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Cycloaddition of "*N*-Acyliminium Ion Pools" with Carbon–Carbon Multiple Bonds

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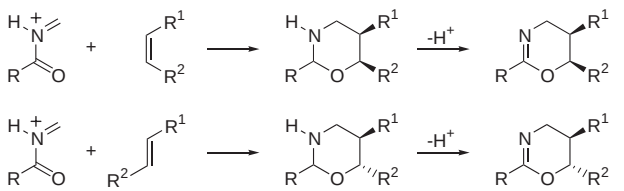
N-Acyliminium ion pools, which are generated from α-silyl carbamates, were found to react with a variety of alkenes and alkynes to give the corresponding cycloadducts. The reaction with styrene derivatives gave rise to the formation of a significant amount of polymeric products. The use of micromixing, however, resulted in a significant increase in the yield of the cycloadduct at the expense of the polymer. Mechanistic studies indicated that a concerted mechanism seems to be most likely for alkyl-substituted alkenes, whereas a stepwise mechanism seems to be reasonable for aryl-substituted alkenes.

N-Acyliminium ions[1] serve as electron-deficient 4π components and undergo [4 + 2] cycloaddition with alkenes and alkynes.[2,3] The reaction has been utilized as a useful method for the construction of heterocycles and acyclic amino alcohols. The reaction can be explained in terms of an inverse electron demand Diels–Alder type process that involves an electron-deficient hetero diene with an electron-rich dienophile.

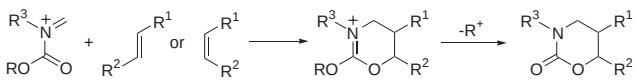
The [4 + 2] cycloaddition reactions of *N*-acyliminium ions having an amide group with alkenes give 4*H*-5,6-dihydro-1,3-oxazine derivatives, as shown in Scheme 1. A concerted mechanism has been suggested because the reaction proceeds stereospecifically.[2]

N-Acyliminium ions having an alkoxycarbonyl group also undergo the [4 + 2] cycloaddition reactions to give perhydro-1,3-oxazin-2-one derivatives (Scheme 2), but only a few reports have appeared in the literature.[4]

Conventionally, *N*-acyliminium ions have been generated by reversible acid-promoted reactions,[5] and have been utilized for [4 + 2] cycloaddition reactions. In such cases *N*-acyliminium ions should be generated in the presence of dienophiles, because *N*-acyliminium ions are usually highly unstable and should be trapped immediately after generation. The reversibility of the generation and an in situ follow-up reaction has made mechanistic studies difficult. Recently, however, we developed the "cation pool" method, which involves an *irreversible* generation and accumulation of carbocations by low-temperature electrochemical oxidation in the absence of other reaction components.[6,7] This method has been successfully applied to *N*-acyliminium ions, which can be characterized as ionic species by NMR and IR spectroscopies.[6,8] In a preliminary study, we found that *N*-acyliminium ions generated by the "cation pool" method underwent [4 + 2] cycloaddition reactions,[9] and herein we report the full details of this study.



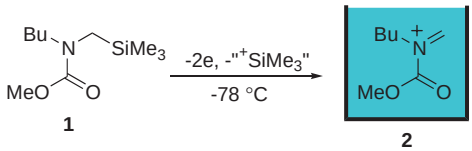
Scheme 1. [4 + 2] Cycloaddition using *N*-acyliminium ions having an amide group.



Scheme 2. [4 + 2] Cycloaddition using *N*-acyliminium ions having an alkoxycarbonyl group.

Results and Discussion

First, we focus on *N*-acyliminium ion **2**, which does not have a substituent on the cationic carbon. Cation **2** was generated by the low-temperature anodic oxidation of carbamate **1** having a silyl group as an electroauxiliary,[10] and was accumulated in a solution (Scheme 3). Bu_4NBF_4/CH_2Cl_2 was used as a supporting electrolyte/solvent system.



Scheme 3. Generation of *N*-acyliminium ion **2** using low temperature electrolysis.

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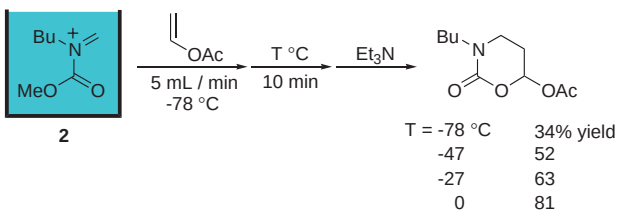
We first examined the reaction of **2** (generated from 0.5 mmol of **1**) with vinyl acetate, which was performed as follows. A solution of vinyl acetate was added to a cation pool **2** by a syringe pump (flow rate, 5.0 mL/min) at −78 °C. The reaction mixture was immediately warmed to the second temperature (T °C) and kept there for 10 min. Then, triethylamine was added at the same temperature to quench the reaction (Scheme 4). The yield of the cycloadduct increased with an increase of the second temperature. At 0 °C the cycloadduct was obtained in 81% yield, but a further increase of the temperature might cause the decomposition of **2**. Therefore, hereafter the reaction was carried out under the condition ($T = 0$ °C) unless otherwise stated (method A).

Using method A, the reactions of **2** with a variety of alkenes were examined to test the generality of the present reaction. As summarized in Table 1, acyclic and cyclic alkenes, 1,2-diphenylethenes, 1-phenyl-1-propenes, and vinylsilanes served as effective dienophiles. It is noteworthy that 1,3-cyclohexadiene behaved as a 2π component in this reaction, and the corresponding cycloadduct was obtained in good yield.

The stereochemistry of the present reaction is interesting. (*E*)-2-Butene gave *trans*-cycloadduct exclusively, while (*Z*)-2-butene gave the *cis*-cycloadduct exclusively. The observed complete stereospecificity suggests a concerted mechanism rather than a stepwise mechanism. The regioselectivity of the reaction with trimethyl(vinyl)silane also implies the concerted mechanism, because the stepwise mechanism involving a less-stable carbocation α to silicon seems to be unlikely.



Scheme 4. The effect of reaction temperature on the reaction of **2** with vinyl acetate (method A).

In order to obtain a deeper insight into the mechanism, we carried out theoretical studies using DFT calculations of a model system (*N*-methoxycarbonyl-*N*-methyliminium ion and ethylene).[11] The geometry optimization gave two structures, and the cisoid structure was found to be more stable (ca. 0.8 kcal) than the transoid structure.[12] The calculations also indicated that the reaction with ethylene proceeds in a concerted fashion, and two new bonds seem to form asynchronously, as shown in Fig. 1. The result of the calculations is consistent with the concerted mechanism suggested by experimental studies using alkyl-substituted alkenes (complete stereospecificity of the reaction).

In contrast to the reaction with alkyl-substituted alkenes, the reactions of aryl-substituted alkenes, such as 1,2-diphenylethenes, seem to proceed by a stepwise mechanism involving cationic intermediates. The reaction with (*Z*)-1,2-diphenylethene led to the formation of a 55:45 mixture of *trans*- and *cis*-cycloadducts, while (*E*)-1,2-diphenylethene exclusively gave *trans*-cycloadduct, the stereochemistry of which was confirmed by X-ray analysis. A partial loss of stereospecificity in the reaction with (*Z*)-1,2-diphenylethene implies that the bond rotation competes the cyclization in cationic intermediate **4**

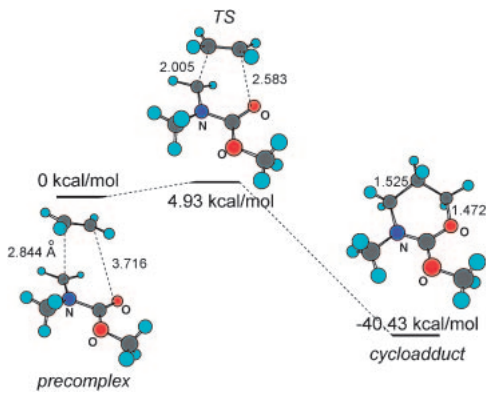
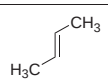
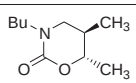
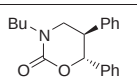
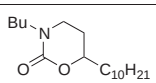
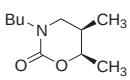
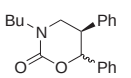
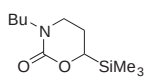
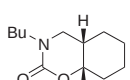
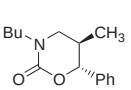
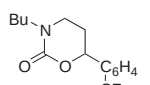
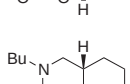
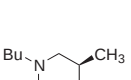
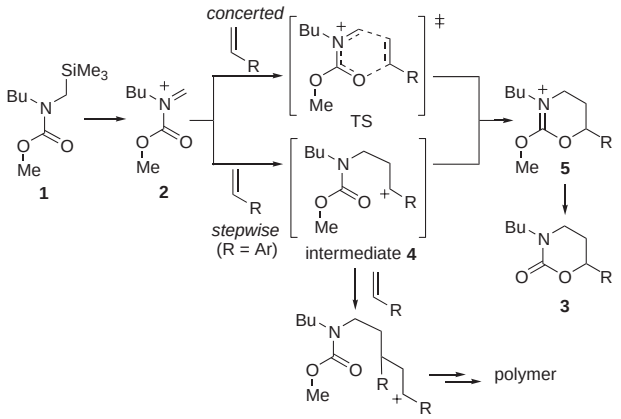


Fig. 1. The energy diagram of the reaction of *N*-methoxycarboyl-*N*-methyliminium ion with ethylene.

