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Rhodium-catalyzed 1,4-addition of alkenylzirconocene chlorides to electron deficient alkenes

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Abstract—The 1,4-conjugated addition of alkenylzirconocene chloride complexes to α,β-enones, α,β-enoic acid esters, and α,β-enoic acid amides can be efficiently achieved by the use of $[RhCl(cod)]_2$ catalyst. A high diastereoselectivity (95% yield, 90% de) was obtained through the reaction of α,β-enoic acid amide derived from Oppolzer's sultam and 2-butenoyl chloride, while the use of Evans' chiral oxazolidinone as a chiral auxiliary in place of Oppolzer's sultam gave a poor diastereoselectivity (98% yield, 26% de).

1. Introduction

The 1,4-addition of organometallic reagents is an important procedure in organic synthesis, and various organometallic reagents or catalysts which lead to an excellent selectivity for the 1,4-addition have been devised.[1] In the past decade, we have witnessed a progress in rhodium (Rh)-catalyzed 1,4-additions of organometallic reagents to activated alkenes, and various kinds of organometallic reagents in Rh(I)-catalyzed reactions have been employed.[2] Particularly, the 1,4-addition of organoboronic acid derivatives to α,β-enone compounds highlights the efficiency of the Rh(I)-catalyst not only for high chemical yields but also for an applicability to enantioselective reaction.[3] Recently, we reported that the $[RhCl(cod)]_2$-catalyzed (2 mol%) nucleophilic addition of alkenylzirconocene chlorides to *N*-*p*-toluenesulfonyl aldimines afforded allylic amine derivatives in excellent yields under mild reaction conditions.[4] The reaction was the first use of the organozirconocene chloride complex as an organometallic reagent in the Rh(I)-catalyzed reactions and also the first catalytic addition of the organozirconocene chloride complex to imine derivatives.[5] Organozirconocene chloride complexes are readily available by the hydrozirconation of alkenes or alkynes with Schwartz reagent (Cp_2ZrHCl)[6] or by the oxidative insertion of a zirconocene equivalent (Cp_2Zr–1-butene complex) to vinyl halide derivatives.[7] Thus, the exploitation of new reactions of the organozirconocene chloride complexes would increase their significance as an organometallic reagent in organic syntheses. The catalytic 1,4-conjugate addition of alkyl- or alkenylzirconocene chlorides to α,β-unsaturated compounds has been reported by the use of a Cu(I) catalyst[8] or by the use of a low valent Ni catalyst generated in situ.[9] In our study of Rh(I)-catalyzed reactions of the organozirconocene chloride complexes, we are tempted to examine the 1,4-conjugate addition to α,β-enone compounds. Herein, we report on an efficient Rh(I)-catalyzed 1,4-conjugate addition of alkenylzirconocene chlorides **1** to electron deficient olefins such as, α,β-enones **2**, α,β-enoic acid esters **3**, and α,β-enoic acid amides **4**, and the diastereoselective 1,4-addition to chiral acid amide derivatives (Scheme 1).

2. Results and discussion

Based on our reported reaction conditions for the Rh(I)-catalyzed additions of alkenylzirconocene chlorides **1** to imines,[5] we examined the 1,4-addition reactions of **1** (2–3 equiv.) to α,β-unsaturated compounds, **2**, **3**, and **4** in the presence of 2 mol% $[RhCl(cod)]_2$ catalyst.

Thus, the 2 mol% $[RhCl(cod)]_2$-catalyzed addition reaction of (*E*)-3,3-dimethyl-1-butenyl zirconocene chloride (**1a**)[10] to **2** in dioxane proceeded smoothly (2 h) at an ambient temperature to give 1,4-addition product **5** in good yields (entries 1–10, Table 1). Although the other Rh(I)-catalysts ($[Rh(cod)_2]BF_3$ or $[Rh(OH)(cod)]_{2)}$ or solvents (toluene or THF) are also efficient in bringing about the reaction, the neutral $[RhCl(cod)_2]$ catalyst, both in terms of the reaction rate and product yield, would be sufficient for the present purpose. The Rh(I)-catalyst did not restrict the 1,4-addition of **1a** to α,β-enones **2**, and thus, α,β-enoic acid esters **3** (entries 11–14) or α,β-enoic acid amides **4** (entries 15–18) are also efficient reactants for the 1,4-addition. In the reactions of **3**, there is not a significant difference in the reactivity of the bulky and small esters **3a-c** (entries 11–13).

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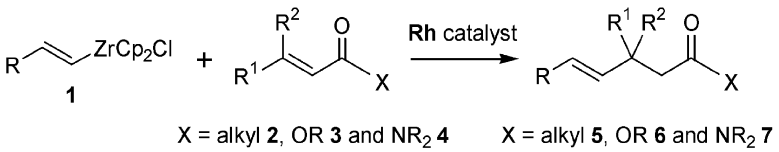


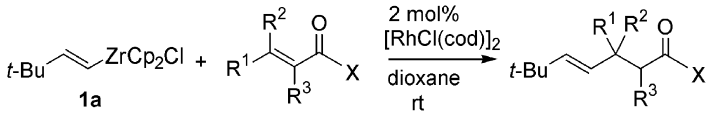
Scheme 1.

