, 1722, 1697, 1390, 1230, 1108, 757, 705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.24 (3H, t, J = 7.1 Hz), 1.28 (3H, d, J = 6.8 Hz), 2.95 (1H, d, J = 14.0 Hz), 3.19 (1H, ddd, J = 7.0, 9.4, 11.0 Hz), 3.25 (1H, m), 3.27 (1H, d, J = 13.9 Hz), 3.78 (1H, ddd, J = 6.7, 9.4, 11.0 Hz), 4.10 (1H, dt, J = 6.7, 9.2 Hz), 4.15−4.23 (2H, m), 4.28 (1H, dt, J = 7.0, 9.2 Hz), 4.39 (1H, dd, J = 9.8, 10.9 Hz), 5.68 (1H, d, J = 9.8 Hz), 7.14−7.26 (7H, m), 7.30−7.32 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5 (CH_3), 14.2 (CH_3), 21.2 (CH_3), 36.9 (CH_2), 42.4 (CH_2), 42.9 (CH), 56.5 (CH), 61.1 (CH_2), 62.1 (CH_2), 79.5 (CH), 88.2 (C), 126.3 (CH), 126.9 (CH), 127.9 (CH), 128.4 (CH), 130.0 (CH), 135.6 (C), 135.7 (C), 137.7 (C), 152.9 (C), 169.5 (C), 171.8 (C); MS (EI) m/z 471 (M^+), 399, 381, 312, 294, 248, 222, 192, 166, 129, 91, 65, 43, 29, 15. Anal. Calcd for $C_{25}H_{26}ClNO_6$: C, 63.63; H, 5.55; N, 2.97. Found: C, 63.84; H, 5.41; N, 2.90.

(2R,3S*,4S*,5R*)-Ethyl 2-benzyl-5-(4-chlorophenyl)-3-methyl-4-(2-oxo-3-oxazolidinylcarbonyl)tetrahydrofuran-2-carboxylate (**5j**):* although **5j** could not be separated by chromatography from a mixture with major **4j** and dipolarophile **3a**, it could be characterized by ^1H NMR; ^1H NMR (400 MHz, $CDCl_3$) δ 1.10 (3H, d, J = 6.8 Hz), 1.22 (3H, t, J = 7.1 Hz), 2.95 (1H, dq, J = 6.8, 10.0 Hz), 3.02 (1H, ddd, J = 6.8, 9.2, 11.0 Hz), 3.39 (1H, d, J = 14.2 Hz), 3.45 (1H, d, J = 14.2 Hz), 3.67 (1H, ddd, J = 6.8, 9.2, 10.9 Hz), 3.97 (1H, dt, J = 7.0, 9.2 Hz), 4.15−4.38 (3H, m), 4.39 (1H, t, J = 10.0 Hz), 5.80 (1H, d, J = 10.0 Hz), 7.09−7.12 (2H, m), 7.25−7.38 (7H, m).

(2S,3S*,4S*,5R*)-Ethyl 2-benzyl-3-methyl-5-(4-nitrophenyl)-4-(2-oxo-3-oxazolidinylcarbonyl)tetrahydrofuran-2-carboxylate (**4k**):* colorless needles; mp 139−143 °C (benzene); IR (KBr) 2974, 1782, 1735, 1688, 1521, 1390, 1348, 743, 709 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.24 (3H, t, J = 7.1 Hz), 1.28 (3H, d, J = 6.8 Hz), 2.95 (1H, d, J = 14.0 Hz), 3.19 (1H, ddd, J = 7.0, 9.4, 11.0 Hz), 3.25 (1H, m), 3.27 (1H, d, J = 14.0 Hz), 3.78 (1H, ddd, J = 6.7, 9.4, 11.0 Hz), 4.10 (1H, dt, J = 6.7, 9.2 Hz), 4.15−4.23 (2H, m), 4.28 (1H, dt, J = 7.0, 9.2 Hz), 4.39 (1H, dd, J = 9.8, 10.9 Hz), 5.68 (1H, d, J = 9.8 Hz), 7.14−7.26 (7H, m), 7.30−7.32 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.2 (CH_3), 14.3 (CH_3), 37.3 (CH_2), 42.4 (CH_2), 43.3 (CH), 56.5 (CH), 61.5 (CH_2), 62.3 (CH_2), 78.9 (CH), 88.8 (C), 123.1 (CH), 126.6 (CH), 127.9 (CH), 128.1 (CH), 130.0 (CH), 135.2 (C), 146.3 (C), 147.5 (C), 153.0 (C), 168.6 (C), 171.5 (C); MS (EI) m/z 482 (M^+), 410, 391, 345, 304, 248, 232, 202, 174, 129, 115, 91, 56, 43, 29, 15. Anal. Calcd for $C_{25}H_{26}N_2O_8$: C, 62.23; H, 5.43; N, 5.81. Found: C, 62.06; H, 5.40; N, 6.02.

(2R,3S*,4S*,5R*)-Ethyl 2-benzyl-3-methyl-5-(4-nitrophenyl)-4-(2-oxo-3-oxazolidinylcarbonyl)tetrahydrofuran-2-carboxylate (**5k**):* although **5k** could not be separated by chromatography from a mixture with major **4k** and dipolarophile **3a**, it could be characterized by ^1H NMR; ^1H NMR (400 MHz, $CDCl_3$) δ 1.11 (3H, d, J = 6.8 Hz), 1.34 (3H, t, J = 7.1 Hz), 3.05 (1H, m), 3.22 (1H, m), 3.27 (1H, d, J = 14.2 Hz), 3.41 (1H, d, J = 14.2 Hz), 3.70 (1H, ddd, J = 6.1, 9.3, 11.0 Hz), 4.06 (1H, dt, J = 6.4, 9.3 Hz), 4.16−4.37 (4H, m), 5.93 (1H, d, J = 10.0 Hz), 6.95−6.98 (2H, m), 7.18−7.31 (7H, m).

(2S,3S*,4S*,5R*)-Ethyl 2-benzyl-3-methyl-5-(2-naphthyl)-4-(2-oxo-3-oxazolidinylcarbonyl)tetrahydrofuran-2-carboxylate (**4l**):* colorless needles; mp 161−163 °C (benzene); IR (KBr) 2972, 1778, 1727, 1696, 1387, 1289, 758, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.28 (3H, t, J = 7.1 Hz), 1.31 (3H, d, J = 7.0 Hz), 2.79 (1H, m), 3.02 (1H, d, J = 14.0 Hz), 3.32 (1H, d, J = 14.0 Hz), 3.36 (1H, m), 3.55−3.63 (2H, m), 4.07 (1H, m), 4.16−4.30 (2H, m), 4.50 (1H, (1H, dd, J = 10.1, 10.9 Hz), 5.87 (1H, d, J = 10.1 Hz), 7.16−7.31 (5H, m), 7.42−7.50 (3H, m), 7.74−7.83 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6 (CH_3), 14.6 (CH_3), 37.0 (CH_2), 42.3 (CH_2), 43.2 (CH), 56.7 (CH), 61.3 (CH_2), 62.1 (CH_2), 79.8 (CH), 88.6 (C), 124.8 (CH), 125.99 (CH), 126.03 (CH), 126.2 (CH), 126.5 (CH), 127.5 (CH), 127.7 (CH), 127.9 (CH), 128.1 (CH), 130.1 (CH), 132.6 (C), 133.1 (C), 135.6 (C), 136.2 (C), 153.1 (C), 169.4 (C), 171.8 (C); MS (EI) m/z 487 (M^+), 415, 397, 332, 309, 283, 264, 235, 207, 182, 166, 141, 91, 65, 43, 29, 15. Anal. Calcd for $C_{29}H_{29}NO_6$: C, 71.44; H, 6.00; N, 2.87. Found: C, 71.36; H, 6.07; N, 2.88.

(2R,3S*,4S*,5R*)-Ethyl 2-benzyl-3-methyl-5-(2-naphthyl)-4-(2-oxo-3-oxazolidinylcarbonyl)tetrahydrofuran-2-carboxylate (**5l**):* although **5l** could not be separated by chromatography from a mixture with major **4l** and dipolarophile **3a**, it could be characterized by ^1H NMR; ^1H NMR (400 MHz, $CDCl_3$) δ 1.14 (3H, d, J = 6.9 Hz), 1.24 (3H, t, J = 7.1 Hz), 2.60 (1H, m), 3.12 (1H, dq, J = 6.9, 11.4 Hz), 3.44 (1H, d, J = 14.0 Hz), 3.45 (1H, m), 3.56 (1H, d, J = 14.0 Hz), 3.97 (1H, dt, J = 7.0, 9.2 Hz), 4.16−4.27 (3H, m), 4.39 (1H, dd, J = 10.3, 11.4 Hz), 5.98 (1H, d, J = 10.3 Hz), 6.89−6.96 (2H, m), 7.13−7.52 (6H, m), 7.74−7.83 (2H, m), 7.94−8.01 (2H, m).