Table 1. [4 + 2] Cycloaddition of *N*-Acyliminium Ion **2** and Alkenes[a)]

Dienophile	Cycloadduct	Yield/%[b)]	Dienophile	Cycloadduct	Yield/%[b)]	Dienophile	Cycloadduct	Yield/%[b)]
		68			87			72
		65			80 (cis/trans 55:45)			86
		84			88			63[c)]
		70			83 (cis/trans 56:44)			

a) The mixing of **2** (generated from 1.2 equiv of **1**) and dienophiles were carried out using method A (see Table 2) at −78 °C. The mixture was stirred at 0 °C for 10 min. Then the reaction mixture was treated with triethylamine. Yields were determined on the basis of dienophiles. b) Isolated yield unless otherwise noted. c) Addition of a solution of an olefin to a solution of **2** at −78 °C. Reactions were immediately quenched by triethylamine.



Scheme 5. A proposed mechanism of [4 + 2] cycloaddition reaction.

Table 2. The Mixing Effect of the Reaction of **2** with Styrene Derivatives[a),b)]

Alkene	Cycloadduct	Yield/%[c)]			
		Method A	Method B	Method C	Micro-[d)] mixing
Ph	Ph	57	20	55	79
C_6H_4-Cl-*p*	C_6H_4-Cl-*p*	43	12	54	70
C_6H_4-Me-*p*	C_6H_4-Me-*p*	45	16	58	66

a) Method A: Addition of a solution of an alkene to a solution of **2** at −78 °C. Method B: Addition of a solution of **2** to a solution of an alkene at −78 °C. Method C: Addition of a solution of an alkene and a solution of **2** into a reaction flask simultaneously at −78 °C. b) Reactions were immediately quenched by triethylamine. c) Isolated yield. Yields were determined on the basis of dienophiles. d) IMM (Institut für Mikrotechnik Mainz GmbH) standard micromixier was used.

(Scheme 5). The cycloadditions of (*E*)- and (*Z*)-1-phenyl-1-propenes proceeded in a similar fashion. A partial loss of stereospecificity is consistent with the stepwise mechanism rather than the concerted mechanism.

It is also note worthy that the reaction with styrene gave rise to the formation of a significant amount of polymer. This observation also suggests the presence of a cationic intermediate, like **4**, which reacts with another molecule of styrene, and eventually gives the polymer. More outstanding is the observation that the product distribution strongly depends upon the method of mixing, as shown in Table 2. Although the addition of a solution of styrene to a solution of **2** (method A; see Table 1 and Scheme 4) gave cycloadduct **3** in 57% yield, the reverse addition of a solution of **2** to a solution of styrene (method B) gave **3** in only 20% yield, and a significant amount of styrene polymer (ca. 80% based on styrene) was obtained. The observation of the mixing effect and the formation of the polymer also designate the presence of cationic intermediate **4**. Presumably, the intramolecular cyclization of **4** gives **3** via cyclic intermediate **5**, and the competing intermolecular reaction with another molecule of styrene leads to the formation of the polymer.[13] The latter reaction seems to be favored in method B because of a higher initial concentration of styrene. The simultaneous addition of two reaction components (method C) gave essentially the same results as those obtained using method A. However, a micromixing[14–16] gave rise to a significant increase of the yield of **3** (79%) at the expense of the amount of the polymer (ca. 20% based on styrene) (Fig. 2). Efficient 1:1 mixing by the micromixer might cause intermediate **4** to be formed at a very low concentration of styrene, which leads to an effective intramolecular reaction to give **3**. Similar mixing effects were also observed for *p*-chloro- and *p*-methylstyrenes. It should be emphasized that the cation pool method is intrinsically suitable for a study of the mixing effect, because cations are formed *irreversibly* and accumulated in a solution, whereas in the conventional method cations are usually generated *reversibly* in situ as an equilibrium mixture.

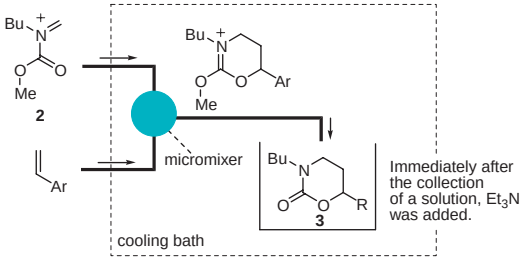


Fig. 2. Schematic diagram of the micromixing.

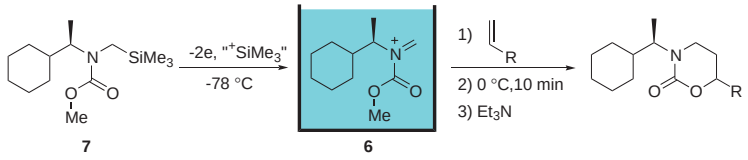
Chiral *N*-acyliminium ion pool **6** generated from **7** was used to investigate the diastereoselectivity in the present reaction. The corresponding cycloadducts were obtained in moderate-to-high yields, as shown in Table 3. The diastereomer ratios of the products were not high (1:1 to 1:3) irrespective of the nature of the substituent on the dienophile.

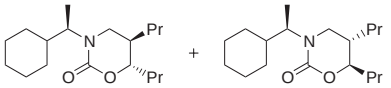
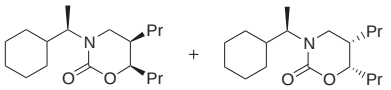
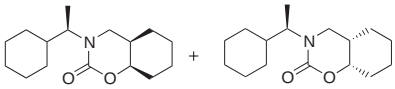
The *N*-acyliminium ion pool was also found to undergo a [4 + 2] cycloaddition reaction with a variety of alkynes. It is synthetically advantageous that alkynes, such as alkyl-, aryl-, and silyl-substituted acetylenes, could also be utilized to obtain the corresponding cycloadducts having a carbon–carbon double bond (Table 4).

N-Acyliminium ions having a substituent on the cationic carbon were also examined. *N*-Methoxycarbonyl-2-trimethylsilylpyrrolidine, *N*-methoxycarbonylpyrrolidine, and *N*-methoxycarbonyldiethylamine were used as precursors of the *N*-acyliminium ions. Among those examined, phenylacetylene was effective as a dienophile, and the corresponding cycloadducts were obtained in moderate yields (Table 5). The reaction with alkenes, such as (*Z*)-1,2-diphenylethene, (*E*)-1,2-diphenylethene, and vinyl acetate using several reaction conditions, were not successful.

In order to obtain a deeper insight into the reaction mechanism, the reaction was analyzed by ^{1}H NMR spectroscopy (Scheme 6). The ^{1}H NMR spectrum of **2** in CD_2Cl_2 has already been reported, and **2** was identified as an single ionic species in the solution.[6i,16b,16c] A solution of *N*-acyliminium ions **2** (generated from 1.2 equiv of **1** in CD_2Cl_2) and a solution of (*E*)-1,2-diphenylethene were mixed by using method A (see Table 1) at −78 °C. After stirring the solution for 10 min at 0 °C, a

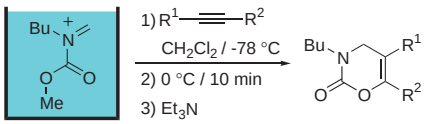
Table 3. [4 + 2] Cycloaddition of *N*-Acyliminium Ion **6** and Alkenes[a)]

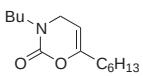
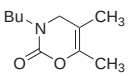
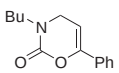
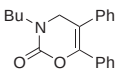
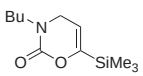


Alkene	Cycloadduct	Yield/%[b)]
		50 (d.r. = 3.3:1)
		86 (d.r. = 1.1:1)
		48 (d.r. = 1.2:1)

a) The mixing of **6** (generated from 1.2 equiv of **7**) and dienophiles were carried out using method A (see Table 2) at −78 °C. The mixture was stirred at 0 °C for 10 min. Then the reaction mixture was treated with triethylamine. Yields were determined on the basis of dienophiles. b) Isolated yield.

Table 4. [4 + 2] Cycloaddition of *N*-Acyliminium Ion **2** and Alkynes[a)]



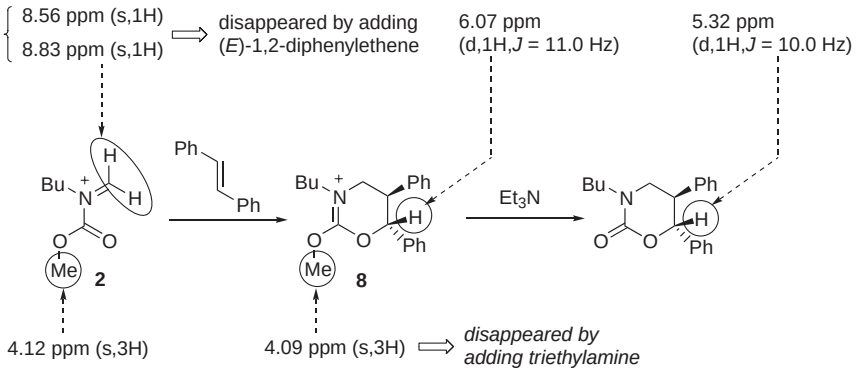
Alkyne	Cycloadduct	Yield/%[b)]	Alkyne	Cycloadduct	Yield/%[b)]
		64			64
		46			48
		90			

a) The mixing of **2** (generated from 1.2 equiv of **1**) and dienophiles were carried out using method A (see Table 2) at −78 °C. The mixture was stirred at 0 °C for 10 min. Then the reaction mixture was treated with triethylamine. Yields were determined on the basis of dienophiles. b) Isolated yield.