In regards to the reactions of **4**, the absence of amide hydrogen is preferable (entry 15), and thus, 1-piperidinyl **4b**[11] or 1-oxazolidin-2-one amide **4c**[12] gave 1,4-adduct **7** in excellent yields (entries 16–18). It has been reported that no reactivity of *N*,*N*-dialkyl derivative such as **4b** in the Rh-catalyzed addition of arylboronic acid.[13] Thus, the present addition of **1a** to **4b** (entry 16) could indicate a high efficiency of organozirconocene chloride complexes under the Rh-catalyzed conditions. In the reactions of β-unsubstituted **2c** and **2e**, a drop in the reaction rate (5 h) and product yield (~30%) was noted, and the improved yields were obtained by the use of 3 equiv of **1a** (entries 3 and 5). The similar β-substituent effect has also been reported in the Rh(I)-catalyzed conjugate addition of organotin compounds to α,β-enones.[14] In the reaction of **3a**, D_2O treatment of the reaction mixture yielded α-deuterated **6a** (>90 %D).[15] It should be mentioned that an alkylzirconocene chloride was an inefficient reagent under the present reaction conditions, and the same inefficiency has been noted in the Rh(I)-catalyzed reaction with imines.[5] Since the transfer of alkyl group from Zr to Rh is slower than the alkenyl group,[16] the present 1,4-addition reaction of **1** is considered to involve the formation of alkenylrhodium species **8** by the transmetalation at the initial stage. The overall process could be depicted as shown in Figure 1, in which the 1,4-adducts are driven out from a catalytic cycle as a Zr-enolate **9**. The addition of a phosphine ligand to the reaction mixture retarded the present Rh(I)-catalyzed 1,4-additions of the alkenylzirconocene chloride **1** to α,β-unsaturated carbonyl compounds.

The efficient additions of **1** to α,β-enoic acid amides **4** under the present conditions led us to examine the diastereoselective 1,4-addition of **1** to chiral α,β-enoic acid amides **10**. The diastereoselective 1,4-additions of **1** to chiral α,β-enoic acid amides **10** derived form 2-butenoyl chloride and chiral amine derivatives are shown in Table 2.

Poor diastereoselectivity has been observed by the use of Evans' chiral oxazolidinone **10a**, **b**[17] (**11a** 96% yield, 11% de and **11b** 98% yield, 26% de) as a chiral auxiliary. A change in the steric environment of the chiral oxazolidinone showed a slight increase in diastereoselectivity (entries 1 and 2). The use of Oppolzer's sultam **10c**,[18] however, induced a much higher diastereoselectivity (88–90% de) to give adducts **11c** and **11d** in an excellent chemical yield, respectively (entries 3 and 4). The diastereomeric ratio of **11** could be determined by HPLC and ^1H NMR analyses of the reaction mixtures. The diastereomeric mixture (95:5) of **11d** was purified by column chromatography to give a pure major isomer of **11d**, $[\alpha]_D^{25}=-65.4$ (*c* 1.02, $CHCl_3$), in 90% yield. The absolute configuration of the newly created chiral center of the major isomer of **11d** was determined to be *S*-configuration by converting to the known methyl

Table 1. 2 mol% $[RhCl(cod)]_2$-catalyzed 1,4-addition reactions of **1a**[a]



Entry	X	R^1	R^2	R^3	Reactant	Product	Yield (%)[b]
1	Ph	Ph	H	H	**2a**	**5a**	93
2	Ph	CH_3	H	H	**2b**	**5b**	60
3	Ph	H	H	CH_3	**2c**	**5c**	72[c]
4	Ph	CH_3	CH_3	H	**2d**	**5d**	56
5	Ph	H	H	H	**2e**	**5e**	98[c]
6	CH_3	Ph	H	H	**2f**	**5f**	94
7	*n*-C_8H_{17}	CH_3	H	H	**2g**	**5g**	53
8		Cyclopent-2-enone			**2h**	**5h**	74
9		Cyclohex-2-one			**2i**	**5i**	93
10		Cyclopent-2-enone			**2j**	**5j**	91
11	CH_3O	Ph	H	H	**3a**	**6a**	93
12	*i*-PrO	Ph	H	H	**3b**	**6b**	90
13	*t*-BuO	Ph	H	H	**3c**	**6c**	96
14	CH_3O	*n*-C_5H_{11}	H	H	**3d**	**6d**	90
15	$PhCH_2NH$	CH_3	H	H	**4a**	**7a**	68
16	Piperidinyl	CH_3	H	H	**4b**	**7b**	92
17	Oxazolidine-2-one	CH_3	H	H	**4c**	**7c**	95
18	Oxazolidine-2-one	CH_3	H	H	**4c**	**7d**	85[d]

[a] A ratio of the reagents; [**1a**]/[Reactant]/$[RhCl(cod)]_2$=2:1:0.02.
[b] Isolated yields.
[c] 3.0 equiv. of **1a** was used.
[d] (*E*)-1-HexenylZrCp_2Cl was used.

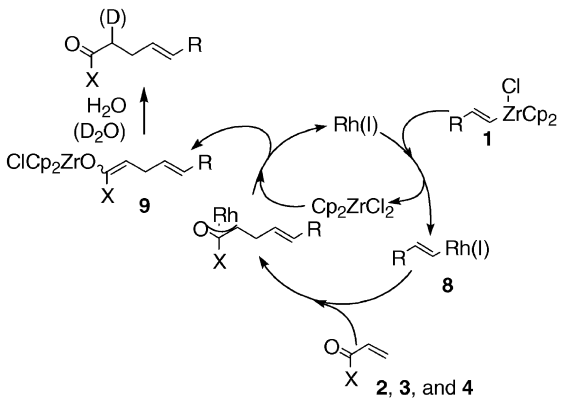
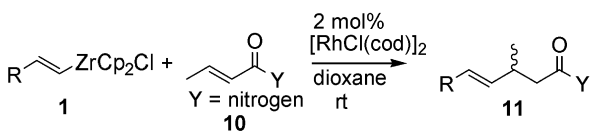
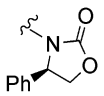
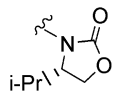
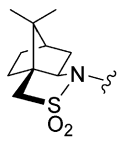


Figure 1. A catalytic cycle for the 1,4-addition reaction of **1**.