General Procedure for the Ni(II)-Catalyzed Reaction Exemplified by the Reaction of Ethyl 2-diazohydrocinnamate (1), Benzaldehyde (2), and (*S*)-3-crotonoyl-4-isopropyl-2-oxazolidinone (7a). To a solution of (*S*)-3-crotonoyl-4-isopropyl-2-oxazolidinone (86.8 mg, 0.44 mmol), Rh_2Piv_4 (1.2 mg, 2.6×10^{-4} mmol), $Ni(BF_4)_2 \cdot 6H_2O$ (13.6 mg, 0.040 mmol), and MS 4 Å (500 mg) in CH_2Cl_2 (4 mL) at −78 °C (dry ice/acetone bath) was added a solution of ethyl 2-diazohydrocinnamate (120.8 mg, 0.52 mmol) and benzaldehyde (41 μL, 0.40 mmol) in CH_2Cl_2 (5 mL) over a period of 1 h using a syringe pump. The syringe was washed with CH_2Cl_2 (1 mL), and then the stirring was continued for 10 min at −78 °C. After the mixture was warmed to room temperature, it was filtered through Celite (1 cm) and a plug of silica gel (3 cm) with AcOEt/hexane (1/1, 80 mL) as an eluent. The solvent was removed in vacuo, and the residue was purified by column chromatography ((98/2)−(95/5), hexane/AcOEt) to provide 153.5 mg (80%) of **8a** and **9a** along with 2.3 mg (3%) of 1,3-dioxolane **6**. The **8a**:**9a** ratio was determined to be 99:1 by ^1H NMR analysis (400 MHz). Cycloadduct **8a** (140.1 mg, 73%) could be separated from the mixture of **8a** and **9a** by careful column chromatography (98:2, hexane/AcOEt).

Cycloadducts **8b** and **9b** (120.5 mg, 61%, **8b**:**9b** = 99:1) were synthesized according to the general procedure. Cycloadduct **8b** (105.7 mg, 54%) could be separated from the mixture of **8b** and **9b** by careful column chromatography.

Cycloadducts **8c** and **9c** (120.0 mg, 59%, **8c**:**9c** = >99:1) were synthesized according to the general procedure.

Cycloadducts **8d** and **9d** (114.9 mg, 53%, **8d**:**9d** = >99:1) were synthesized according to the general procedure.

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Cycloadducts **8e** and **9e** (125.4 mg, 75%, **8e**:**9e** = 99:1) were synthesized according to the general procedure. Cycloadduct **8e** (114.5 mg, 68%) could be separated from the mixture of **8e** and **9e** by careful column chromatography.

Cycloadducts **8f** and **9f** (146.1 mg, 82%, **8f**:**9f** = >99:1) were synthesized according to the general procedure.

Cycloadducts **8g** and **9g** (167.6 mg, 79%, **8g**:**9g** = >99:1) were synthesized according to the general procedure.

Cycloadducts **8h** and **9h** (138.4 mg, 70%, **8h**:**9h** = 99:1) were synthesized according to the general procedure. Cycloadduct **8h** (129.7 mg, 67%) could be separated from the mixture of **8h** and **9h** by careful column chromatography.

Cycloadducts **8i** and **9i** (137.9 mg, 67%, **8i**:**9i** = 99:1) were synthesized according to the general procedure. Cycloadduct **8i** (125.9 mg, 61%) could be separated from the mixture of **8i** and **9i** by careful column chromatography.

Cycloadducts **8j** and **9j** (142.6 mg, 68%, **8j**:**9j** = 99:1) were synthesized according to the general procedure. Cycloadduct **8j** (134.7 mg, 64%) could be separated from the mixture of **8j** and **9j** by careful column chromatography.

Cycloadducts **8k** and **9k** (150.6 mg, 71%, **8k**:**9k** = >99:1) were synthesized according to the general procedure.

Cycloadducts **8l** and **9l** (145.1 mg, 78%, **8l**:**9l** = 99:1) were synthesized according to the general procedure. Cycloadduct **8l** (135.8 mg, 73%) could be separated from the mixture of **8l** and **9l** by careful column chromatography.

Cycloadducts **8m** and **9m** (148.4 mg, 73%, **8m**:**9m** = >99:1) were synthesized according to the general procedure.

*(2S,3S,4S,5R)-Ethyl 2-benzyl-4-[(S)-4-isopropyl-2-oxo-3-oxazolidinylcarbonyl]-3-methyl-5-phenyltetrahydrofuran-2-carboxylate (**8a**):* colorless needles; mp 125−127 °C (benzene); $[\alpha]_D^{25}$ = −34.0° (*c* 1.00, $CHCl_3$); IR (KBr) 2981, 1775, 1725, 1702, 1495, 1380, 1276, 1218, 1105, 746, 704 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.77 (3H, d, *J* = 6.9 Hz), 0.78 (3H, d, *J* = 6.9 Hz), 1.23 (3H, t, *J* = 7.1 Hz), 1.30 (3H, d, *J* = 6.8 Hz), 2.15 (1H, m), 2.98 (1H, d, *J* = 13.9 Hz), 3.26−3.34 (3H, m), 3.49−3.56 (2H, m), 3.94 (1H, m), 4.11−4.25 (2H, m), 4.49 (1H, dd, *J* = 9.8, 10.8 Hz), 5.62 (1H, d, *J* = 9.8 Hz), 7.14−7.30 (8H, m), 7.34−7.37 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6 (CH_3), 14.2 (CH_3), 14.9 (CH_3), 17.9 (CH_3), 28.9 (CH), 36.7 (CH_2), 43.4 (CH), 56.7 (CH), 58.9 (CH), 61.1 (CH_2), 63.5 (CH_2), 79.5 (CH), 88.3 (C), 126.3 (CH), 127.3 (CH), 127.86 (CH), 127.94 (CH), 128.2 (CH), 130.0 (CH), 135.6 (C), 138.4 (C), 153.7 (C), 169.5 (C), 171.7 (C); MS (EI) *m*/*z* 479 (M^+), 406, 389, 370, 342, 324, 299, 277, 260, 203, 185, 159, 143, 128, 103, 91, 86, 77, 65, 52, 43, 39, 30. Anal. Calcd for $C_{28}H_{33}NO_6$: C, 70.13; H, 6.94; N, 2.92. Found: C, 70.50; H, 6.91; N, 2.58.

*(2R,3S,4S,5R)-Ethyl 2-benzyl-4-[(S)-4-isopropyl-2-oxo-3-oxazolidinylcarbonyl]-3-methyl-5-phenyltetrahydrofuran-2-carboxylate (**9a**):* although **9a** could not be separated by chromatography from a mixture with major **8a** and dipolarophile **7a**, it could be characterized by ^1H NMR; ^1H NMR (400 MHz, $CDCl_3$) δ 0.72 (3H, d, *J* = 6.9 Hz), 0.73 (3H, d, *J* = 6.9 Hz), 1.13 (3H, d, *J* = 7.0 Hz), 1.36 (3H, t, *J* = 7.0 Hz), 2.09 (1H, m), 3.04 (1H, dq, *J* = 11.1, 7.0 Hz), 3.25 (1H, d, *J* = 14.2 Hz), 3.33−3.43 (2H, m), 3.86 (1H, dd, *J* = 1.8, 8.4 Hz), 4.11−4.23 (3H, m), 4.38 (1H, dd, *J* = 10.2, 11.1 Hz), 5.75 (1H, d, *J* = 10.2 Hz), 6.88−6.90 (2H, m), 7.25−7.31 (8H, m).