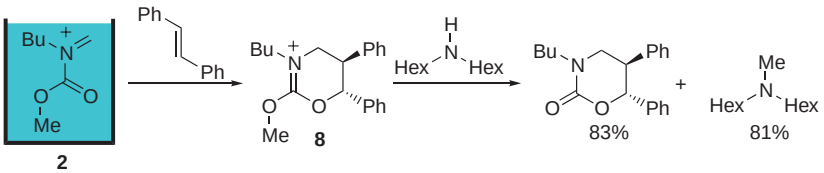
^{1}H NMR measurement was carried out at 0 °C. Two methylene proton signals (8.56 and 8.83 ppm) of **2** disappeared and an alternative benzylic proton signal (6.07 ppm, $J = 11.0$ Hz) appeared. The coupling constant was similar to that observed in the corresponding cycloadduct (5.32 ppm, $J = 10.0$ Hz), indicating the formation of a cyclic intermediate, such as **8**. The signal of the methoxy group at 4.12 ppm of **2** shifted slightly to 4.09 ppm by the addition of (*E*)-1,2-diphenylethene. The addition of triethylamine to the mixture gave rise to an extensive change of the spectrum. The methoxy signal was absolutely disappeared and the signal of the benzylic proton shifted to 5.32 ppm. The observation indicated that triethylamine plays a significant role in the formation of the cycloadduct.

To clarify the function of the triethylamine, the following experiments were carried out. When dihexylamine was used instead of triethylamine to quench the reaction, the cycloadduct was obtained together with dihexylmethylamine (Scheme 7). The yield of dihexylmethylamine was almost equal to that of the cycloadduct. The present result obviously indicates that a methyl group was transferred from cyclic intermediate **8** to an amine in the final step of the reaction.

It is also noteworthy that the intermediate **8** was reduced to the cyclic compound **9** by sodium borohydride in 78% yield (Scheme 8). The reduction may be carried out stepwise. The observation also strongly suggests the intermediacy of **8** in this cycloaddition reaction.

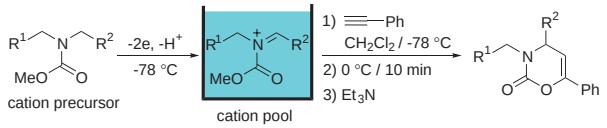


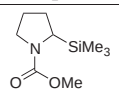
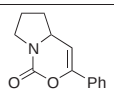
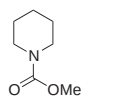
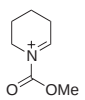
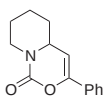
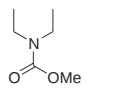
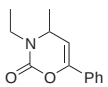
Scheme 6. Analysis of the reaction using ^{1}H NMR spectroscopy (500 MHz, CD_2Cl_2, 0 °C).



Scheme 7. Removal of methyl group from cyclic intermediate **8**.

Table 5. [4 + 2] Cycloaddition of *N*-Acyliminium Ion Having a Substituent on the Cationic Carbon and Phenylacetylene[a)]

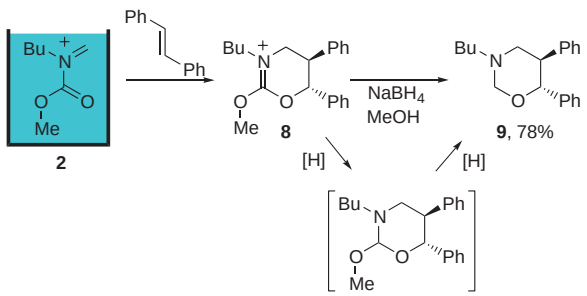


Cation precursor	Cation pool	Product	Yield/%[b)]
			61
			36
			59

a) The mixing of a cation pool (generated from 1.2 equiv of a cation precursor) and dienophiles were carried out using method A (see Table 2) at −78 °C. The mixture was stirred at 0 °C for 10 min. Then the reaction mixture was treated with triethylamine. Yields were determined on the basis of dienophiles. b) Isolated yield.

Conclusion

N-Acyliminium ion pool was found to undergo a cycloaddition reaction with a variety of dienophiles, such as alkenes and acetylenes. The reaction mechanism depends on the nature of the dienophile. A concerted mechanism seems to be most likely for alkyl-substituted alkenes, as suggested by DFT calculations in the gas phase, whereas a stepwise mechanism plays the major role for aryl-substituted olefins. A remarkable mixing effect observed for styrene derivatives is consistent with the



Scheme 8. Reduction of cyclic intermediate **8**.

stepwise mechanism. The NMR analysis revealed that a cationic adduct was formed. Upon a work-up with an amine, the methyl group was removed to give the final cycloadduct. The present study sheds light on the mechanistic features of the [4 + 2] cycloaddition reactions of *N*-acyliminium ions and high potential of the cation pool method for a mechanistic study on carbocation chemistry was well demonstrated.

Experimental

General Remarks. GC analysis was performed on a gas chromatograph (SHIMADZU GC-14B) equipped with a flame ionization detector using a fused-silica capillary. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Varian GEMINI-2000 (^{1}H 300 MHz, ^{13}C 75 MHz), Varian MERCURYplus-400 (^{1}H 400 MHz, ^{13}C 100 MHz), JEOL A-500 (^{1}H 500 MHz, ^{13}C 125 MHz), and JEOL ECA-600 (^{1}H 600 MHz, ^{13}C 150 MHz) spectrometers with Me_4Si as an internal standard unless otherwise noted. NMR spectra of the carbamates were usually very broad, and sometimes separated into two signals due to the existence of rotamers. EI mass spectra were recorded on a JMS-SX102A spectrometer. FAB mass spectra were recorded on a JMS-HX110A spectrometer. IR spectra were measured with a SHIMADZU FTIR 1600 spectrometer. Thin-layer chromatography (TLC) was carried out using Merck precoated silica gel F_{254} plates (thickness 0.25 mm). Flash chro-

matography was carried out on a column of silica gel (Kanto Chem. Co., Silica Gel N, spherical, neutral, 40–100 μm). Gel permeation chromatography (GPC) was carried out on a Japan Analytical Industry LC-908 equipped with JAIGEL-1H and 2H using $CHCl_3$ as an eluent. All reactions were carried out under an Ar atmosphere unless otherwise noted. A micromixer was purchased from Institut für Mikrotechnik Mainz GmbH (IMM). A micromixer constructed of stainless steel body had 40 μm mixing channels (silver) which were fabricated by means of the LIGA (Lithographie, Galvanoformung, Abformung) process. The introduction of two solutions to the mixer was performed by two syringe pumps, Harvard Model 11. DFT calculations were carried out at the B3LYP/6-31G(d) level using the Gaussian 98W, Revision A.7 (See Supporting Information).

Materials. Tetrabutylammonium tetrafluoroborate was purchased from TCI and dried at 50 °C/1 mmHg overnight before use. Dichloromethane was washed with water, distilled from P_2O_5, redistilled from dried K_2CO_3 to remove a trace amount of acid, and stored over molecular sieves 4A. THF was purchased from Kanto as a dehydrated solvent.

***N*-Methoxycarbonyl-*N*-(trimethylsilylmethyl)butylamine (1).** To a suspension of sodium hydride (60 wt % dispersion in mineral oil, 7.91 g, 197 mmol) in DMF (200 mL), *N*-(methoxycarbonyl)-butylamine (21.6 g, 165 mmol) was added at 0 °C. The mixture was stirred for 120 min at 60 °C and iodo(trimethylsilyl)methane (42.6 g, 199 mmol) was added at 0 °C. The reaction mixture was stirred for 14.5 h at 60 °C, and then poured into water (300 mL). The organic phase was separated and the aqueous phase was extracted with ether (300 mL × 3). The combined organic phase was dried over Na_2SO_4, and the solvent was removed to give the crude product. After purification with flash chromatography (hexane/ethyl acetate 10:1), the compound was further purified by distillation (120 °C, 20 mmHg) to obtain the title compound (36.0 g, 76%): $^tR = 6.92$ min (column, OV-17; 0.25 mm × 25 m; oven temperature, 100 °C; rate of temperature increase, 10 °C/min): TLC R_f 0.54 (hexane/ethyl acetate 5:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.03 (s, 9H), 0.90 (t, 3H, $J = 7.2$ Hz), 1.16–1.36 (m, 2H), 1.39–1.55 (m, 2H), 2.68 (s) and 2.72 (s) (total 2H, two rotamers), 3.06–3.26 (m, 2H), 3.64 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.8 and −1.6, 13.7, 19.8, 29.4 and 29.8, 37.9 and 38.6, 48.7 and 49.3, 51.9 and 52.3, 156.6. IR (neat) 2957, 1701, 1473, 1225 cm^{-1}. LRMS (EI) m/z 217 (M^+), 202 ($M^+ - CH_3$), 186 ($M^+ - OMe$), 158 ($M^+ - CO_2Me$). HRMS (EI) calcd for $C_{10}H_{23}NO_2Si$ (M^+): 217.1498, found: 217.1501.