Table 2. Diastereoselective 1,4-addition reactions of **1** to **10**

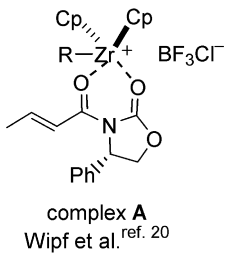


Entry	Y	10	R	11	Yield (%)[a]	de (%)[b]
1		**10a**	*t*-Bu	**11a**	96	11[c]
2		**10b**	*t*-Bu	**11b**	98	26[c]
3		**10c**	*t*-Bu	**11c**	92	88
4		**10c**	*n*-Bu	**11d**	95	90

[a] A mixture of diastereomers.
[b] Determined by HPLC and NMR analyses.
[c] Relative stereochemistry was undetermined.

(3*S*)-3-methyl-4-oxobutanoate (Scheme 2).[19] The relative stereochemistry of the major isomer of **11c** was assigned by analogy with **11d**.

It should be mentioned that in the reported Cu(I)-$BF_3{\cdot}OEt_2$-catalyzed 1,4-additions of alkylzirconocene chloride to **10**,[20] Oppolzer's sultam was a poor auxiliary (19% yield, 9% de), while the Evans' chiral oxazolidinone **10a**, **b** was highly efficient (60–84% yield, 90% de), and the addition of $BF_3{\cdot}OEt_2$ was essential to attain the high diastereoselectivity. It has been proposed that a conformationally rigid cationic zirconocene complex formed by the extrusion of chloride from Cp_2Zr–Cl bond with $BF_3{\cdot}OEt_2$ would have attributed to the high diastereoselectivity (a complex **A** in Fig. 2).[20]



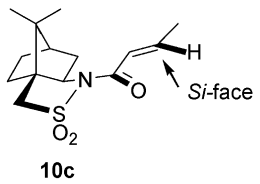
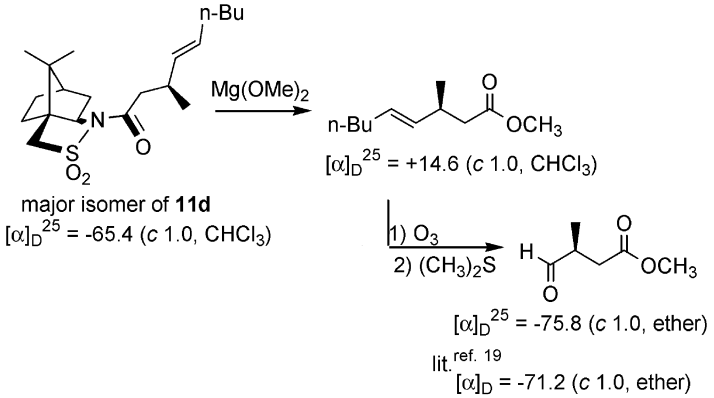


Figure 2. Possible conformation of amide **10c**.

In the present Rh(I)-catalyzed 1,4-addition of **1**, however, the formation of such chelated cationic zirconocene complex is impossible because of the absence of $BF_3{\cdot}OEt_2$, and thus, the use of Evans' chiral oxazolidinone auxiliary poorly discriminated the diastereoface of the carbon–carbon double bond of **10a**, **b** (entries 1 and 2, Table 2). The stereochemical outcome of **11c**, **d** can be explained by invoking a preferential SO_2/C=O *syn* disposition with an *s*–*cis* carbonyl/double bond conformation followed by an attack of alkenyl rhodium **8** to the less hindered alkene *Si*-face at β-carbon (Fig. 2).[21]

3. Conclusion

It has been demonstrated that the highly efficient conjugate addition reactions of alkenylzirconocene chlorides to α,β-enones, -enoic acid esters and -enoic acid amides were brought about by the use of Rh(I) catalyst. The application of the reaction to α,β-enoic acid chiral amides indicated that Oppolzer's sultam turned out to be an excellent chiral auxiliary in terms of diastereoselectivity and chemical yield.



Scheme 2. Absolute stereochemistry of **11e**.

4. Experimental

All non-aqueous reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions. Anhydrous solvents were purchased and used directly without further purification. Materials purchased from commercial suppliers were used without further purification unless otherwise noted. Schwartz reagent (Cp_2ZrHCl) was prepared according to the procedure described by Buchwald et al.[22] Purification of the products was carried out by silica gel column chromatography. Purification by medium pressure silica gel column chromatography (MPLC) was carried out using hexane/ethyl acetate as an eluting solvent and a UV detector at 254 nm. NMR spectra were measured at 300 or 400 MHz for ^1H, and 75.5 or 100.6 MHz for ^{13}C. MS analyses were performed on a spectrometer equipped with a positive electrospray ionization mode (ESI).

4.1. General procedure for the hydrozirconation

Alkyne (1.1 mmol) was added to a suspension of Cp_2ZrHCl (1.0 mmol) in dry CH_2Cl_2 (4 mL) at an ambient temperature, and the mixture was allowed to stir for 15 min. After the removal of the solvent in vacuum, the resulting alkenylzirconocene chloride **1** was dissolved in dry dioxane (4 mL), and the solution was directly used as a 1.0 mmol solution of **1** for the next reaction.