*(2S,3S,4S,5R)-Ethyl 2-benzyl-3-ethyl-4-[(S)-4-isopropyl-2-oxo-3-oxazolidinylcarbonyl]-5-phenyltetrahydrofuran-2-carboxylate (**8b**):* colorless needles; mp 189−191 °C (benzene); $[\alpha]_D^{25}$ = −31.2° (*c* 1.00, $CHCl_3$); IR (KBr) 2964, 1776, 1725, 1770, 1387, 1264, 1206, 1088, 751, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.76 (6H, d, *J* = 7.4 Hz), 0.91 (3H, t, *J* = 7.4 Hz), 1.23 (3H, t, *J* = 7.1 Hz), 1.56 (1H, m), 1.99−2.15 (2H, m), 3.02 (1H, d, *J* = 14.1 Hz), 3.28 (1H, d, *J* = 14.1 Hz), 3.26 (1H, m), 3.45 (1H, t, *J* = 8.2 Hz), 3.49 (1H, ddd, *J* = 1.8, 4.0, 8.2 Hz), 3.90 (1H, dd, *J* = 1.8, 8.2 Hz), 4.10−4.62 (2H, m), 4.62 (1H, t, *J* = 9.8 Hz), 5.59 (1H, d, *J* = 9.8 Hz), 7.15−7.31 (8H, m), 7.38−7.40 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.2 (CH_3), 14.1 (CH_3), 14.9 (CH_3), 17.8 (CH_3), 22.8 (CH_2), 28.8 (CH), 36.4 (CH_2), 50.5 (CH), 54.9 (CH), 58.7 (CH), 61.2 (CH_2), 63.4 (CH_2), 80.0 (CH), 88.4 (C), 126.4 (CH), 127.7 (CH), 127.8 (CH), 128.0 (CH), 128.3 (CH), 130.1 (CH), 135.8 (C), 138.0 (C), 153.8 (C), 170.4 (C), 172.0 (C); MS (EI) *m*/*z* 493(M^+), 403, 291, 273, 217, 199, 171, 145, 130, 105, 91, 77, 57, 43, 29, 15. Anal. Calcd for $C_{29}H_{35}NO_6$: C, 70.57; H, 7.15; N, 2.84. Found: C, 70.78; H, 7.02; N, 2.75.

*(2R,3S,4S,5R)-Ethyl 2-benzyl-3-ethyl-4-[(S)-4-isopropyl-2-oxo-3-oxazolidinylcarbonyl]-5-phenyltetrahydrofuran-2-carboxylate (**9b**):* although **9b** could not be separated by chromatography from a mixture with major **8b** and dipolarophile **7b**, it could be characterized by ^1H NMR; ^1H NMR (400 MHz, $CDCl_3$) δ 0.72 (6H, d, *J* = 7.1 Hz), 0.96 (3H, t, *J* = 7.3 Hz), 1.27 (3H, t, *J* = 7.1 Hz), 1.53 (1H, m), 1.77 (1H, m), 2.04 (1H, m), 2.99 (1H, dq, *J* = 11.0, 7.1 Hz), 3.25 (1H, d, *J* = 14.2 Hz), 3.49−3.55 (2H, m), 3.85 (1H, m), 4.14−4.31 (3H, m), 4.55 (1H, dd, *J* = 9.8, 11.0 Hz), 5.79 (1H, d, *J* = 9.8 Hz), 6.99−7.02 (2H, m), 7.15−7.37 (8H, m).

*(2S,3S,4S,5R)-Ethyl 2-benzyl-4-[(S)-4-isopropyl-2-oxo-3-oxazolidinylcarbonyl]-5-phenyl-3-propyltetrahydrofuran-2-carboxylate (**8c**):* colorless needles; mp 179−182 °C (benzene); $[\alpha]_D^{25}$ = −26.5° (*c* 1.00, $CHCl_3$); IR (KBr) 2963, 1775, 1731, 1702, 1388, 1211, 1091, 754, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.75 (6H, d, *J* = 7.0 Hz), 0.95 (3H, t, *J* = 7.3 Hz), 1.23 (3H, t, *J* = 7.1 Hz), 1.15−1.32 (2H, m), 1.54 (1H, m), 1.92 (1H, m), 2.10 (1H, m), 3.02 (1H, d, *J* = 14.0 Hz), 3.29 (1H, d, *J* = 14.0 Hz), 3.33 (1H, m), 3.45 (1H, t, *J* = 8.2 Hz), 3.48 (1H, ddd, *J* = 1.7, 4.1, 8.2 Hz), 3.90 (1H, dd, *J* = 1.7, 8.2 Hz), 4.11−4.26 (2H, m,), 4.64 (1H, t, *J* = 9.8 Hz), 5.58 (1H, d, *J* = 9.8 Hz), 7.13−7.31 (8H, m), 7.38−7.40 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2 (CH_3), 14.4 (CH_3), 14.9 (CH_3), 17.8 (CH_3), 21.9 (CH_2), 28.8 (CH), 32.1 (CH_2), 36.4 (CH_2), 48.7 (CH), 55.2 (CH), 58.7 (CH), 61.1 (CH_2), 63.4 (CH_2), 80.0 (CH), 88.4 (C), 126.3 (CH), 127.6 (CH), 127.7 (CH), 127.9 (CH), 128.2 (CH), 130.0 (CH), 135.8 (C), 137.9 (C), 153.7 (C), 170.3 (C), 171.8 (C); MS (EI) *m*/*z* 507 (M^+), 435, 418, 371, 343, 306, 289, 242, 213, 186, 158, 131, 115, 91, 77, 55, 29, 15. Anal. Calcd for $C_{30}H_{37}NO_6$: C, 70.98; H, 7.45; N, 2.76. Found: C, 70.86; H, 7.30; N, 2.94.

*(2R,3S,4S,5R)-Ethyl 2-benzyl-4-[(S)-4-isopropyl-2-oxo-3-oxazolidinylcarbonyl]-5-phenyl-3-propyltetrahydrofuran-2-carboxylate (**9c**):* although **9c** could not be separated by chromatography from a mixture with major **8c** and dipolarophile **7c**, it could be characterized by ^1H NMR; ^1H NMR (400 MHz, $CDCl_3$) δ 0.72 (6H, d, *J* = 6.8 Hz), 0.98 (3H, t, *J* = 7.3 Hz), 1.31 (3H, t, *J* = 7.1 Hz), 1.56 (1H, m), 1.66−173 (2H, m), 2.03−2.09 (2H, m), 2.83 (1H, ddd, *J* = 6.8, 9.8, 10.5 Hz), 3.10 (1H, m), 3.35 (1H, d, *J* = 14.2 Hz), 3.47 (1H, d, *J* = 14.2 Hz), 3.51 (1H, m), 3.84 (1H, m), 4.13−4.25 (2H, m), 4.56 (1H, dd, *J* = 9.8, 10.0 Hz), 5.79 (1H, d, *J* = 9.8 Hz), 6.98−7.01 (2H, m), 7.11−7.34 (8H, m).

*(2S,3S,4S,5R)-Ethyl 2-benzyl-3,5-diphenyl-4-[(S)-4-isopropyl-2-oxo-3-oxazolidinylcarbonyl]-3-propyltetrahydrofuran-2-carboxylate (**8d**):* colorless prisms; mp 213-215 °C (benzene); $[\alpha]_D^{25}$ = −35.7° (*c* 1.00, $CHCl_3$); IR (KBr) 2965, 1776, 1735, 1702, 1388, 1204, 1085, 755, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.59 (3H, d, *J* = 6.9 Hz), 0.64 (3H, d, *J* = 6.9 Hz), 1.21 (3H, t, *J* = 7.1 Hz), 1.98 (1H, m), 2.80 (1H, d, *J* = 14.0 Hz), 3.05 (1H, d, *J* = 14.0 Hz), 3.50−3.51 (2H, m), 3.90 (1H, m), 4.11−4.23 (2H, m), 4.55 (1H, d, *J* = 10.3 Hz), 5.43 (1H, dd, *J* = 9.7, 10.3 Hz), 5.86 (1H, d, *J* = 9.7 Hz), 7.10−7.19 (5H, m), 7.28−7.41 (8H, m), 7.51−7.53 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6 (CH_3), 14.6 (CH_3), 17.8 (CH_3), 28.5 (CH), 38.4 (CH_2), 54.3 (CH), 54.8 (CH), 58.9 (CH), 61.2 (CH_2), 63.4 (CH_2), 80.2 (CH), 88.7(C), 126.3 (CH), 127.4 (CH), 127.6 (CH), 127.8 (CH), 128.0 (CH), 128.3 (CH), 128.4 (CH), 129.1 (CH), 130.1 (CH), 135.4 (C), 135.6 (C), 138.2 (C), 153.8 (C), 169.3 (C), 171.3 (C); MS (EI) *m*/*z* 541 (M^+), 469, 451, 405, 377, 340, 322, 294, 276, 248, 220, 192, 130, 115, 91, 65, 29, 15. Anal. Calcd for $C_{33}H_{35}NO_6$: C, 73.18; H, 6.51; N, 2.59. Found: C, 73.33; H, 6.57; N, 2.37.

*(2R,3S,4S,5R)-Ethyl 2-benzyl-3,5-diphenyl-4-[(S)-4-isopropyl-2-oxo-3-oxazolidinylcarbonyl]-3-propyltetrahydrofuran-2-carboxylate (**9d**):* although **9d** could not be separated by chromatography from a mixture with major **8d** and dipolarophile **7d**, it could be characterized by ^1H NMR; ^1H NMR (400 MHz, $CDCl_3$) δ 0.56 (3H, d, *J* = 6.8 Hz), 0.62 (3H, d, *J* = 6.8 Hz), 0.99 (3H, t, *J* = 7.1 Hz), 1.86 (1H, m), 3.28 (1H, d, *J* = 13.6 Hz), 3.41 (1H, d, *J* = 13.6 Hz), 3.51

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(1H, m), 3.74 (1H, m), 3.82 (1H, dd, J = 1.7, 8.3 Hz), 3.90−3.99 (2H, m), 4.26 (1H, d, J = 10.2 Hz), 5.34 (1H, dd, J = 9.5, 10.2 Hz), 6.10 (1H, d, J = 9.5 Hz), 7.18−7.24 (2H, m), 7.24−7.46 (13H, m).