***N*-Methoxycarbonyl-*N*-(trimethylsilylmethyl)-(*R*)-(−)-1-cyclohexylethylamine (7).** To a suspension of sodium hydride (60 wt % dispersion in mineral oil, 1.9 g, 47.0 mmol) in DMF (150 mL), *N*-(methoxycarbonyl)-(*R*)-(−)-1-cyclohexylethylamine (7.2 g, 39.0 mmol) was added at 0 °C. After being stirred for 60 min at room temperature, the reaction mixture was stirred for 3 h at 60 °C, and then iodo(trimethylsilyl)methane (10.1 g, 47.0 mmol) was added at 0 °C. After being stirred for 60 min at room temperature, the reaction mixture was stirred for 2 h at 60 °C, and then water (160 mL) was added at 0 °C. The organic phase was separated and the aqueous phase was extracted with ether (200 mL × 3). The combined organic phase was washed with water, dried over Na_2SO_4, and evaporated. Flash chromatography of the residue (hexane/ethyl acetate 50:1) afforded the title compound (7.1 g, 67%): TLC R_f 0.53 (hexane/ethyl acetate 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.03 (s) and 0.08 (s) (total 9H, two rotamers), 0.78–1.00 (m, 2H), 1.02–1.28 (m, 6H), 1.28–1.40 (m, 1H), 1.54–1.66 (m, 2H), 1.66–1.78 (m, 3H), 2.33 (s) and 2.35 (s) (total 1H, two rotamers), 2.49 (s) and 2.51 (s) (total 1H, two rotamers), 3.66 (s, 3H), 3.88 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ −1.9 and 0.80, 16.5 and 16.8, 26.0, 26.2 and 26.3, 29.9, 30.2 and 30.3, 33.2 and 33.8, 40.9 and 41.0, 51.8 and 52.4, 57.1 and 57.2, 157.1 and 157.3. IR (neat) 2932, 1700, 1460, 1246 cm^{-1}. LRMS (EI) m/z 271 (M^+), 256 ($M^+ - CH_3$), 240 ($M^+ - OMe$), 212 ($M^+ - CO_2Me$). HRMS (EI) calcd for $C_{14}H_{29}NO_2Si$ (M^+): 271.1968, found: 271.1972.

***N*-Methoxycarbonyl-2-trimethylsilylpyrrolidine.** To a solution of *N*-boc-2-trimethylsilylpyrrolidine (30.0 g, 0.123 mol), which was prepared as reported, in CH_2Cl_2 (500 mL) was added TFA (70.2 g, 0.616 mol) at 0 °C. The solution was stirred for 14 h at room temperature and dry Na_2CO_3 (117.4 g, 1.108 mol) was added slowly at 0 °C. The solution was stirred for 1 h at room temperature and methyl chlorocarbonate (20.9 g, 0.221 mol) was added at 0 °C. The mixture was stirred over night at room temperature. Water (100 mL) was added. The mixture was extracted with ether (150 mL × 3), and the organic phase was dried over $MgSO_4$. After removal of the solvent, the crude product was purified with flash column chromatography (hexane/ethyl acetate 25:1) and distillation (72.0 °C, 1.1 mmHg) to obtain the title compound (15.5 g, 63%): TLC R_f 0.37 (hexane/ethyl acetate 5:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.03 (s, 9H), 1.62–1.83 (m, 3H), 1.88–2.00 (m, 1H), 3.07–3.18 (m, 2H), 3.44–3.58 (m, 1H), 3.591 (s) and 3.594 (s) (total 3H, two rotamers). ^{13}C NMR (75 MHz, $CDCl_3$) δ −2.4, 25.6, 28.4, 47.1, 48.1, 51.8, 155.5. IR (neat) 1705, 1452, 1387, 841 cm^{-1}. LRMS (EI) m/z 201 (M^+), 186 ($M^+ - CH_3$), 142 ($M^+ - COOMe$), 128 ($M^+ - SiMe_3$). HRMS (EI) calcd for $C_9H_{19}NO_2Si$ (M^+): 201.1185, found: 201.1186; Anal. calcd for $C_9H_{19}NO_2Si$: C, 53.69; H, 9.51; N, 6.96%. found: C, 53.81; H, 9.75; N, 6.87%.

Genaration of *N*-Acyliminium Cation Pool 2. Typical Procedure: The anodic oxidation was carried out in an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon JF-20-P7, ca. 320 mg, dried at 250 °C/1 mmHg for 1 h before use) and a platinum plate cathode (60 mm × 30 mm). In the anodic chamber was placed a solution of **1** (610.3 mg, 2.81 mmol) in 0.3 M Bu_4NBF_4/CH_2Cl_2 (56.0 mL). In the cathodic chamber were placed 0.3 M Bu_4NBF_4/CH_2Cl_2 (56.0 mL) and trifluoromethanesulfonic acid (1.05 g, 7.00 mmol). Constant-current electrolysis (30 mA) was carried out at −78 °C with magnetic stirring until 2.5 F/mol of electricity was consumed.

NMR Analysis of Intermediate 8 in the Reaction of 2 with (*E*)-Diphenylethene. ^{1}H and ^{13}C NMR spectra were recorded in CD_2Cl_2 on a JEOL A-500 spectrometer. Chemical shifts were reported using methylene signals at δ 5.32 (^{1}H NMR) and δ 53.80 (^{13}C NMR) as standards. The anodic oxidation was carried out in a divided cell equipped with a carbon felt anode and a platinum plate cathode. In the anodic chamber was placed a solution of **8** (43.2 mg, 0.199 mmol) in 4.0 mL of 0.3 M Bu_4NBF_4/CD_2Cl_2. In the cathodic chamber were placed trifluoromethanesulfonic acid (75.7 mg, 0.504 mmol) and 0.3 M Bu_4NBF_4/CD_2Cl_2 (4.0 mL). Constant-current electrolysis (4.0 mA) was carried out at −78 °C with magnetic stirring. After 2.5 F/mol of electricity was consumed, to the *N*-Acyliminium ion pool **2** thus generated in the anodic chamber was added (*E*)-1,2-diphenylethene (53.8 mg, 0.298 mmol) in CD_2Cl_2 (0.75 mL) at −78 °C and the reaction mixture of the anodic chamber was transferred to a 5 mm NMR tube with a septum cap under Ar atmosphere at −78 °C. A NMR measurement was carried out at 0 °C: ^{1}H NMR (500 MHz, CD_2Cl_2, selected) δ 3.50–3.76 (m, 4H), 4.09 (s, 3H), 6.07 (d, $J = 11.0$ Hz, 1H). ^{13}C NMR (125 MHz, CD_2Cl_2, selected) δ

13.5, 20.0, 28.3, 43.2, 51.0, 51.5, 59.2, 88.4, 158.4. In the NMR spectra the other signals could not be assigned because of an overlap of the signals of Bu_4NBF_4 used as an electrolyte and (*E*)-1,2-diphenylethene.

General Procedure of Batch Mixing (Method A). To a cation pool (**2**, 10 mL, cooled at −78 °C) generated from **1** (0.500 mmol) was added a solution of an alkene (0.417 mmol) in CH_2Cl_2 (10 mL, cooled at −78 °C) by syringe pump (flow rate, 5.0 mL/min). After mixing, the reaction mixture was immediately quenched by the addition of Et_3N (1 mL) at the same temperature. Otherwise, after the reaction mixture was quickly warmed from −78 °C to X °C, the reaction mixture was stirred for 10 min at X °C. Et_3N (1 mL) was added at the same temperature to quench the reaction. The mixture was warmed to room temperature. The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (10 cm) of silica gel to remove Bu_4NBF_4. The silica gel was washed with ether (300 mL). The combined filtrate was concentrated to give a crude product, which was purified by flash chromatography.

General Procedure of Batch Mixing (Method B). To a solution of an alkene (0.417 mmol) in CH_2Cl_2 (10 mL, cooled at −78 °C) was added a cation pool (**2**, 10 mL, cooled at −78 °C) generated from **1** (0.500 mmol) by a syringe pump (flow rate, 5.0 mL/min) (The solutions of **2** were quickly transferred to a syringe, which were kept cool with dry ice, and immediately introduced to a mixer cooled at −78 °C. Decomposition of **2** was thus avoided.). Immediately after mixing, the reaction was quenched by the addition of Et_3N (1 mL) at the same temperature. The mixture was warmed to room temperature. The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (10 cm) of silica gel to remove Bu_4NBF_4. The silica gel was washed with ether (300 mL). The combined filtrate was concentrated to give a crude product, which was purified by flash chromatography.

General Procedure of Batch Mixing (Method C). A solution of an alkene (0.417 mmol) in CH_2Cl_2 (10 mL, cooled at −78 °C) and a cation pool (**2**, 10 mL, cooled at −78 °C) generated from **1** (0.500 mmol) were simultaneously introduced to the reaction vessel using syringe pumps (flow rate of 5.0 mL/min). Immediately after mixing, the reaction was quenched by the addition of Et_3N (1 mL) at the same temperature. The mixture was warmed to room temperature. The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (10 cm) of silica gel to remove Bu_4NBF_4. The silica gel was washed with ether (300 mL). The combined filtrate was concentrated to give a crude product, which was purified by flash chromatography.