4.2. General procedure for the 1,4-conjugate addition

A solution of α,β-enones **2**, α,β-enoic acid esters **3**, or α,β-enoic acid amides **4** (0.5 mmol) in dry dioxane (1 mL) and $[RhCl(cod)]_2$ (0.01 mmol) were successively added to a 1.0 mmol solution of **1**, prepared as described, at ambient temperature. The reaction mixture was stirred for 1 h before being quenched with saturated aqueous $NaHCO_3$. The solution was extracted with ethyl acetate, and the combined organic layer was washed with brine and dried over $MgSO_4$. The filtered solution was concentrated to dryness in vacuo to give a crude product, which was purified by silica gel column chromatography (hexane/ethyl acetate; a ratio of 10:1 for **5** and **6**, a ratio of 4:1 for **7** and **11**) to give a pure product. Preparation of the analytical sample was carried out by MPLC (hexane/ethyl acetate). The structures of **5b**, **5h**, and **5i** were confirmed by comparing with the authentic samples.[9]

4.2.1. (*E*)-6,6-Dimethyl-1,3-diphenyl-4-hepten-1-one (5a). Mp 51–52 °C. IR (KBr) ν 1686 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.80 (s, 9H), 3.18 (dd, J=6.9, 15.8 Hz, 1H), 3.24 (dd, J=7.8, 15.8 Hz, 1H), 3.91 (q, J=7.1 Hz, 1H), 5.33 (d, J=15.7 Hz, 1H), 5.40 (dd, J=6.8, 15.7 Hz, 1H), 7.03–7.39 (m, 8H), 7.77–7.79 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 29.5, 32.7, 44.1, 44.9, 126.2, 126.7, 127.5, 128.0, 128.4, 128.5, 132.8, 137.4, 141.8, 144.1, 198.7; ESI m/z 315 $[M+Na]^+$; HRMS Calcd for $C_{21}H_{24}ONa$: 315.1725. Found: 315.1749; Anal. Calcd for $C_{21}H_{24}O$: C, 86.26; H, 8.27; O, 5.47. Found: C, 86.27; H, 8.27.

4.2.2. (*E*)-2,6,6-Trimethyl-1-phenyl-4-hepten-1-one (5c). IR (neat) ν 1671 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.92 (s, 9H), 1.07 (d, J=6.9 Hz, 3H), 2.14 (ddd, J=7.0, 7.4, 13.8 Hz 1H), 2.44 (ddd, J=6.4, 7.4, 13.8 Hz, 1H), 3.46 (m, 1H), 5.26 (dd, J=7.0, 15.6 Hz, 1H), 5.45 (d, J=15.6 Hz, 1H), 7.41–7.55 (m, 3H), 7.92–7.94 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 16.7, 29.5, 32.8, 36.9, 41.0, 121.4, 128.2, 128.5, 132.7, 136.8, 144.0, 204.0; ESI m/z 253 $[M+Na]^+$; Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63; O, 6.95. Found: C, 83.33; H, 9.62.

4.2.3. (*E*)-3,3,6,6-Tetramethyl-1-phenyl-4-hepten-1-one (5d). IR (neat) ν 1674 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.83 (s, 9H), 1.14 (s, 6H), 2.91 (s, 2H), 5.27 (d, J=16.0 Hz, 1H), 5.33 (d, J=16.0 Hz, 1H), 7.42 (t, J=7.6 Hz, 2H), 7.51 (t, J=7.3 Hz, 1H), 7.89 (d, J=7.6 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 28.0, 29.5, 32.4, 35.8, 50.0, 128.3, 128.4, 132.5, 133.4, 137.3, 138.6, 200.2; ESI m/z 267 $[M+Na]^+$; HRMS Calcd for $C_{17}H_{24}ONa$: 267.1725. Found: 267.1745.

4.2.4. (*E*)-6,6-Dimethyl-1-phenyl-4-hepten-1-one (5e). IR (neat) ν 1687 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.97 (s, 9H), 2.42 (q, J=7.2 Hz, 2H), 3.00 (t, J=7.4 Hz, 2H), 5.38 (td, J=6.6, 15.5 Hz, 1H), 5.51 (td, J=1.1, 15.7 Hz, 1H), 7.43–7.56 (m, 3H), 7.94–7.96 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 27.4, 29.6, 32.7, 38.7, 123.0, 128.0, 128.5, 132.8, 137.1, 142.6, 199.8; ESI m/z 217 $[M+1]^+$; Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32; O, 7.40. Found: C, 83.24; H, 9.40.

4.2.5. (*E*)-7,7-Dimethyl-4-phenyl-5-octen-2-one (5f). IR (neat) ν 1718 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.98 (s, 9H), 2.06 (s, 3H), 2.84 (d, J=7.4 Hz, 2H), 3.85 (bq, J=6.9 Hz, 1H), 5.45 (dd, J=5.9, 15.6 Hz, 1H), 5.50 (d, J=15.6 Hz, 1H), 7.17–7.31 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 29.5, 30.6, 32.8, 43.9, 50.0, 126.3, 126.7, 127.4, 128.4, 141.9, 143.8, 207.3; ESI m/z 231 $[M+1]^+$; Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63; O, 6.95. Found: C, 83.20; H, 9.49.