(2S,3S,4S,5R)-Ethyl 2-ethyl-4-[(S)-4-isopropyl-2-oxo-3-oxazolidinylcarbonyl]-3-methyl-5-phenyltetrahydrofuran-2-carboxylate ***(8e)****:* colorless oil; $[\alpha]_D^{25}$ = −34.7° (c 0.50, $CHCl_3$); IR (neat) 2967, 1780, 1748, 1701, 1389, 1251, 1133, 741, 703 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.76 (6H, d, J = 6.8 Hz), 0.97 (3H, t, J = 7.4 Hz), 1.15 (3H, d, J = 6.9 Hz), 1.36 (3H, t, J = 7.1 Hz), 1.70 (1H, dq, J = 14.2, 7.4 Hz), 2.01 (1H, dq, J = 14.2, 7.4 Hz), 2.13 (1H, m), 3.22 (1H, dq, J = 10.6, 6.8 Hz), 3.46−3.51 (2H, m), 3.91 (1H, m), 4.22−4.40 (3H, m), 5.36 (1H, d, J = 9.8, Hz), 7.25−7.37 (5H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 8.1 (CH_3), 13.3 (CH_3), 14.3 (CH_3), 14.9 (CH_3), 17.8 (CH_3), 24.0 (CH_2), 28.9 (CH), 42.8 (CH), 56.8 (CH), 59.0 (CH), 61.2 (CH_2), 63.5 (CH_2), 79.4 (CH), 88.5 (C), 127.5 (CH), 128.1 (CH), 128.4 (CH), 138.9 (C), 154.0 (C), 170.2 (C), 172.7 (C); MS (EI) m/z 417 (M^+), 344, 275, 215, 187, 159, 130, 105, 57; HRMS (ESI-TOF) calcd for $C_{23}H_{32}NO_6$ $(M + H)^+$ 418.2224, found 418.2228.

(2R,3S,4S,5R)-Ethyl 2-ethyl-4-[(S)-4-isopropyl-2-oxo-3-oxazolidinylcarbonyl]-3-methyl-5-phenyltetrahydrofuran-2-carboxylate ***(9e)****:* although **9e** could not be separated by chromatography from a mixture with major **8e** and dipolarophile **7a**, it could be characterized by ^1H NMR; ^1H NMR (500 MHz, $CDCl_3$) δ 0.71 (3H, d, J = 6.8 Hz), 0.80 (3H, d, J = 6.8 Hz), 1.02 (3H, t, J = 7.1 Hz), 1.16 (3H, d, J = 6.9 Hz), 1.36 (3H, t, J = 7.1 Hz), 1.67−1.75 (2H, m), 2.09 (1H, m), 3.06 (1H, dq, J = 11.0, 6.9 Hz), 3.47 (1H, m), 3.71 (1H, m), 3.86 (1H, dd, J = 1.8, 8.6 Hz), 4.17−4.24 (2H, m), 4.37 (1H, dd, J = 10.0, 11.0 Hz), 5.42 (1H, d, J = 10.0, Hz), 7.19−7.30 (5H, m).

(2S,3S,4S,5R)-Ethyl 2-isobutyl-4-[(S)-4-isopropyl-2-oxo-3-oxazolidinylcarbonyl]-3-methyl-5-phenyltetrahydrofuran-2-carboxylate ***(8f)****:* colorless oil; $[\alpha]_D^{25}$ = −28.7° (c 0.80, $CHCl_3$); IR (neat) 2962, 1780, 1727, 1701, 1388, 1211, 1139, 762, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.75 (3H, d, J = 6.9 Hz), 0.76 (3H, d, J = 6.9 Hz), 0.89 (3H, d, J = 6.5 Hz), 1.02 (3H, d, J = 6.5 Hz), 1.13 (3H, d, J = 6.8 Hz), 1.36 (3H, t, J = 7.1 Hz), 1.63 (1H, dd, J = 5.0, 13.6 Hz), 1.80−1.91 (2H, m), 2.12 (1H, m), 3.14 (1H, dq, J = 10.9, 6.8 Hz), 3.46−3.50 (2H, m), 3.91 (1H, m), 4.23−4.35 (2H, m), 4.36 (1H, dd, J = 9.9, 10.9 Hz), 5.36 (1H, d, J = 9.9 Hz), 7.25−7.31 (3H, m), 7.35−7.37 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.1 (CH_3), 14.2 (CH_3), 14.9 (CH_3), 17.8 (CH_3), 23.0 (CH_3), 24.2 (CH_3), 24.5 (CH), 28.9 (CH), 38.8 (CH_2), 44.0 (CH), 56.8 (CH), 59.0 (CH), 61.1 (CH_2), 63.6 (CH_2), 79.5 (CH), 87.4 (C), 127.6 (CH), 128.1 (CH), 128.4 (CH), 139.0 (C), 154.0 (C), 170.2 (C), 173.3 (C); MS (EI) m/z 445 (M^+), 374, 324, 277, 245, 185, 130, 105, 77, 69; HRMS (ESI-TOF) calcd for $C_{25}H_{36}NO_6$ $(M + H)^+$ 446.2537, found 446.2542.

(2R,3S,4S,5R)-Ethyl 2-isobutyl-4-[(S)-4-isopropyl-2-oxo-3-oxazolidinylcarbonyl]-3-methyl-5-phenyltetrahydrofuran-2-carboxylate ***(9f)****:* although **9f** could not be separated by chromatography from a mixture with major **8f** and dipolarophile **7a**, it could be characterized by ^1H NMR; ^1H NMR (500 MHz, $CDCl_3$) δ 0.68 (3H, d, J = 6.8 Hz), 0.72 (3H, d, J = 6.8 Hz), 0.82 (3H, d, J = 6.6 Hz), 0.95 (3H, d, J = 6.6 Hz,), 1.17 (3H, d, J = 6.9 Hz), 1.34 (3H, t, J = 7.1 Hz), 1.71−1.84 (2H, m), 1.96−2.09 (2H, m), 3.06 (1H, dq, J = 11.0, 6.9 Hz), 3.44−3.53 (2H, m), 3.81 (1H, m), 4.15−4.26 (2H, m), 4.30 (1H, dd, J = 9.6, 10.3 Hz), 5.42 (1H, d, J = 9.6 Hz), 7.07−7.32 (5H, m).

(2S,3S,4S,5R)-Ethyl 4-[(S)-4-isopropyl-2-oxo-3-oxazolidinylcarbonyl]-3-methyl-2-(1-naphthylmethyl)-5-phenyltetrahydrofuran-2-carboxylate ***(8g)****:* colorless prisms; mp 132−134 °C (benzene); $[\alpha]_D^{25}$ = −30.5° (c 0.50, $CHCl_3$); IR (KBr) 2966, 1777, 1720, 1700, 1457, 1206, 1076, 776, 701 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.79 (3H, d, J = 6.9 Hz), 0.81 (3H, d, J = 6.9 Hz), 1.07 (3H, t, J = 7.3 Hz), 1.45 (3H, d, J = 6.9 Hz), 2.18 (1H, m), 3.38 (1H, dq, J = 6.9, 11.0 Hz), 3.43 (1H, d, J = 14.8 Hz), 3.56 (1H, m), 3.61 (1H, t, J = 8.7 Hz), 3.85 (1H, d, J = 14.8 Hz), 3.98 (1H, dd, J = 2.2, 8.7 Hz), 4.06 (2H, dq, J = 1.1, 7.3 Hz), 4.65 (1H, dd, J = 9.8, 11.0 Hz), 5.68 (1H, d, J = 9.8 Hz), 7.23−7.27 (3H, m), 7.30−7.32 (2H, m), 7.34−7.37 (1H, m), 7.42−7.45 (1H, m), 7.52−7.55 (2H, m), 7.69−7.70 (1H, m), 7.79−7.81 (1H, m), 8.14−8.15 (1H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.7 (CH_3), 14.1 (CH_3), 14.9 (CH_3), 17.8 (CH_3), 28.9 (CH), 32.6 (CH_2), 43.7 (CH), 56.8 (CH), 59.0 (CH), 61.2 (CH_2), 63.6 (CH_2), 79.9 (CH), 88.3 (C), 123.9 (CH), 125.2 (CH), 125.4 (CH), 125.7 (CH), 127.35 (CH), 127.42 (CH), 128.0 (CH), 128.1 (CH), 128.4 (CH), 128.7 (CH), 132.2 (C), 132.8 (C), 133.9 (C), 138.9 (C), 154.0 (C), 169.8 (C), 172.6 (C); MS (EI) m/z 529 (M^+), 388, 324, 259, 231, 213, 187, 157, 141, 130; HRMS (ESI-TOF) calcd for $C_{32}H_{36}NO_6$ $(M + H)^+$ 530.2537, found 530.2530.