General Procedure of Micromixing. A solution of an alkene (0.417 mmol) in CH_2Cl_2 (10 mL, cooled at −78 °C) and a cation pool (**2**, 10 mL, cooled at −78 °C) generated from **1** (0.500 mmol) were simultaneously introduced to the micromixer (channel width = 40 μm), which was dipped in a coolant at −78 °C, using syringe pumps (flow rate is 5.0 mL/min). Then, the reaction mixture coming out from the outlet of the micromixer was collected with a round-bottom flask, and immediately quenched by Et_3N (1 mL) at −78 °C. The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (10 cm) of silica gel to remove Bu_4NBF_4. The silica gel was washed with ether (300 mL). The combined filtrate was concentrated to give a crude product, which was purified by flash chromatography.

3-Butyl-6-decylperhydro-1,3-oxazin-2-one. Prepared from **1** (10.0 mL, 0.499 mmol) and 1-dodecene (71.4 mg, 0.424 mmol) by Method A (X = 0 °C): Isolated yield 72% (91.3 mg, purified with flash chromatography, hexane/ethyl acetate 6:1): TLC R_f 0.61 (hexane/ethyl acetate 3:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 3H, J = 6.8 Hz), 0.93 (d, 3H, J = 7.4 Hz), 1.18–1.39 (m, 17H), 1.41–1.62 (m, 4H), 1.62–1.85 (m, 2H), 1.90–2.03 (m, 1H), 3.20–3.42 (m, 4H), 4.10–4.24 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, Some of the ^{13}C NMR signals overlapped) δ 13.8, 14.1, 19.9, 22.6, 24.7, 27.2, 29.1, 29.2, 29.4, 29.4, 29.5, 29.5, 31.8, 34.9, 44.4, 49.0, 76.9, 153.7. IR (neat) 2923, 1688, 1667, 1487 cm^{-1}. LRMS (EI) m/z 297 (M^+), 282 ($M^+ - Me$), 254 ($M^+ - C_3H_7$), 240 ($M^+ - C_4H_9$). HRMS (EI) calcd for $C_{18}H_{35}NO_2$ (M^+): 297.2668, found: 297.2664.

3-Butyl-*trans*-5,6-dimethylperhydro-1,3-oxazin-2-one.[17] Prepared from **1** (10.0 mL, 0.491 mmol) and (*E*)-2-butene (23.3 mg, 0.415 mmol) by Method A (X = −27 °C): Isolated yield 68% (52.5 mg, purified with flash chromatography, hexane/ethyl acetate 3:1): TLC R_f 0.21 (hexane/ethyl acetate 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.93 (t, 3H, J = 7.4 Hz), 0.98 (d, 3H, J = 6.9 Hz), 1.33 (tq, 2H, J = 7.4 Hz, J = 7.4 Hz), 1.34 (d, 3H, J = 6.3 Hz), 1.45–1.65 (m, 2H), 1.70–1.95 (m, 1H), 2.98 (dd, 1H, J = 10.7 Hz, J = 11.6 Hz), 3.18 (dd, 1H, J = 5.6 Hz, J = 11.9 Hz), 3.20–3.45 (m, 2H), 3.98 (dq, 1H, J = 9.5 Hz, J = 6.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.7, 14.0, 18.7, 19.8, 29.0, 33.1, 48.7, 51.5, 78.2, 153.5. IR (neat) 2961, 1694, 1491, 1248 cm^{-1}. LRMS (EI) m/z 185 (M^+), 170 ($M^+ - Me$), 142 ($M^+ - C_3H_7$). HRMS (EI) calcd for $C_{10}H_{19}NO_2$ (M^+): 185.1416, found: 185.1415.

3-Butyl-*cis*-5,6-dimethylperhydro-1,3-oxazin-2-one.[17] Prepared from **1** (10.0 mL, 0.503 mmol) and (*Z*)-2-butene (23.5 mg, 0.419 mmol) by Method A (X = −27 °C): Isolated yield 65% (50.2 mg, purified with flash chromatography, hexane/ethyl acetate 3:1): TLC R_f 0.21 (hexane/ethyl acetate 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, 3H, J = 7.4 Hz), 1.02 (d, 3H, J = 7.2 Hz), 1.28 (d, 3H, J = 6.6 Hz), 1.33 (tq, 2H, J = 7.5 Hz, J = 7.5 Hz), 1.45–1.53 (m, 2H), 2.09–2.22 (m, 1H), 3.01 (dd, 1H, J = 5.3 Hz, J = 11.6 Hz), 3.20–3.40 (m, 2H), 3.40 (dd, 1H, J = 5.1 Hz, J = 11.4 Hz), 4.43 (dq, 1H, J = 3.0 Hz, J = 6.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.5, 13.7, 16.4, 19.8, 28.9, 29.9, 48.9, 50.6, 75.4, 153.1. IR (neat) 2961, 1694, 1491, 1237 cm^{-1}. LRMS (EI) m/z 185 (M^+), 170 ($M^+ - Me$), 156 ($M^+ - C_2H_5$), 142 ($M^+ - C_3H_7$), 128 ($M^+ - C_4H_9$). HRMS (EI) calcd for $C_{10}H_{19}NO_2$ (M^+): 185.1416, found: 185.1416.

3-Butyl-5,6-*cis*-tetramethyleneperhydro-1,3-oxazin-2-one.[18] Prepared from **1** (10.0 mL, 0.507 mmol) and cyclohexene (34.7 mg, 0.423 mmol) by Method A (X = 0 °C): Isolated yield 84% (75.1 mg, purified with flash chromatography, hexane/ethyl acetate 1:1): TLC R_f 0.32 (hexane/ethyl acetate 1:2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, 3H, J = 7.3 Hz), 1.27 (tq, 2H, J = 7.4 Hz, J = 7.4 Hz), 1.36–1.62 (m, 8H), 1.80–1.98 (m, 2H), 2.88 (dd, 1H, J = 2.0 Hz, J = 11.8 Hz), 3.12–3.35 (m, 2H), 3.42 (dd, 1H, J = 5.0 Hz, J = 11.3 Hz), 4.38 (d, 1H, J = 3.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.7, 19.3, 19.7, 24.1, 24.6, 28.9, 29.8, 32.1, 48.7, 50.1, 74.6, 153.3. IR (neat) 2934, 1686, 1489, 1233 cm^{-1}. LRMS (EI) m/z 211 (M^+), 196 ($M^+ - Me$), 168 ($M^+ - C_3H_7$). HRMS (EI) calcd for $C_{12}H_{21}NO_2$ (M^+): 211.1572, found: 211.1574.

3-Butyl-6-trimethylsilylperhydro-1,3-oxazin-2-one. Prepared from **1** (10.0 mL, 0.491 mmol) and trimethyl(vinyl)silane (40.2 mg, 0.401 mmol) by Method A (X = 0 °C): Isolated yield 86% (79.3 mg, purified with flash chromatography, hexane/ethyl acetate 3:1): TLC R_f 0.49 (hexane/ethyl acetate 1:1). ^{1}H NMR

(300 MHz, $CDCl_3$) δ 0.07 (s, 9H), 0.89 (t, 3H, $J = 7.2$ Hz), 1.29 (tq, 2H, $J = 7.5$ Hz, $J = 7.5$ Hz), 1.43–1.64 (m, 2H), 1.87–2.04 (m, 2H), 3.12–3.28 (m, 2H), 3.29–3.48 (m, 2H), 3.91 (dd, 1H, $J =$ 4.1 Hz, $J = 10.7$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.4, 13.8, 19.9, 23.5, 29.1, 46.5, 49.3, 71.8, 154.8. IR (neat) 2957, 1684, 1456, 1250 cm^{-1}. LRMS (EI) m/z 229 (M^+), 214 ($M^+ - Me$), 186 ($M^+ - C_3H_7$). HRMS (EI) calcd for $C_{11}H_{23}NO_2Si$ (M^+): 229.1498, found: 229.1493.

6-Acetoxy-3-butylperhydro-1,3-oxazin-2-one. Prepared from **1** (10.0 mL, 0.491 mmol) and vinyl acetate (35.4 mg, 0.411 mmol) by Method A (X = 0 °C): GC yield 81% (72.0 mg, ^tR 16.7 min, column, OV-1; 0.80 mm × 1 m; oven temperature, 100 °C; rate of temperature increase, 10 °C/min): TLC R_f 0.48 (hexane/ethyl acetate 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (t, 3H, $J = 7.2$ Hz), 1.29 (tq, 2H, $J = 7.5$ Hz, $J = 7.5$ Hz), 1.53–1.68 (m, 2H), 1.96–2.10 (m, 1H), 2.12 (s, 3H), 2.13–2.28 (m, 1H), 3.18–3.32 (m, 1H), 3.37 (dt, 2H, $J = 4.5$ Hz, $J = 7.2$ Hz), 3.55 (dt, 1H, $J = 4.8$ Hz, $J = 14.0$ Hz), 6.48 (dd, 1H, $J =$ 3.6 Hz, $J = 4.2$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.7, 19.7, 20.8, 25.3, 28.9, 40.3, 49.3, 90.2, 150.6, 168.6. IR (neat) 2959, 1759, 1718, 1491 cm^{-1}. LRMS (EI) m/z 215 (M^+), 172 ($M^+ - C_3H_7$), 156 ($M^+ - CH_3CO_2$). HRMS (EI) calcd for $C_{10}H_{17}NO_4$ (M^+): 215.1158, found: 215.1157.