4.2.6. (*E*)-2,2,5-Trimethyl-3-pentadecen-7-one (5g). IR (neat) ν 1715 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, J=6.8 Hz, 3H), 0.94 (s, 9H), 0.96 (d, J=6.7 Hz, 3H), 1.24–1.29 (m, 10H), 1.50–1.55 (m, 2H,), 2.25–2.39 (m, 4H), 2.61 (sep, J=6.9 Hz, 1H), 5.19 (dd, 1H, J=7.4, 15.6 Hz), 5.40 (d, 1H, J=15.6 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.0, 20.7, 22.6, 23.6, 29.1, 29.2, 29.3, 29.6, 31.7, 32.5, 32.9, 43.5, 50.2, 128.9, 140.3, 210.6; ESI m/z 289 $[M+Na]^+$; HRMS Calcd for $C_{18}H_{34}ONa$: 289.2507. Found: 289.2543.

4.2.7. 3-[(*E*)-3,3-Dimethyl-1-butenyl]cycloheptanone (5j). IR (neat) ν 1701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.94 (s, 9H), 1.36–1.90 (m, 6H), 2.43–2.61 (m, 5H), 5.23 (dd, J=7.2, 15.6 Hz, 1H), 5.42 (dd, J=1.0, 15.6 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 24.0, 28.4, 29.6, 32.6, 37.5, 39.0, 44.0, 50.0, 128.8, 140.1, 214.0; ESI m/z 195 $[M+1]^+$; Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41; O, 8.32. Found: C, 80.29; H, 11.40.

4.2.8. Methyl (*E*)-6,6-dimethyl-3-phenyl-4-heptenoate (6a). IR (neat) ν 1723 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (s, 9H), 2.60 (d, J=7.8 Hz, 2H), 3.51 (s, 3H), 3.70 (q, J=7.6 Hz, 1H), 5.38 (dd, J=7.1, 15.7 Hz, 1H), 5.46 (d, J=15.7 Hz, 1H), 7.09–7.23 (m, 5H); ^{13}C NMR (75.5 MHz,

$CDCl_3$) δ 29.6, 32.8, 41.2, 44.9, 51.3, 126.3, 126.4, 126.7, 127.3, 128.5, 142.2, 143.5, 172.3; ESI *m/z* 269 $[M+Na]^+$; HRMS Calcd for $C_{16}H_{22}O_2Na$: 269.1517. Found: 269.1518; Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.09; O, 12.99. Found: C, 77.99; H, 9.02.

4.2.9. *iso*-Propyl (*E*)-6,6-dimethyl-3-phenyl-4-heptenoate (6b). IR (neat) ν 1733 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.99 (s, 9H), 1.14 (d, *J*=6.3 Hz, 3H), 1.18 (d, *J*=6.3 Hz, 3H), 2.65 (d, *J*=7.8 Hz, 2H), 3.79 (q, *J*=7.6 Hz, 1H), 4.93 (sep, *J*=6.3 Hz, 1H), 5.45–5.51 (dd, *J*=7.0, 15.7 Hz, 1H), 5.56 (d, *J*=15.7 Hz, 1H), 7.18–7.32 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.7, 21.8, 29.6, 32.8, 41.6, 44.9, 67.5, 126.3, 126.5, 127.4, 128.4, 141.9, 143.6, 171.5; ESI *m/z* 297 $[M+Na]^+$; HRMS Calcd for $C_{18}H_{26}O_2Na$: 297.1831. Found: 297.1815; Anal. Calcd for $C_{18}H_{26}O_2$: C, 78.77; H, 9.56; O, 11.66. Found: C, 78.77; H, 9.56.

4.2.10. *tert*-Butyl (*E*)-6,6-dimethyl-3-phenyl-4-heptenoate (6c). IR (neat) ν 1733 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.00 (s, 9H), 1.37 (s, 9H), 2.60 (d, *J*=7.8 Hz, 2H), 3.77 (q, *J*=7.6 Hz, 1H), 5.45–5.51 (dd, *J*=6.9, 15.7 Hz, 1H), 5.57 (d, *J*=15.7 Hz, 1H), 7.18–7.31 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 28.0, 29.6, 32.8, 42.3, 44.9, 80.1, 126.2, 126.7, 127.4, 128.3, 141.7, 143.8, 171.2; ESI *m/z* 311 $[M+Na]^+$; HRMS Calcd for $C_{19}H_{28}O_2Na$: 311.1987. Found: 311.1988; Anal. Calcd for $C_{19}H_{28}O_2$: C, 79.12; H, 9.78; O, 11.09. Found: C, 79.08; H, 9.75.

4.2.11. Methyl 3-[(*E*)-3,3-dimethyl-1-butene-1-yl]octanoate (6d). IR (neat) ν 1743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.84 (t, *J*=6.7 Hz, 3H), 0.96 (s, 9H), 1.21–1.34 (m, 8H), 2.21 (dd, *J*=8.6, 14.0 Hz, 1H), 2.33 (dd, *J*=6.0, 14.0 Hz, 1H), 2.38–2.42 (m, 1H), 3.62 (s, 3H), 5.06 (dd, *J*=8.6, 15.6 Hz, 1H), 5.44 (d, *J*=15.6 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.0, 22.5, 26.6, 29.7, 31.6, 32.7, 34.9, 39.7, 40.9, 51.2, 126.9, 142.4, 173.2; ESI *m/z* 263 $[M+Na]^+$; HRMS Calcd for $C_{15}H_{28}O_2Na$: 263.1987. Found: 263.1980.