(2R,3S,4S,5R)-Ethyl 4-[(S)-4-isopropyl-2-oxo-3-oxazolidinylcarbonyl]-3-methyl-2-(1-naphthylmethyl)-5-phenyltetrahydrofuran-2-carboxylate ***(9g)****:* although **9g** could not be separated by chromatography from a mixture with major **8g** and dipolarophile **7a**, it could be characterized by ^1H NMR; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.71 (3H, d, J = 6.9 Hz), 0.74 (3H, d, J = 6.9 Hz), 1.12 (3H, t, J = 7.1 Hz), 1.39 (3H, d, J = 6.9 Hz), 2.11 (1H, m), 3.24 (1H, dq, J = 11.1, 6.9 Hz), 3.30 (1H, d, J = 14.8 Hz), 3.45 (1H, d, J = 14.8 Hz), 3.58 (1H, m), 3.90 (1H, m), 4.14−4.39 (3H, m), 4.52 (1H, dd, J = 9.8, 11.1 Hz), 5.75 (1H, d, J = 9.8 Hz), 6.98−7.05 (2H, m), 7.41−7.56 (6H, m), 7.64−7.79 (2H, m), 8.05−8.10 (1H, m), 8.12−8.18 (1H, m).

(2S,3S,4S,5R)-Ethyl 2-benzyl-4-[(S)-4-isopropyl-2-oxo-3-oxazolidinylcarbonyl]-3-methyl-5-(p-tolyl)tetrahydrofuran-2-carboxylate ***(8h)****:* colorless needles; mp 138−140 °C (benzene); $[\alpha]_D^{25}$ = −39.4° (c 1.00, $CHCl_3$); IR (KBr) 2976, 2881, 1779, 1724, 1697, 1387, 1209, 1084, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.780 (3H, d, J = 6.8 Hz), 0.784 (3H, d, J = 6.8 Hz), 1.22 (3H, t, J = 7.1 Hz), 1.29 (3H, d, J = 6.7 Hz), 2.14 (1H, m), 2.30 (3H, s), 2.97 (1H, d, J = 13.8 Hz), 3.27 (1H, d, J = 13.8 Hz), 3.28 (1H, m), 3.52−3.59 (2H, m), 3.95 (1H, t, J = 6.5 Hz), 4.09−4.24 (2H, m), 4.47 (1H, dd, J = 10.0, 11.0 Hz), 5.59 (1H, d, J = 10.0 Hz), 7.06−7.08 (2H, m), 7.13−7.36 (7H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6 (CH_3), 14.2 (CH_3), 15.0 (CH_3), 17.9 (CH_3), 21.3 (CH_3), 28.9 (CH), 36.8 (CH_2), 43.4 (CH), 56.7 (CH), 58.9 (CH), 61.1 (CH_2), 63.6 (CH_2), 79.4 (CH), 88.2 (C), 126.3 (CH), 127.2 (CH), 128.0 (CH), 128.5 (CH), 130.1 (CH), 135.5 (C), 135.7 (C), 137.8 (C), 153.7 (C), 169.6 (C), 171.8 (C); MS (EI) m/z 493 (M^+), 421, 402, 291, 273, 245, 201, 171, 145, 130, 105, 91, 77, 69, 57, 43, 29, 15. Anal. Calcd for $C_{29}H_{35}NO_6$: C, 70.57; H, 7.15; N, 2.84. Found: C, 70.57; H, 7.16; N, 2.82.

(2R,3S,4S,5R)-Ethyl 2-benzyl-4-[(S)-4-isopropyl-2-oxo-3-oxazolidinylcarbonyl]-3-methyl-5-(p-tolyl)tetrahydrofuran-2-carboxylate ***(9h)****:* although **9h** could not be separated by chromatography from a mixture with major **8h** and dipolarophile **7a**, it could be characterized by ^1H NMR; ^1H NMR (400 MHz, $CDCl_3$) δ 0.72 (3H, d, J = 6.9 Hz,), 0.73 (3H, d, J = 6.9 Hz), 1.13 (3H, d, J = 7.0 Hz), 1.35 (3H, t, J = 7.0 Hz), 2.09 (1H, m), 2.44 (3H, s), 3.04 (1H, dq, J = 11.1, 7.0 Hz), 3.23 (1H, d, J = 14.2 Hz), 3.34−3.46 (2H, m), 3.75 (1H, m), 3.84 (1H, dd, J = 1.8, 8.4 Hz), 4.11−4.24 (2H, m), 4.35 (1H, dd, J = 9.6, 11.1 Hz), 5.75 (1H, d, J = 9.6 Hz), 7.04−7.11 (2H, m), 7.25−7.31 (7H, m).

(2S,3S,4S,5R)-Ethyl 2-benzyl-5-(4-chlorophenyl)-4-[(S)-4-isopropyl-2-oxo-3-oxazolidinylcarbonyl]-3-methyltetrahydrofuran-2-carboxylate ***(8i)****:* colorless needles; mp 148−151 °C (benzene); $[\alpha]_D^{25}$ = −35.7° (c 1.00, $CHCl_3$); IR (KBr) 2976, 2881, 1779, 1728, 1699, 1388, 1206, 1086, 756, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.796 (3H, d, J = 6.9 Hz), 0.802 (3H, d, J = 6.8 Hz), 1.23 (3H, t, J = 7.1 Hz), 1.29 (3H, d, J = 6.8 Hz), 2.17 (1H, m), 2.95 (1H, d, J = 13.9 Hz), 3.28 (1H, d, J = 13.9 Hz), 3.26 (1H, m), 3.67−3.69 (2H, m), 4.02 (1H, m), 4.12−4.25 (2H, m), 4.47 (1H, dd, J = 9.8, 10.9 Hz), 5.62 (1H, d, J = 9.8 Hz), 7.15−7.32 (9H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5 (CH_3), 14.2 (CH_3), 14.9 (CH_3), 17.9 (CH_3), 28.8 (CH), 36.8 (CH_2), 43.4 (CH), 56.7 (CH), 58.7 (CH), 61.2 (CH_2), 63.6 (CH_2), 78.9 (CH), 88.4 (C), 126.4 (CH), 128.0 (CH), 128.0 (CH), 128.6 (CH), 130.0 (CH), 133.9 (C), 135.4 (C), 137.2 (C), 153.6 (C), 169.2 (C), 171.6 (C); MS (EI) m/z 513 (M^+), 441, 423, 311, 298, 266, 247, 222, 191, 166, 130, 91, 65, 29, 15; HRMS (EI) calcd for $C_{23}H_{32}ClNO_6$ (M^+) 513.1918, found 513.1913.

(2R,3S,4S,5R)-Ethyl 2-benzyl-5-(4-chlorophenyl)-4-[(S)-4-isopropyl-2-oxo-3-oxazolidinylcarbonyl]-3-methyltetrahydrofuran-2-carboxylate ***(9i)****:* although **9i** could not be separated by chromatography from a mixture with major **8i** and dipolarophile **7a**, it could be characterized by ^1H NMR; ^1H NMR (400 MHz, $CDCl_3$) δ 0.74 (3H, d, J = 6.8 Hz), 0.75 (3H, d, J = 6.8 Hz), 1.12 (3H, d, J = 6.8 Hz), 1.33 (3H, t, J = 7.1 Hz), 2.10 (1H, m), 3.01 (1H, dq, J = 11.2, 6.8 Hz), 3.26 (1H, d, J = 14.2 Hz), 3.38 (1H, d, J = 14.2 Hz), 3.52 (1H, m), 3.93

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(1H, m), 4.14−4.29 (3H, m), 4.36 (1H, dd, J = 10.0, 11.2 Hz), 5.74 (1H, d, J = 10.0 Hz), 7.11−7.15 (2H, m), 7.20−7.37 (7H, m).