4-Butyl-2-oxa-4-aza-*cis*-bicyclo[4.4.0]dec-9-en-3-one. Prepared from **1** (10.0 mL, 0.507 mmol) and 1,3-cyclohexadiene (33.9 mg, 0.423 mmol) by Method A (X = 0 °C): Isolated yield 70% (61.9 mg, purified with flash chromatography, hexane/ethyl acetate 1:1): TLC R_f 0.32 (hexane/ethyl acetate 1:2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.93 (t, 3H, $J = 7.4$ Hz), 1.33 (tq, 2H, $J =$ 7.4 Hz, $J = 7.4$ Hz), 1.48–1.70 (m, 3H), 1.71–1.89 (m, 1H), 2.10–2.24 (m, 3H), 3.10 (dd, 1H, $J = 4.2$ Hz, $J = 12.0$ Hz), 3.21–3.40 (m, 2H), 3.50 (dd, 1H, $J = 5.6$ Hz, $J = 12.2$ Hz), 4.73 (d, 1H, $J =$ 4.1 Hz), 5.80–5.90 (m, 1H), 5.92–6.04 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 19.8, 21.5, 24.0, 29.1, 30.1, 48.5, 49.0, 72.1, 124.6, 132.1, 152.6. IR (neat) 2957, 1699, 1487, 1244 cm^{-1}. LRMS (EI) m/z 209 (M^+), 180 ($M^+ - C_2H_5$), 166 ($M^+ - C_3H_7$). HRMS (EI) calcd for $C_{12}H_{19}NO_2$ (M^+): 209.1416, found: 209.1416.

3-Butyl-*trans*-5,6-diphenylperhydro-1,3-oxazin-2-one. Prepared from **1** (10.0 mL, 0.496 mmol) and (*E*)-1,2-diphenylethene (76.0 mg, 0.422 mmol) by Method A (X = 0 °C): Isolated yield 87% (113.7 mg, purified with flash chromatography, hexane/ethyl acetate 3.5:1): TLC R_f 0.57 (hexane/ethyl acetate 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (t, 3H, $J = 7.4$ Hz), 1.37 (tq, 2H, $J =$ 7.5 Hz, $J = 7.5$ Hz), 1.57–1.72 (m, 2H), 3.23–3.61 (m, 4H), 3.68 (dd, 2H, $J = 11.0$ Hz, $J = 11.9$ Hz), 5.34 (d, 1H, $J = 9.6$ Hz), 7.01–7.29 (m, 10H). ^{13}C NMR (125.65 MHz, $CDCl_3$, Some of the ^{13}C NMR signals overlapped) δ 13.8, 19.9, 29.1, 45.9, 49.2, 51.0, 83.0 and 83.1, 126.7, 127.6, 128.0, 128.2, 128.7, 136.7, 137.3, 153.2. IR (KBr) 2963, 1690, 1482, 1238 cm^{-1}. LRMS (FAB) m/z 310 (MH^+). HRMS (FAB) calcd for $C_{20}H_{25}NO_2$ (MH^+): 310.1807, found: 310.1807. X-ray data: $C_{20}H_{23}NO_2'$, MW = 309.41, monoclinic, space group $P2_1/c$ (No. 14), $a =$ 10.1579(8) Å, $b = 10.7574(8)$ Å, $c = 16.195(2)$ Å, $V =$ 1723.1(2) Å^3, $Z = 4$, $Dc = 1.193$ g/cm^3, $\mu = 0.76$ cm^{-1}. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The data were collected at 23 ± 1 °C to a maximum 2θ value of 55.0°. A total of 14787 reflections were collected. The structure was solved by direct methods and expanded using the Fourier technique. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included, but not refined.

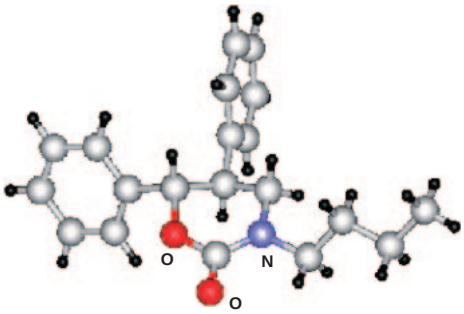


Fig. 3. The molecular structure of 3-butyl-*trans*-5,6-diphenylperhydro-1,3-oxazin-2-one.

The final cycle of full-matrix least-squares refinement on F was based on 2013 observed reflections ($I > 3.00\sigma(I)$) and 244 variable parameters, and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of $R = 0.055$ ($R_W = 0.112$). The standard deviation of an observation of unit weight was 2.41. The calculation was performed using the CrystalStructure crystallographic software package (Fig. 3). Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-275680. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

3-Butyl-*cis*-5,6-diphenylperhydro-1,3-oxazin-2-one. Prepared from **1** (10.0 mL, 0.495 mmol) and (*Z*)-1,2-diphenylethene (73.1 mg, 0.406 mmol) by Method A (X = 0 °C): Isolated yield 80% (95.9 mg, purified with flash chromatography, hexane/ethyl acetate 1:1)(cis/trans 55:45 by ^{1}H NMR): TLC R_f 0.57 (hexane/ethyl acetate 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97 (t, 3H, $J =$ 7.4 Hz), 1.40 (tq, 2H, $J = 7.4$ Hz, $J = 7.4$ Hz), 1.57–1.76 (m, 2H), 3.42–3.62 (m, 4H), 3.72 (t, 1H, $J = 7.1$ Hz), 5.62 (d, 1H, $J =$ 3.0 Hz), 6.78–6.95 (m, 4H), 7.09–7.30 (m, 6H). ^{13}C NMR (125.65 MHz, $CDCl_3$, Some of the ^{13}C NMR signals overlapped) δ 13.9, 20.1, 29.0, 43.1, 48.7, 49.4, 80.8, 126.2, 127.8, 128.3, 128.5, 136.4, 136.4, 153.4. IR (KBr) 2957, 1680, 1497, 1264 cm^{-1}. LRMS (EI) m/z 309 (M^+), 266 ($M^+ - C_3H_7$). HRMS (EI) calcd for $C_{20}H_{25}NO_2$ (M^+): 309.1729, found: 309.1726.

3-Butyl-*trans*-5-methyl-6-phenylperhydro-1,3-oxazin-2-one. Prepared from **1** (10.0 mL, 0.496 mmol) and (*E*)-1-phenyl-1-propene (49.1 mg, 0.415 mmol) by Method A (X = 0 °C): Isolated yield 88% (90.6 mg, purified with flash chromatography, hexane/ethyl acetate 3:1): TLC R_f 0.49 (hexane/ethyl acetate 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.83 (d, 3H, $J = 6.9$ Hz), 0.96 (t, 3H, $J = 7.4$ Hz), 1.36 (tq, 2H, $J = 7.5$ Hz, $J = 7.5$ Hz), 1.50–1.73 (m, 2H), 2.17–2.36 (m, 1H), 3.12 (dd, 1H, $J = 11.6$ Hz, $J = 10.4$ Hz), 3.18–3.50 (m, 3H), 4.80 (d, 1H, $J = 9.6$ Hz), 7.28–7.42 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 14.2, 19.9, 29.1, 33.4, 49.0, 51.5, 84.2, 126.8, 128.4, 128.5, 137.6, 153.4. IR (KBr) 2956, 1676, 1483, 1256 cm^{-1}. LRMS (EI) m/z 247 (M^+), 232 ($M^+ - Me$), 204 ($M^+ - C_3H_7$). HRMS (EI) calcd for $C_{15}H_{21}NO_2$ (M^+): 247.1572, found: 247.1575.

3-Butyl-*cis*-5-methyl-6-phenylperhydro-1,3-oxazin-2-one. Prepared from **1** (10.0 mL, 0.493 mmol) and (*Z*)-1-phenyl-1-propene (48.9 mg, 0.414 mmol) by Method A (X = 0 °C): Isolated yield 83% (85.4 mg, purified with flash chromatography, hexane/ethyl acetate 3:1) (cis/trans 56:44 by ^{1}H NMR): TLC R_f 0.49 (hexane/ethyl acetate 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ

0.85 (d, 3H, $J = 7.2$ Hz), 0.96 (t, 3H, $J = 7.4$ Hz), 1.37 (tq, 2H, $J = 7.4$ Hz, $J = 7.4$ Hz), 1.50–1.73 (m, 2H), 2.35–2.48 (m, 1H), 3.05 (dd, 1H, $J = 11.7$ Hz, $J = 3.6$ Hz), 3.25–3.50 (m, 2H), 3.60 (dd, 1H, $J = 11.6$ Hz, $J = 5.0$ Hz), 5.40 (d, 1H, $J = 2.7$ Hz), 7.28–7.42 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.3, 13.8, 19.9, 29.0, 31.5, 49.1, 50.1, 80.2, 125.5, 127.7, 128.2, 137.5, 153.0. IR (KBr) 2961, 1689, 1489, 1279 cm^{-1}. LRMS (EI) m/z 247 (M^+), 232 ($M^+ - Me$), 204 ($M^+ - C_3H_7$). HRMS (EI) calcd for $C_{15}H_{21}NO_2$ (M^+): 247.1572, found: 247.1573.