4.2.12. (*E*)-*N*-Benzyl-3,6,6-trimethyl-4-heptenamide (7a). Crystals, mp 56–58 °C; IR (neat) ν 3270, 1641 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.94 (s, 9H), 0.98 (d, *J*=6.8 Hz, 3H), 2.14 (dd, *J*=6.9, 14.1 Hz, 1H), 2.20 (dd, *J*=7.5, 14.0 Hz, 1H), 2.62 (sep, *J*=6.9 Hz, 1H), 4.39 (m, 2H), 5.22 (dd, *J*=7.4, 15.7 Hz, 1H), 5.47 (d, *J*=15.6 Hz, 1H), 6.05 (bs, 1H), 7.24–7.32 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 20.7, 29.6, 32.5, 33.9, 43.4, 44.4, 127.3, 127.7, 128.5, 128.8, 138.3, 140.8, 171.8; ESI *m/z* 282 $[M+Na]^+$; HRMS Calcd for $C_{17}H_{25}NONa$: 282.1834; Found: 282.1811.

4.2.13. (*E*)-3,6,6-Trimethyl-1-(1-piperidinyl)-4-hepten-1-one (7b). IR (neat) ν 1642 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.95 (s, 9H), 1.01 (d, *J*=6.7 Hz, 3H), 1.49–1.64 (m, 6H), 2.20 (dd, *J*=7.9, 14.2 Hz, 1H), 2.33 (dd, *J*=6.6, 14.2 Hz, 1H), 2.61 (sep, *J*=6.9 Hz, 1H), 3.37–3.56 (m, 4H), 5.24 (dd, *J*=7.3, 15.6 Hz, 1H), 5.43 (d, *J*=15.6 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 20.5, 24.5, 25.6, 26.6, 29.7, 32.5, 33.9, 40.6, 42.6, 47.0, 129.1, 140.0, 170.0; ESI *m/z* 260 $[M+Na]^+$; HRMS Calcd for $C_{15}H_{27}ONNa$: 260.1990. Found: 260.2011.

4.2.14. 3-[(*E*)-3,6,6-Trimethyl-4-heptenoyl]-1,3-oxazolidin-2-one (7c). Mp 33–34 °C; IR (neat) ν 1770, 1698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.94 (s, 9H), 1.04 (d, *J*=6.7 Hz, 3H), 2.65 (sep, *J*=7.0 Hz, 1H), 2.82 (dd, *J*=6.9, 15.3 Hz, 1H), 2.98 (dd, *J*=7.5, 15.3 Hz, 1H), 3.96 (t, *J*=8.1 Hz, 2H), 4.35 (t, *J*=8.1 Hz, 2H), 5.24 (dd, *J*=7.7, 15.6 Hz, 1H), 5.43 (d, *J*=15.6 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 20.6, 29.6, 32.5, 33.6, 42.0, 42.4, 61.8, 128.5, 140.6, 153.4, 172.4; ESI *m/z* 262 $[M+Na]^+$; HRMS Calcd for $C_{13}H_{21}O_3NNa$: 262.1419. Found: 262.1433.

4.2.15. 3-[(*E*)-3-Methyl-4-nonenoyl]-1,3-oxazolidin-2-one (7d). IR (neat) ν 1781, 1700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.82 (t, *J*=7.1 Hz, 3H), 1.02 (d, *J*=6.8 Hz, 3H), 1.22–1.30 (m, 4H), 1.90–1.95 (m, 2H), 2.67 (sep, *J*=6.8 Hz, 1H), 2.80 (dd, *J*=6.8, 15.7 Hz, 1H), 2.96 (dd, *J*=8.1, 15.7 Hz, 1H), 3.96 (t, *J*=8.1 Hz, 2H), 4.07 (t, *J*=8.1 Hz, 2H), 5.30–5.43 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 13.8, 20.5, 22.0, 31.5, 32.0, 33.1, 41.9, 42.4, 61.8, 129.5, 133.9, 153.3, 172.2; ESI *m/z* 262 $[M+Na]^+$; HRMS Calcd for $C_{13}H_{21}O_3NNa$: 262.1419. Found: 262.1424.

4.2.16. (4*R*)-4-Phenyl-3-[(3,4*E*)-3,6,6-trimethyl-4-heptenoyl]-1,3-oxazolidine-2-one (minor-11a). Less polar isomer, oil; $[\alpha]_D^{25}=-73.8$ (*c* 0.86, $CHCl_3$); IR (neat) ν 1778, 1702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (s, 9H), 0.98 (d, *J*=6.7 Hz, 3H), 2.64 (sep, *J*=6.9 Hz, 1H), 2.88 (dd, *J*=6.4, 15.4 Hz, 1H), 2.96 (dd, *J*=7.8, 15.4 Hz, 1H), 4.25 (dd, *J*=3.7, 8.9 Hz, 1H), 4.65 (t, *J*=8.8 Hz, 1H), 5.20 (dd, *J*=7.6, 15.6 Hz, 1H), 5.37 (dd, *J*=0.7, 15.3 Hz, 1H), 5.41 (dd, *J*=3.7, 8.8 Hz, 1H), 7.28–7.39 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 20.7, 29.6, 32.5, 33.5, 42.5, 57.5, 69.8, 125.9, 128.4, 128.6, 129.1, 139.2, 140.7, 153.7, 171.6; ESI *m/z* 338 $[M+Na]^+$; HRMS Calcd for $C_{19}H_{25}O_3NNa$: 338.1732. Found: 338.1703.