*(2S,3S,4S,5R)-Ethyl 2-benzyl-4-[(S)-4-isopropyl-2-oxo-3-oxazolidinylcarbonyl]-3-methyl-5-(4-nitrophenyl)tetrahydrofuran-2-carboxylate (**8j**):* colorless prisms; m.p 145−147 °C (benzene); $[\alpha]_D^{25}$ = −49.6° (c 0.40, $CHCl_3$); IR (KBr) 2968, 1778, 1733, 1700, 1523, 1388, 1202, 854, 741, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.80 (6H, d, J = 6.9 Hz), 1.23 (3H, t, J = 7.1 Hz), 1.26 (3H, d, J = 7.1 Hz), 2.18 (1H, m), 2.96 (1H, d, J = 13.9 Hz), 3.26 (1H, dq, J = 11.4, 6.9 Hz), 3. 31 (1H, d, J = 13.9 Hz), 3.75 (1H, ddd, J = 3.0, 4.1, 9.0 Hz), 3.82 (1H, t, J = 9.0 Hz), 4.07 (1H, dd, J = 3.0, 9.0 Hz), 4.17−4.27 (2H, m), 4.55 (1H, dd, J = 9.9, 11.4 Hz), 5.76 (1H, d, J = 9.9 Hz), 7.19−7.26 (5H, m), 7.55−7.59 (2H, m), 8.12−8.16 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.1 (CH_3), 14.2 (CH_3), 14.7 (CH_3), 17.7 (CH_3), 28.4 (CH), 37.2 (CH_2), 43.8 (CH), 56.9 (CH), 58.6 (CH), 61.5 (CH_2), 63.6 (CH_2), 78.8 (CH), 88.9 (C), 123.3 (CH), 126.9 (CH), 128.2 (CH), 128.3 (CH), 130.2 (CH), 135.5 (C), 146.5 (C), 147.9 (C), 154.0 (C), 169.2 (C), 171.8 (C); MS (EI) m/z 524 (M^+), 451, 433, 304, 232, 202, 130, 91; HRMS (ESI-TOF) calcd for $C_{28}H_{33}N_2O_8$ $(M + H)^+$ 525.2231, found 525.2226.

*(2R,3S,4S,5R)-Ethyl 2-benzyl-4-[(S)-4-isopropyl-2-oxo-3-oxazolidinylcarbonyl]-3-methyl-5-(4-nitrophenyl)tetrahydrofuran-2-carboxylate (**9j**):* although **9j** could not be separated by chromatography from a mixture with major **8j** and dipolarophile **7a**, it could be characterized by ^1H NMR; ^1H NMR (400 MHz, $CDCl_3$) δ 0.80 (6H, d, J = 6.8 Hz), 1.12 (3H, d, J = 6.8 Hz), 1.33 (3H, t, J = 7.1 Hz), 2.10 (1H, m), 3.01 (1H, dq, J = 11.2, 6.8 Hz), 3.26 (1H, d, J = 14.2 Hz), 3.38 (1H, d, J = 14.2 Hz), 3.52 (1H, m), 3.93 (1H, m), 4.14−4.29 (3H, m), 4.36 (1H, dd, J = 10.0, 11.2 Hz), 5.74 (1H, d, J = 10.0 Hz), 7.11−7.15 (2H, m), 7.20−7.37 (7H, m).

*(2S,3S,4S,5R)-Ethyl 2-benzyl-4-[(S)-4-isopropyl-2-oxo-3-oxazolidinylcarbonyl]-3-methyl-5-(2-naphthalenyl)tetrahydrofuran-2-carboxylate (**8k**):* colorless needles; mp 201−204 °C (benzene); $[\alpha]_D^{25}$ = −30.7° (c 1.00, $CHCl_3$); IR (KBr) 2978, 1777, 1720, 1695, 1387, 1280, 1218, 1105, 759, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.67 (3H, d, J = 6.9 Hz), 0.73 (3H, d, J = 6.9 Hz), 1.27 (3H, t, J = 7.1 Hz), 1.33 (3H, d, J = 6.8 Hz), 2.05 (1H, m), 3.01 (1H, t, J = 9.0 Hz), 3.03 (1H, d, J = 13.9 Hz), 3.32 (1H, d, J = 13.9 Hz), 3.37 (1H, dq, J = 6.9, 11.0 Hz), 3.30 (1H, ddd, J = 2.4, 4.3, 9.0 Hz), 3.76 (1H, dd, J = 2.4, 9.0 Hz), 4.15−4.29 (2H, m), 4.56 (1H, dd, J = 10.0, 11.0 Hz), 5.81 (1H, d, J = 10.0 Hz), 7.15−7.30 (5H, m), 7.45−7.51 (3H, m), 7.75−7.80 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6 (CH_3), 14.3 (CH_3), 15.0 (CH_3), 17.83 (CH_3), 28.9 (CH), 36.2 (CH_2), 43.5 (CH), 56.8 (CH), 58.7 (CH), 61.2 (CH_2), 63.5 (CH_2), 79.7 (CH), 88.5 (C), 124.9 (CH), 126.0 (CH), 126.1 (CH), 126.2 (CH), 126.4 (CH), 127.5 (CH), 127.8 (CH), 127.8 (CH), 128.0 (CH), 130.1 (CH), 132.5 (C), 133.1 (C), 135.7 (C), 136.0 (C), 153.9 (C), 169.4 (C), 171.8 (C); MS (EI) m/z 531 (M^+), 439, 375, 328, 311, 292, 264, 236, 208, 166, 130, 93, 91, 65, 41, 29, 15. Anal. Calcd for $C_{32}H_{35}NO_6$: C, 72.57; H, 6.66; N, 2.64. Found: C, 72.21; H, 6.76; N, 2.90.

*(2R,3S,4S,5R)-Ethyl 2-benzyl-4-[(S)-4-isopropyl-2-oxo-3-oxazolidinylcarbonyl]-3-methyl-5-(2-naphthalenyl)tetrahydrofuran-2-carboxylate (**9k**):* although **9k** could not be separated by chromatography from a mixture with major **8k** and dipolarophile **7a**, it could be characterized by ^1H NMR; ^1H NMR (400 MHz, $CDCl_3$) δ 0.71 (3H, d, J = 6.9 Hz), 0.72 (3H, d, J = 6.9 Hz), 1.15 (3H, d, J = 6.9 Hz), 1.37 (3H, t, J = 7.0 Hz), 2.11 (1H, m), 3.05 (1H, dq, J = 11.1, 6.9 Hz), 3.25 (1H, d, J = 14.2 Hz), 3.33−3.43 (2H, m), 3.88 (1H, dd, J = 1.8, 8.4 Hz), 4.10−4.25 (3H, m), 4.36 (1H, dd, J = 10.3, 11.1 Hz), 5.80 (1H, d, J = 10.3 Hz), 6.90−7.42 (12H, m).

*(2S,3S,4S,5R)-Methyl 2-benzyl-4-[(S)-4-isopropyl-2-oxo-3-oxazolidinylcarbonyl]-3-methyl-5-phenyltetrahydrofuran-2-carboxylate (**8l**):* colorless needles; mp 131−133 °C (benzene); $[\alpha]_D^{25}$ = −32.6° (c 0.40, $CHCl_3$); IR (KBr) 2974, 1774, 1719, 1699, 1502, 1382, 1276, 1120, 743, 704 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.76 (3H, d, J = 6.9 Hz), 0.77 (3H, d, J = 6.9 Hz), 1.30 (3H, d, J = 6.8 Hz), 2.14 (1H, m), 2.98 (1H, d, J = 13.9 Hz), 3.27 (1H, d, J = 13.9 Hz), 3.31 (1H, dq, J = 10.9, 6.8 Hz), 3.46−3.52 (2H, m), 3.69 (3H, s), 3.92 (1H, m), 4.50 (1H, dd, J = 9.8, 10.9 Hz), 5.62 (1H, d, J = 9.8 Hz), 7.14−7.30 (8H, m), 7.33−7.36 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.5 (CH_3), 14.9 (CH_3), 17.8 (CH_3), 28.9 (CH), 36.8 (CH_2), 43.4 (CH), 52.2 (CH_3), 56.7 (CH), 59.0 (CH), 63.6 (CH_2), 79.7 (CH), 88.7 (C), 126.7 (CH), 127.6 (CH), 128.2 (CH), 128.3 (CH), 128.5 (CH), 130.2 (CH), 135.8 (C), 138.6 (C), 154.0 (C), 169.9 (C), 172.6 (C); MS (EI) m/z 465 (M^+), 392, 374, 287, 227, 213, 185, 157, 143, 129, 103, 91, 86, 77, 65, 52, 43; HRMS (ESI-TOF) calcd for $C_{27}H_{32}NO_6$ $(M + H)^+$ 466.2224, found 466.2216.