3-Butyl-6-(*p*-trifluoromethylphenyl)perhydro-1,3-oxazin-2-one. Prepared from **1** (10.0 mL, 0.503 mmol) and *p*-(trifluoromethyl)styrene (73.8 mg, 0.429 mmol) by Method A (X = 0 °C): Isolated yield 63% (80.9 mg, purified with flash chromatography, hexane/ethyl acetate 2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (t, 3H, $J = 7.5$ Hz), 1.23–1.42 (m, 2H), 1.49–1.70 (m, 2H), 2.01–2.17 (m, 1H), 2.21–2.36 (m, 1H), 3.22–3.55 (m, 4H), 5.35 (dd, 1H, $J = 1.8$ Hz, $J = 9.9$ Hz), 7.49 (s) and 7.52 (s) (2H), 7.62 (s) and 7.65 (s) (2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.6, 19.8, 28.9, 29.5, 44.0, 49.1, 77.1, 125.39, 125.43, 125.8, 143.0, 152.9. IR (KBr) 2965, 1682, 1489, 1329 cm^{-1}. LRMS (EI) m/z 301 (M^+), 282 ($M^+ - F$), 258 ($M^+ - C_3H_7$). HRMS (EI) calcd for $C_{15}H_{18}F_3NO_2$ (M^+): 301.1290, found: 301.1287.

3-Butyl-6-octyl-3,4-dihydro-2*H*-1,3-oxazin-2-one. Prepared from **1** (10.0 mL, 0.503 mmol) and 1-octyne (46.8 mg, 0.425 mmol) by Method A (X = 0 °C): Isolated yield 64% (64.6 mg, purified with flash chromatography, hexane/ethyl acetate 15:1): TLC R_f 0.32 (hexane/ethyl acetate 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 3H, $J = 7.2$ Hz), 0.94 (t, 3H, $J = 7.2$ Hz), 1.20–1.65 (m, 12H), 2.09 (dt, 2H, $J = 0.9$ Hz, $J = 7.5$ Hz), 3.34 (dd, 2H, $J = 8.6$ Hz, $J = 7.5$ Hz), 3.49–3.68 (m, 2H), 4.78 (t, 2H, $J = 3.2$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 14.0, 19.9, 22.5, 25.9, 28.3, 28.6, 31.5, 32.3, 45.2, 48.6, 93.6, 150.7, 151.8. IR (neat) 2957, 1725, 1456, 1173 cm^{-1}. LRMS (EI) m/z 239 (M^+), 238 ($M^+ - H$). HRMS (EI) calcd for $C_{14}H_{25}NO_2$ (M^+): 239.1885, found: 239.1883.

3-Butyl-6-pheny-3,4-dihydro-2*H*-1,3-oxazin-2-one. Prepared from **1** (10.0 mL, 0.500 mmol) and phenylacetylene (43.0 mg, 0.421 mmol) by Method A (X = 0 °C): Isolated yield 46% (44.6 mg, purified with flash chromatography, hexane/ethyl acetate 10:1): TLC R_f 0.76 (hexane/ethyl acetate 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (t, 3H, $J = 7.2$ Hz), 1.38 (dd, 2H, $J = 7.4$ Hz, $J = 7.4$ Hz), 1.57–1.70 (m, 2H), 3.41 (dd, 2H, $J = 6.6$ Hz, $J = 8.4$ Hz), 4.01 (d, 2H, $J = 3.3$ Hz), 5.56 (t, 1H, $J = 3.6$ Hz), 7.34–7.43 (m, 3H), 7.57–7.69 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 19.9, 28.4, 45.5, 48.7, 65.8, 94.1, 124.5, 128.4, 129.1, 131.7, 148.8, 150.4. IR (neat) 2959, 1723, 1449, 1227 cm^{-1}. LRMS (EI) m/z 231 (M^+), 203 ($M^+ - CO$), 187 ($M^+ - CO_2$). HRMS (EI) calcd for $C_{14}H_{17}NO_2$ (M^+): 231.1259, found: 231.1258.

3-Butyl-6-(trimethylsilyl)-3,4-dihydro-2*H*-1,3-oxazin-2-one. Prepared from **1** (10.0 mL, 0.504 mmol) and (trimethylsilyl)acetylene (41.2 mg, 0.419 mmol) by Method A (X = 0 °C): Isolated yield 90% (85.5 mg, purified with flash chromatography, hexane/ethyl acetate 10:1): TLC R_f 0.69 (hexane/ethyl acetate 3:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.16 (s, 9H), 0.94 (t, 3H, $J = 7.2$ Hz), 1.35 (tq, 2H, $J = 7.6$ Hz, $J = 7.6$ Hz), 1.52–1.66 (m, 2H), 3.33 (dd, 2H, $J = 6.6$ Hz, $J = 8.4$ Hz), 3.85 (d, 2H, $J = 3.3$ Hz), 5.25 (t, 1H, $J = 3.5$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 3.1, 13.7, 19.8, 28.2, 45.7, 48.7, 108.5, 150.8, 158.0. IR (neat) 2959, 1717, 1483, 1250 cm^{-1}. LRMS (EI) m/z 227 (M^+), 212 ($M^+ - Me$), 199 ($M^+ - CO$). HRMS (EI) calcd for $C_{11}H_{21}NO_2Si$ (M^+): 227.1342, found: 227.1342.

3-Butyl-5,6-diphenyl-3,4-dihydro-2*H*-1,3-oxazin-2-one. Prepared from **1** (10.0 mL, 0.496 mmol) and diphenylacetylene (73.5 mg, 0.412 mmol) by Method A (X = 0 °C): Isolated yield 48% (64.0 mg, purified with flash chromatography, hexane/ethyl acetate 10:1): TLC R_f 0.47 (hexane/ethyl acetate 3:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.97 (t, 3H, $J = 7.6$ Hz), 1.41 (tq, 2H, $J = 7.6$ Hz, $J = 7.6$ Hz), 1.64–1.71 (m, 2H), 3.47 (t, 2H, $J = 7.6$ Hz), 4.20 (s, 2H), 7.08–7.35 (m, 10H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.8, 20.0, 28.5, 48.6, 50.6, 109.4, 127.7, 127.8, 128.66, 128.74, 128.79, 132.2, 135.8, 145.3, 150.5. IR (neat) 3060, 2959, 1728, 1447 cm^{-1}. LRMS (EI) m/z 307 (M^+). HRMS (EI) calcd for $C_{20}H_{21}NO_2$ (M^+): 307.1572, found: 307.1574.

3-Butyl-5,6-dimethyl-3,4-dihydro-2*H*-1,3-oxazin-2-one. Prepared from **1** (10.0 mL, 0.496 mmol) and 2-butyne (46.3 mg, 0.421 mmol) by Method A (X = 0 °C): Isolated yield 64% (64.0 mg, purified with flash chromatography, hexane/ethyl acetate 10:1): TLC R_f 0.50 (hexane/ethyl acetate 3:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.89 (t, 3H, $J = 6.8$ Hz), 0.90 (t, 3H, $J = 7.6$ Hz), 0.92 (t, 3H, $J = 7.6$ Hz), 1.33 (tq, 2H, $J = 7.6$ Hz, $J = 7.6$ Hz), 1.39 (tq, 2H, $J = 7.6$ Hz, $J = 7.6$ Hz), 1.50–1.61 (m, 4H), 1.96 (t, 2H, $J = 7.6$ Hz), 2.11 (t, 2H, $J = 7.5$ Hz), 3.32 (t, 2H, $J = 8.3$ Hz), 3.68 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.6, 13.7, 13.8, 19.9, 20.1, 21.0, 28.4, 30.5, 30.7, 48.29, 48.34, 105.6, 145.9, 151.2. IR (neat) 3337, 2963, 1725, 1466 cm^{-1}. LRMS (EI) m/z 239 (M^+), 224 ($M^+ - Me$), 196 ($M^+ - C_3H_7$). HRMS (EI) calcd for $C_{14}H_{25}NO_2$ (M^+): 239.1889, found: 239.1885.

3-Butyl-6-phenylperhydro-1,3-oxazin-2-one.[19] Prepared from **1** (10.0 mL, 0.492 mmol) and styrene (43.2 mg, 0.414 mmol) by Method A: Isolated yield 57% (55.3 mg, purified with flash chromatography, hexane/ethyl acetate 2:1) with polymeric product (15.5 mg, 35% yield based on styrene, purified with gel permeation chromatography): Prepared from **1** (10.0 mL, 0.492 mmol) and styrene (43.2 mg, 0.414 mmol) by Method B: Isolated yield 20% (19.4 mg, purified with flash chromatography, hexane/ethyl acetate 2:1) with polymeric product (43.3 mg, 98% yield based on styrene, purified with gel permeation chromatography): Prepared from **1** (10.0 mL, 0.497 mmol) and styrene (43.1 mg, 0.414 mmol) by Method C: Isolated yield 55% (53.0 mg, purified with flash chromatography, hexane/ethyl acetate 2:1) with polymeric product (24.5 mg, 56% yield based on styrene, purified with gel permeation chromatography): Prepared from **1** (10.0 mL, 0.491 mmol) and styrene (45.3 mg, 0.435 mmol) by micromixing: Isolated yield 79% (79.8 mg, purified with flash chromatography, hexane/ethyl acetate 2:1) with polymeric product (10.1 mg, 23% yield based on styrene, purified with gel permeation chromatography): TLC R_f 0.32 (hexane/ethyl acetate 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (t, 3H, $J = 6.3$ Hz), 1.35 (tq, 2H, $J = 7.4$ Hz, $J = 7.4$ Hz), 1.52–1.69 (m, 2H), 2.02–2.34 (m, 2H), 3.21–3.52 (m, 4H), 5.28 (dd, 1H, $J = 2.7$ Hz, $J = 9.6$ Hz), 7.25–7.42 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 19.9, 29.1, 29.6, 44.2, 49.2, 77.9, 125.5, 128.2, 128.5, 139.0, 153.4.