4.2.17. (4*R*)-4-Phenyl-3-[(3,4*E*)-3,6,6-trimethyl-4-heptenoyl]-1,3-oxazolidine-2-one (major-11a). More polar isomer, crystals, mp 46–47 °C; $[\alpha]_D^{25}=-114.33$ (*c* 0.22, $CHCl_3$); IR (neat) ν 1778, 1702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (s, 9H), 0.97 (d, *J*=6.8 Hz, 3H), 2.66 (sep, *J*=6.8 Hz, 1H), 2.85 (dd, *J*=7.5, 16.2 Hz, 1H), 3.0 (dd, *J*=6.6, 16.2 Hz, 1H), 4.27 (dd, *J*=3.7, 8.9 Hz, 1H), 4.67 (t, *J*=8.9 Hz, 1H), 5.21 (dd, *J*=7.2, 15.7 Hz, 1H), 5.40 (dd, *J*=1.0, 15.7 Hz, 1H), 5.42 (dd, *J*=3.7, 8.7 Hz, 1H), 7.27–7.38 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 20.4, 29.6, 32.5, 32.6, 42.6, 57.6, 69.8, 125.9, 128.6, 128.7, 129.1, 139.1, 140,153.7,171.6; ESI *m/z*338 $[M+Na]^+$; HRMS Calcd for $C_{19}H_{25}O_3NNa$: 338.32. Found: 338.1714.

4.2.18. (4*S*)-4-*iso*-Propyl-3-[(3*,4*E*)-3,6,6-trimethyl-4-heptenoyl]-1,3-oxazolidine-2-one (minor-11b). Less polar isomer, oil; $[\alpha]_D^{25}=+73.3$ (*c* 1.12, $CHCl_3$); IR (neat) ν 1783, 1701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.86 (d, *J*=6.9 Hz, 3H), 0.90 (d, *J*=7.0 Hz, 3H), 0.95 (s, 9H), 1.06 (d, *J*=6.7 Hz, 3H), 2.29–2.36 (m, 1H), 2.68 (sep, *J*=7.0 Hz, 1H), 2.84 (dd, *J*=8.0, 14.8 Hz, 1H), 2.97 (dd, *J*=6.3, 14.9 Hz, 1H), 4.18 (dd, *J*=3.3, 9.1 Hz, 1H), 4.22 (t, *J*=8.6 Hz, 1H), 4.41 (dt, *J*=3.5, 8.2 Hz, 1H), 5.24 (dd, *J*=7.8, 15.6, 1 Hz), 5.44 (dd, 1H, *J*=0.6, 15.7 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.6, 17.9, 21.0, 28.4, 29.7,

32.6, 34.0, 42.6, 58.3, 63.1, 128.6, 140.7, 154.0, 172.1; ESI *m/z* 304 $[M+Na]^+$; HRMS Calcd for $C_{16}H_{27}O_3NNa$: 304.1889. Found: 304.1901.

4.2.19. (4*S*)-4-*iso*-Propyl-3-[(3*,4*E*)-3,6,6-trimethyl-4-heptenoyl]-1,3-oxazolidine-2-one (major-11b). More polar isomer, oil; $[\alpha]_D^{25}=+28.3$ (*c* 0.72, $CHCl_3$); IR (neat) ν 1783, 1701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.86 (d, *J*=6.9 Hz, 3H), 0.90 (d, *J*=7.0 Hz, 3H), 0.96 (s, 9H), 1.04 (d, *J*=6.7 Hz, 3H), 2.30–2.37 (m, 1H), 2.72 (sep, *J*=7.0 Hz, 1H), 2.79 (dd, *J*=8.0, 14.8 Hz, 1H), 3.05 (dd, *J*=6.3, 14.9 Hz, 1H), 4.18 (dd, *J*=3.3, 9.1 Hz, 1H), 4.24 (t, *J*=8.6 Hz, 1H), 4.42 (dt, *J*=3.5, 8.2 Hz, 1H), 5.27 (dd, *J*=7.8, 15.6, 1 Hz), 5.47 (dd, *J*=0.6, 15.7 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.7, 17.9, 20.6, 28.4, 29.7, 32.6, 32.9, 42.5, 58.4, 63.2, 128.6, 140.5, 154.0, 172.1; ESI *m/z* 304$[M+Na]^+$; HRMS Calcd for $C_{16}H_{27}O_3NNa$: 304.1889. Found: 304.1901.

4.2.20. (4*E*,3*R*)-3,6,6-Trimethyl-4-heptenoyl (*S*)-sultam (minor 11c). Less polar isomer, oil; $[\alpha]_D^{25}=-59.8$ (*c* 1.02, $CHCl_3$); IR (neat) ν 1698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.96 (s, 9H), 0.97 (s, 3H), 1.02 (d, *J*=6.4 Hz, 3H), 1.10 (s, 3H), 1.34–1.42 (m, 2H), 1.84–1.90 (m, 3H), 2.07 (d, *J*=6.3 Hz, 2H), 2.57 (dd, *J*=6.9, 17.6 Hz, 1H), 2.72–2.80 (m, 2H), 3.42 (d, *J*=13.8 Hz, 1H), 3.47 (d, *J*=13.8 Hz, 1H), 3.87 (t, *J*=6.3 Hz, 1H), 5.24 (dd, *J*=7.2, 15.7 Hz, 1H), 5.44 (dd, *J*=0.6, 15.7 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 19.9, 20.6, 20.8, 26.4, 29.7, 32.6, 32.8, 33.9, 38.6, 43.2, 44.6, 47.7, 48.2, 53.0, 65.2, 128.6, 140.6, 171.0; ESI *m/z* 390 $[M+Na]^+$; HRMS Calcd for $C_{21}H_{33}NO_3SNa$: 390.2079. Found: 390.2062.