*(2R,3S,4S,5R)-Methyl 2-benzyl-4-[(S)-4-isopropyl-2-oxo-3-oxazolidinylcarbonyl]-3-methyl-5-phenyltetrahydrofuran-2-carboxylate (**9l**):* although **9l** could not be separated by chromatography from a mixture with major **8l** and dipolarophile **7a**, it could be characterized by ^1H NMR; ^1H NMR (300 MHz, $CDCl_3$) δ 0.70 (3H, d, J = 6.8 Hz), 0.72 (3H, d, J = 6.8 Hz), 1.12 (3H, d, J = 7.0 Hz), 2.09 (1H, m), 3.04 (1H, dq, J = 11.0, 7.0 Hz), 3.27 (1H, d, J = 13.9 Hz), 3.33−3.43 (2H, m), 3.72 (3H, s), 3.84 (1H, m), 4.19 (1H, m), 4.40 (1H, dd, J = 9.8, 11.0 Hz), 5.79 (1H, d, J = 9.8 Hz), 6.91−6.98 (2H, m), 7.22−7.34 (8H, m).

*(2S,3S,4S,5R)-tert-Butyl 2-benzyl-4-[(S)-4-isopropyl-2-oxo-3-oxazolidinylcarbonyl]-3-methyl-5-phenyltetrahydrofuran-2-carboxylate (**8m**):* colorless prisms; mp 140−142 °C (hexane); $[\alpha]_D^{25}$ = −38.3° (c 1.00, $CHCl_3$); IR (KBr) 2979, 1776, 1720, 1702, 1386, 1290, 739, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.77 (3H, d, J = 6.8 Hz), 0.78 (3H, d, J = 6.8 Hz), 1.27 (3H, d, J = 6.8 Hz), 1.43 (9H, s), 2.15 (1H, m), 2.94 (1H, d, J = 14.0 Hz), 3.25 (1H, d, J = 14.0 Hz), 3.25 (1H, m), 3.50 (1H, m), 3.55 (1H, t, J = 8.4 Hz), 3.94 (1H, dd, J = 2.0, 8.4 Hz), 4.47 (1H, dd, J = 10.0, 11.0 Hz), 5.60 (1H, d, J = 10.0 Hz), 7.14−7.32 (8H, m), 7.37−7.39 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6 (CH_3), 15.0 (CH_3), 17.9 (CH_3), 28.0 (CH_3), 28.9 (CH), 36.3 (CH_2), 43.5 (CH), 56.9 (CH), 58.9 (CH), 63.6 (CH_2), 79.4 (CH), 81.6 (C), 88.2 (C), 126.2 (CH), 127.3 (CH), 127.8 (CH), 127.8 (CH), 128.1 (CH), 130.2 (CH), 136.0 (C), 138.8 (C), 153.7 (C), 169.6 (C), 170.6 (C); MS (EI) m/z 507 (M^+), 407, 361, 277, 231, 213, 185, 160, 131, 91, 77, 57, 41, 15. Anal. Calcd for $C_{30}H_{37}NO_6$: C, 70.98; H, 7.35; N, 2.76. Found: C, 70.87; H, 7.36; N, 2.85.

Conversion of Cycloadduct 8a to (2*S*,3*S*,4*S*,5*R*)-Ethyl 2-Benzyl-4-hydroxymethyl-3-methyl-5-phenyltetrahydrofuran-2-carboxylate. To a solution of cycloadduct **8a** (100.7 mg, 0.21 mmol) in THF (4 mL) and water (1 mL) was added $NaBH_4$ (31.8 mg, 0.84 mmol) at room temperature. After the mixture was stirred for 20 h at room temperature, the mixture was quenched with 1 mol/L hydrochloric acid (15 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic layers were dried over Na_2SO_4, and then the solvent was removed in vacuo. The residue was purified by silica gel column chromatography (9/1, hexane/AcOEt) to give 65.1 mg (81%) of the corresponding alcohol. The enantiomeric excess (>99% ee) was determined by HPLC analysis (Chiralpak AD-H, 2/8 *i*PrOH/hexane, flow rate 0.5 mL/min, 35 °C) t_R(minor) = 11.72 min, t_R(major) = 13.44 min: colorless needles; mp 143−145 °C (Et_2O); $[\alpha]_D^{25}$ = −10.6° (c 0.40, $CHCl_3$); IR (KBr) 3536, 2978, 1736, 1454, 1195, 1060, 739, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.83 (1H, bs), 1.24 (3H, t, J = 7.1 Hz), 1.30 (3H, d, J = 6.6 Hz), 2.41−2.56 (2H, m), 2.91 (1H, d, J = 13.9 Hz), 3.23 (1H, d, J = 13.9 Hz), 3.25 (1H, dd, J = 6.7, 11.6 Hz), 3.43 (1H, dd, J = 3.4, 11.6 Hz), 4.10−4.24 (2H, m), 5.41 (1H, d, J = 8.4 Hz), 7.14−7.35 (8H, m), 7.47−7.50 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5 (CH_3), 14.3 (CH_3), 37.9 (CH_2), 42.7 (CH), 51.8 (CH), 61.0 (CH_2), 61.2 (CH_2), 81.5 (CH), 88.2 (C), 126.3 (CH), 126.7 (CH), 127.6 (CH), 127.9 (CH), 128.2 (CH), 130.2 (CH), 136.1 (C), 139.8 (C), 172.8 (C); MS (EI) m/z 354 (M^+), 281, 263, 233, 171, 159, 145, 131, 117, 105, 91, 77, 43, 29, 15. Anal. Calcd for $C_{22}H_{26}O_4$: C, 74.55; H, 7.39. Found: C, 74.40; H, 7.37.

Conversion of Cycloadduct 8m to (2*S*,3*S*,4*S*,5*R*)-*tert*-Butyl 2-Benzyl-4-hydroxymethyl-3-methyl-5-phenyltetrahydrofuran-2-carboxylate. A procedure similar to that for $NaBH_4$ reduction of **8a** was employed. The enantiomeric excess (>99% ee) was determined by HPLC analysis (Chiralpak IC, 1/9 *i*PrOH/hexane, flow rate 0.5 mL/min, 35 °C) t_R(minor) = 10.92 min, t_R(major) = 33.63 min: colorless prisms; mp 160−162 °C (Et_2O); $[\alpha]_D^{25}$ = −10.2° (c 0.5, $CHCl_3$); IR (KBr) 3482, 2975, 1718, 1496, 1368, 1155, 847 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.74 (1H, bs), 1.29 (3H, d, J = 6.8 Hz), 1.42 (9H, s), 2.40−2.53 (2H, m), 2.90 (1H, d, J = 13.9 Hz), 3.19 (1H, d, J = 13.9 Hz), 3.29 (1H, m), 3.43 (1H, dd, J = 3.9, 11.7 Hz), 5.40 (1H, d, J = 8.5 Hz), 7.14−7.18 (1H, m), 7.21−7.60 (8H, m), 7.53−

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7.55 (1H, m);^{13}C NMR (125 MHz) δ 13.6 (CH_3), 28.0 (CH_3), 37.6 (CH_2), 42.8 (CH), 52.1 (CH), 61.3 (CH_2), 81.3 (CH), 81.6 (C), 88.1 (C), 126.4 (CH), 126.9 (CH), 127.8 (CH), 128.0 (CH), 128.4 (CH), 130.5 (CH), 136.7 (C), 140.2 (C), 172.2 (C); MS (EI) m/z 382 (M^+), 281, 235, 217, 205, 171, 143, 91, 57; HRMS (ESI-TOF) calcd for $C_{24}H_{30}O_4Na$ $(M + Na)^+$ 405.2036, found 405.2038.

Conversion of (2*S*,3*S*,4*S*,5*R*)-Ethyl 2-Benzyl-4-hydroxymethyl-3-methyl-5-phenyltetrahydrofuran-2-carboxylate to (2*S*,3*S*,4*S*,5*R*)-2-Benzyl-2,4-bis(hydroxymethyl)-3-methyl-5-phenyltetrahydrofuran (10). To a solution of (2*S*,3*S*,4*S*,5*R*)-ethyl 2-benzyl-4-hydroxymethyl-3-methyl-5-phenyltetrahydrofuran-2-carboxylate (58.6 mg, 0.165 mmol) in diethyl ether (5 mL) was added $LiAlH_4$ (7.2 mg, 0.190 mmol), and then the mixture was stirred at romm temperature for 2 h. The mixture was poured into a saturated Na_2SO_4 solution (30 mL) and stirred for 20 min at room temperature. The mixture was extracted with ethyl acetate (10 mL × 3). The combined extracts were washed with saturated sodium chloride solution, and the dried over Na_2SO_4. The residue was chromatographed over silica gel (8/2 hexane/AcOEt) to give 50.0 mg (94%) of the corresponding diol **10**. The enantiomeric excess was determined by HPLC analysis (Chiralpak IC, 2/8 *i*PrOH/hexane, flow rate 0.5 mL/min, 35 °C) t_R(minor) = 10.50 min, t_R(major) = 19.85 min: colorless prism; mp 161−164 °C (Et_2O); $[\alpha]_D^{25}$ = −125.6° (c 0.60, $CHCl_3$); IR (KBr) 3290, 2932, 2874, 1485, 1455, 1067, 1031, 741, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (1H, bs), 1.15 (3H, d, J = 6.5 Hz), 1.88 (1H, bs) 2.48−2.62 (2H, m), 2.59 (1H, d, J = 14.2 Hz), 2.97 (1H, d, J = 14.2 Hz), 3.31 (1H, dd, J = 7.6, 11.4 Hz), 3.45 (1H, dd, J = 4.4, 11.4 Hz), 3.53 (1H, d, J = 11.8 Hz), 3.64 (1H, d, J = 11.8 Hz), 5.34 (1H, d, J = 8.6 Hz), 7.18−7.41 (10H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7 (CH_3), 36.4 (CH_2), 39.1 (CH), 52.1 (CH), 62.5 (CH_2), 64.0 (CH_2), 80.2 (CH), 86.0 (C), 126.1 (CH), 127.1 (CH), 127.8 (CH), 127.9 (CH), 128.3 (CH), 130.4 (CH), 136.9 (C), 139.8 (C); MS (EI) m/z 312 (M^+), 310, 280, 267, 185, 183, 157, 155, 139, 104, 76, 49. Anal. Calcd for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74. Found: C, 76.62; H, 7.94.

Conversion of (2*S*,3*S*,4*S*,5*R*)-*tert*-Butyl 2-Benzyl-4-hydroxymethyl-3-methyl-5-phenyltetrahydrofuran-2-carboxylate to (2*S*,3*S*,4*S*,5*R*)-2-Benzyl-2,4-bis(hydroxymethyl)-3-methyl-5-phenyltetrahydrofuran (10). A similar procedure for $LiAlH_4$ reduction of (2*S*,3*S*,4*S*,5*R*)-ethyl 2-benzyl-4-hydroxymethyl-3-methyl-5-phenyltetrahydrofuran-2-carboxylate was employed.

Conversion of Cycloadduct 8a to (2*S*,3*S*,4*S*,5*R*)-2-Benzyl-2,4-bis(hydroxymethyl)-3-methyl-5-phenyltetrahydrofuran (10). To a solution of cycloadduct **8a** (60.0 mg, 0.125 mmol) in diethyl ether (10 mL) was added $LiAlH_4$ (11.9 mg, 0.313 mmol), and then the mixture was heated under reflux for 30 min. After the mixture was cooled to room temperature, it was poured into a saturated Na_2SO_4 solution (30 mL) and stirred for 20 min at room temperature. The mixture was extracted with ethyl acetate (20 mL × 3). The combined extract was washed with saturated sodium chloride solution and then dried over Na_2SO_4. The residue was chromatographed over silica gel (8/2 hexane/AcOEt) to give 32.8 mg (84%) of the corresponding diol **10**.

Conversion of Cycloadducts 8a and 9a to (2*S*,3*S*,4*S*,5*R*)-2-benzyl-2,4-bis(hydroxymethyl)-3-methyl-5-phenyltetrahydrofuran (10) and (2*R*,3*S*,4*S*,5*R*)-2-benzyl-2,4-bis(hydroxymethyl)-3-methyl-5-phenyltetrahydrofuran (11). To a solution of cycloadducts **8a** and **9a** (**8a**:**9a** = 65:35, 107.4 mg, 0.224 mmol) in diethyl ether (20 mL) was added $LiAlH_4$ (21.3 mg, 0.56 mmol), and then the mixture was heated under reflux for 30 min. After the mixture was cooled to room temperature, it was poured into a saturated Na_2SO_4 solution (30 mL) and stirred for 20 min at room temperature. The mixture was extracted with ethyl acetate (20 mL × 3). The combined extracts were washed with saturated sodium chloride solution and then dried over Na_2SO_4. The residue was chromatographed over silica gel (8/2 hexane/AcOEt) to give 38.4 mg of diol **10** and 19.0 mg of diol **11** (total yield 82%, **10**:**11** = 67:33). The enantiomeric excess of **11** was determined by HPLC analysis (Chiralpak IC, 2/8 *i*PrOH/hexane, flow rate 0.5 mL/min, 35 °C) t_R(major) = 13.35 min, t_R(minor) = 14.48 min.

(2R,3S,4S,5R)-2-Benzyl-2,4-bis(hydroxymethyl)-3-methyl-5-phenyltetrahydrofuran (11): colorless viscous oil; $[\alpha]_D^{25}$ = −17.1° (c 0.40, $CHCl_3$); IR (KBr) 3446, 2959, 1719, 1590, 1270, 1102, 1011, 755, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.67 (1H, bs), 0.93 (3H, d, J = 7.0 Hz), 2.09 (1H, dq, J = 10.3, 7.0 Hz), 2.11 (1H, bs), 2.48 (1H, m), 2.98 (1H, d, J = 13.8 Hz), 3.07 (1H, dd, J = 7.8, 11.4 Hz), 3.22 (1H, d, J = 13.8 Hz), 3.23 (1H, m), 3.49 (1H, d, J = 11.4 Hz), 3.76 (1H, d, J = 11.4 Hz), 5.16 (1H, d, J = 9.2 Hz), 6.98−7.00 (2H, m), 7.22−7.35 (8H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.6 (CH_3), 40.15 (CH_2), 40.19 (CH), 52.5 (CH), 62.3 (CH_2), 62.9 (CH_2), 80.2 (CH), 86.0 (C), 126.5 (CH), 127.0 (CH), 127.8 (CH), 128.1 (CH), 128.4 (CH), 131.2 (CH),136.7 (C), 139.6 (C); MS (EI) m/z 312 (M^+), 310, 280, 267, 185, 183, 157, 155, 139, 104, 76, 49; HRMS (EI) calcd for $C_{20}H_{24}O_3$ (M^+) 312.1725, found 312.1722.

Conversion of Cycloadducts 4d and 5d to (2*S,3*S**,4*S**,5*R**)-2-Benzyl-2,4-bis(hydroxymethyl)-3-methyl-5-phenyltetrahydrofuran (10) and (2*R**,3*S**,4*S**,5*R**)-2-Benzyl-2,4-bis(hydroxymethyl)-3-methyl-5-phenyltetrahydrofuran (11).** To a solution of cycloadducts **4d** and **5d** (**4d**:**5d** = 88:12, 136.5 mg, 0.312 mmol) in diethyl ether (20 mL) was added $LiAlH_4$ (29.6 mg, 0.78 mmol), and then the mixture was heated under reflux for 30 min. After the mixture was cooled to room temperature, it was poured into a saturated Na_2SO_4 solution (30 mL) and stirred for 20 min at room temperature. The mixture was extracted with ethyl acetate (10 mL × 3). The combined extracts were washed with saturated sodium chloride solution and then dried over Na_2SO_4. The residue was chromatographed over silica gel (8/2 hexane/AcOEt) to give 68.0 mg of diol **10** and 13.9 mg of diol **11** (total yield 84%, **10**:**11** = 83:17).

Preparation of (*S*)-4-Isopropyl-3-[(*E*)-2-hexenoyl]-2-oxazolidinone (7c). 2-Oxazolidinone **7c** was prepared according to the procedure reported for the preparation of (*S*)-4-isopropyl-3-[(*E*)-2-pentenoyl]-2-oxazolidinone (**7b**)[15] in the literature: colorless oil; $[\alpha]_D^{25}$ = +89.7° (c 1.00, $CHCl_3$); IR (neat) 2963, 1775, 1685, 1636, 1365, 1203, 714 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (3H, d, J = 6.8 Hz), 0.93 (3H, d, J = 6.8 Hz), 0.96 (3H, t, J = 7.4 Hz), 1.53 (2H, sext, J = 7.4 Hz), 2.26 (2H, q, J = 7.4 Hz), 2.41 (1H, m), 4.22 (1H, dd, J = 3.0, 9.0 Hz), 4.28 (1H, t, J = 9.0 Hz), 4.49 (1H, m), 7.15 (1H, m), 7.27 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7 (CH_3), 14.7 (CH_3), 18.0 (CH_3), 21.4 (CH_2), 28.5 (CH), 34.6 (CH_2), 58.5 (CH), 63.3 (CH_2), 120.5 (CH), 151.3 (CH), 154.1 (C), 165.1 (C); MS (EI) m/z 225 (M^+), 182, 130, 97, 71, 55; HRMS (ESI-TOF) calcd for $C_{12}H_{19}NO_3Na$ $(M + Na)^+$ 248.1257, found 248.1263.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, tables, figures, and a CIF file giving X-ray crystallographic data for **8m** and ^{1}H and ^{13}C NMR spectra of cycloadducts. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*H.S.: tel, +81-26-269-5392; fax, +81-26-269-5424; e-mail, sugahio@shinshu-u.ac.jp.

Notes

The authors declare no competing financial interest.

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