4.2.21. (4*E*,3*S*)-3,6,6-Trimethyl-4-heptenoyl (*S*)-sultam (major 11c). More polar isomer, crystals, mp 109–111 °C; $[\alpha]_D^{25}=-77.4$ (*c* 0.32, $CHCl_3$); IR (neat) ν 1681 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.94 (s, 3H), 0.96 (s, 3H), 1.03 (d, *J*=6.6 Hz, 3H), 1.15 (s, 3H), 1.31–1.42 (m, 2H), 1.84–1.90 (m, 3H), 2.05 (d, *J*=5.6, 14.6 Hz, 2H), 2.53 (dd, *J*=6.9 Hz, 1H), 2.74–2.84 (m, *J*=7.8, 14.6 Hz, 2H), 3.41 (d, *J*=13.8 Hz, 1H), 3.48 (d, *J*=13.8 Hz, 1H), 3.86 (t, *J*=6.3 Hz, 1H), 5.23 (dd, *J*=6.9, 15.4 Hz, 1H), 5.45 (d, *J*=6.3, 15.4 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 19.8, 20.7, 21.0, 26.4, 29.6, 32.6, 32.8, 33.3, 38.5, 42.6, 44.7, 47.7, 48.2, 53.0, 65.2, 128.3, 140.6, 170.9; Anal. Calcd for $C_{20}H_{33}NO_3S$: C, 65.36; H, 9.05; N, 3.81. Found: C, 65.39; H, 8.90; N, 3.80.

4.2.22. (4*E*,3*R*)-3-Methyl-4-nonenoyl (*S*)-sultam (minor 11d). Less polar isomer, oil; $[\alpha]_D^{25}=-61.0$ (*c* 1.0, $CHCl_3$); IR (neat) ν 1698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J*=7.1 Hz, 3H), 0.97 (s, 3H), 1.04 (d, *J*=6.5 Hz, 3H), 1.17 (s, 3H), 1.29–1.40 (m, 7H), 1.85–2.08 (m, 7H), 2.59–2.80 (m, 3H), 3.40 (d, *J*=13.8 Hz), 1H, 3.47 (d, *J*=13.8 Hz, 1H), 3.86 (t, *J*=6.3 Hz, 1H), 5.36 (dd, *J*=6.5, 15.4 Hz, 1H), 5.43 (dt, *J*=6.1, 12.1 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 13.9, 19.9, 20.4, 20.8, 22.1, 26.5, 31.7, 32.1, 32.9, 33.7, 38.6, 43.0, 44.8, 47.7, 48.3, 53.1, 65.3, 129.7, 133.0, 170.0.

4.2.23. (4*E*,3*S*)-3-Methyl-4-nonenoyl (*S*)-sultam (major 11d). More polar isomer, oil; $[\alpha]_D^{25}=-65.4$ (*c* 1.0, $CHCl_3$); IR (neat) ν 1697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.84 (t, *J*=6.9 Hz, 3H), 0.94 (s, 3H), 1.01 (d, 3H, *J*=6.6 Hz), 1.12 (s, 3H), 1.23–1.37 (m, 6H), 1.67–2.03 (m, 7H), 2.49 (dd, *J*=5.6, 14.6 Hz, 1H), 2.77 (sep, *J*=6.9 Hz, 1H), 2.81 (dd, *J*=7.8, 14.6 Hz, 1H), 3.39 (d, *J*=13.8 Hz, 1H), 3.47 (d, *J*=13.8 Hz, 1H), 3.84 (t, *J*=6.3 Hz, 1H), 5.31 (dd, *J*=6.9, 15.4 Hz, 1H), 5.40 (dt, *J*=6.3, 15.4 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 13.8, 19.8, 20.6, 20.7, 22.1, 26.4, 31.4, 32.0, 32.7, 33.7, 38.4, 42.4, 44.6, 47.6, 48.1, 53.0, 65.1, 129.6, 133.6, 170.9; Anal. Calcd for $C_{20}H_{33}NO_3S$: C, 65.36; H, 9.05; N, 3.81. Found: C, 65.38; H, 8.99; N, 3.58.

4.2.24. (3*S*)-3-Methyl-4-oxobutanoate. To a solution of major-**11d**, $[\alpha]_D^{25}=-65.4$ (*c* 1.0, $CHCl_3$), (377 mg, 1.02 mmol) in MeOH (20 mL) was added a 6–10 wt% solution of $Mg(OMe)_2$ in MeOH (2.1 mL, ca. 2.0 mmol) at 0 °C and the mixture was stirred at 60 °C for 2 h. After adding H_2O, the reaction mixture was extracted with ether. The combined organic layer was washed with brine and dried over $MgSO_4$. The filtered solution was concentrated in vacuo to dryness and the residual oil was purified by silica gel column chromatography (pentane/ether=50:1) to give pure methyl ester, $[\alpha]_D^{25}=+14.6$ (*c* 1.0, $CHCl_3$), (110 mg, 0.6 mmol) in 58% yield. The ester (50 mg, 0.27 mmol) was treated with O_3 in CH_2Cl_2 (6 mL) at −78 °C for 15 min. After bubbling through the mixture with N_2 for 30 min, Me_2S was added at-78 °C and the mixture was stirred at ambient temperature for 1 h. The reaction mixture was dissolved into ether and the solution was washed with brine before drying ($MgSO_4$). The filtered solution was concentrated in vacuo to give a crude product which was purified by silica gel flash column chromatography (pentane/ether=10:1) to give (3*S*)-3-methyl-4-oxobutanoate, $[\alpha]_D^{25}=-75.8$ (*c* 1.0, ether). The NMR spectral data and specific rotation value showed a good agreement to the authentic material reported in Ref. 19.

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