3-Butyl-6-*p*-chlorophenylperhydro-1,3-oxazin-2-one. Prepared from **1** (10.0 mL, 0.500 mmol) and *p*-chlorostyrene (60.9 mg, 0.440 mmol) by Method A: Isolated yield 43% (50.1 mg, purified with flash chromatography, hexane/ethyl acetate 2:1) with polymeric product (39.2 mg, 64% yield based on *p*-chlorostyrene, purified with gel permeation chromatography): Prepared from **1** (10.0 mL, 0.500 mmol) and *p*-chlorostyrene (60.9 mg, 0.440 mmol) by Method B: Isolated yield 12% (14.6 mg, purified with flash chromatography, hexane/ethyl acetate 2:1) with polymeric product (50.9 mg, 83% yield based on *p*-chlorostyrene, purified

with gel permeation chromatography): Prepared from **1** (10.0 mL, 0.500 mmol) and *p*-chlorostyrene (60.9 mg, 0.440 mmol) by Method C: Isolated yield 54% (63.3 mg, purified with flash chromatography, hexane/ethyl acetate 2:1) with polymeric product (34.1 mg, 56% yield based on *p*-chlorostyrene, purified with gel permeation chromatography): Prepared from **1** (10.0 mL, 0.500 mmol) and *p*-chlorostyrene (60.9 mg, 0.440 mmol) by micromixing: Isolated yield 70% (82.1 mg, purified with flash chromatography, hexane/ethyl acetate 2:1) with polymeric product (25.4 mg, 42% yield based on *p*-chlorostyrene, purified with gel permeation chromatography). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, 3H, $J = 7.4$ Hz), 1.34 (tq, 2H, $J = 7.4$ Hz, $J = 7.4$ Hz), 1.49–1.70 (m, 2H), 1.89–2.17 (m, 1H), 2.18–2.28 (m, 1H), 3.20–3.52 (m, 4H), 5.25 (dd, 1H, $J = 2.9$ Hz, $J = 10.1$ Hz), 7.28–7.39 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.7, 19.8, 29.0, 29.5, 44.0, 49.1, 77.2, 126.9, 128.6, 133.9, 137.6, 153.0. IR (KBr) 2959, 1678, 1489, 1096 cm^{-1}. LRMS (EI) m/z 267 (M^+), 252 ($M^+ - Me$), 224 ($M^+ - C_3H_7$), 210 ($M^+ - C_4H_9$). HRMS (EI) calcd for $C_{14}H_{18}ClNO_2$ (M^+): 267.1026, found: 267.1024.

3-Butyl-6-(*p*-methylphenyl)perhydro-1,3-oxazin-2-one. Prepared from **1** (10.0 mL, 0.504 mmol) and *p*-methylstyrene (50.6 mg, 0.428 mmol) by Method A: Isolated yield 45% (47.4 mg, purified with flash chromatography, hexane/ethyl acetate 3:1) with polymeric product (39.5 mg, 78% yield based on *p*-methylstyrene, purified with gel permeation chromatography): Prepared from **1** (10.0 mL, 0.503 mmol) and *p*-methylstyrene (50.4 mg, 0.426 mmol) by Method B: Isolated yield 16% (16.5 mg, purified with flash chromatography, hexane/ethyl acetate 3:1) with polymeric product (50.8 mg, 100% yield based on *p*-methylstyrene, purified with gel permeation chromatography): Prepared from **1** (10.0 mL, 0.503 mmol) and *p*-methylstyrene (50.4 mg, 0.426 mmol) by Method C: Isolated yield 58% (60.9 mg, purified with flash chromatography, hexane/ethyl acetate 3:1) with polymeric product (43.0 mg, 85% yield based on *p*-methylstyrene, purified with gel permeation chromatography): Prepared from **1** (10.0 mL, 0.503 mmol) and *p*-methylstyrene (50.4 mg, 0.426 mmol) by micromixing: Isolated yield 66% (69.3 mg, purified with flash chromatography, hexane/ethyl acetate 3:1) with polymeric product (24.5 mg, 49% yield based on *p*-methylstyrene, purified with gel permeation chromatography). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97 (t, 3H, $J = 7.5$ Hz), 1.37 (tq, 2H, $J = 7.5$ Hz, $J = 7.5$ Hz), 1.52–1.71 (m, 2H), 2.05–2.33 (m, 2H), 2.38 (s, 3H), 3.21–3.52 (m, 4H), 5.28 (dd, 1H, $J = 3.0$ Hz, $J = 9.6$ Hz), 7.17–7.32 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 19.9, 21.1, 29.1, 29.6, 44.2, 49.2, 77.9, 125.5, 129.2, 136.1, 138.0, 153.5. IR (KBr) 2957, 1682, 1495, 1460 cm^{-1}. LRMS (EI) m/z 247 (M^+), 232 ($M^+ - Me$), 204 ($M^+ - C_3H_7$). HRMS (EI) calcd for $C_{15}H_{21}NO_2$ (M^+): 247.1572, found: 247.1574.

3-((*R*)-(−)-1-cyclohexylethyl)-*trans*-5,6-dipropyl-perhydro-1,3-oxazin-2-one. Prepared from **7** (113.6 mg, 0.418 mmol) and *trans*-4-octene (114.1 mg, 1.017 mmol) by Method A (X = 0 °C): Isolated yield 50% (62.4 mg, purified with flash chromatography, hexane/ethyl acetate 5:1). This compound was characterized as a mixture of two diastereomers (3.3:1 by ^{1}H NMR): TLC R_f 0.20 (hexane/ethyl acetate 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.82–1.78 (m, 26H), 1.09 (d, $J = 6.9$ Hz) and 1.10 (d, $J = 6.9$ Hz) (total 3H, two diastereomers), 2.66 (dd, $J = 9.7$ Hz, $J = 11.7$ Hz) and 2.79 (dd, $J = 8.9$ Hz, $J = 13.3$ Hz) (total 1H, two diastereomers), 3.08 (dd, $J = 4.8$ Hz, $J = 11.6$ Hz) and 3.18 (dd, $J = 4.9$ Hz, $J = 11.7$ Hz) (total 1H, two diastereomers), 3.82–3.93 (m, 1H), 3.95–4.06 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.8, 13.95 and 14.0, 15.3 and 15.6, 17.6 and 17.7, 19.7, 25.78 and 25.84, 26.0, 26.1, 29.74 and 29.88, 29.91 and 30.01, 31.5, 34.6 and 35.0, 35.1 and 35.5, 39.7 and 40.0, 42.8 and 43.0, 56.2 and 56.3, 80.0, 153.5 and 153.7. IR (neat) 2930, 1682, 1489, 1435 cm^{-1}. LRMS (EI) m/z 295 (M^+). HRMS (EI) calcd for $C_{18}H_{33}NO_2$ (M^+): 295.2511, found: 295.2518.

3-((*R*)-(−)-1-cyclohexylethyl)-*cis*-5,6-dipropyl-perhydro-1,3-oxazin-2-one. Prepared from **7** (113.0 mg, 0.416 mmol) and *cis*-4-octene (120.4 mg, 1.073 mmol) by Method A (X = 0 °C): Purified with flash chromatography (hexane/ethyl acetate 3:1) to give two diastereomers (total 105.9 mg, 86%, diastereomer ratio was 1.1:1).

The major diastereomer (56.2 mg, 46%): TLC R_f 0.73 (hexane/ethyl acetate 1:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.91 (t, 6H, $J = 6.8$ Hz), 1.04–1.45 (m, 12H), 1.11 (d, 3H, $J = 6.8$ Hz), 1.50–1.64 (m, 4H), 1.64–1.75 (m, 3H), 1.90–1.99 (m, 1H), 2.89 (dd, 1H, $J = 6.2$ Hz, $J = 11.7$ Hz), 3.12 (dd, 1H, $J = 4.8$ Hz, $J = 11.7$ Hz), 4.01 (dq, 1H, $J = 10.3$ Hz, $J = 6.9$ Hz), 4.18 (dt, 1H, $J = 8.9$ Hz, $J = 4.9$ Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.8, 14.0, 15.5, 18.7, 20.2, 25.8, 26.0, 26.1, 28.2, 29.9, 30.0, 32.2, 34.3, 39.8, 42.0, 56.4, 78.4, 153.4. IR (neat) 2932, 1682, 1489, 1435 cm^{-1}. LRMS (EI) m/z 295 (M^+), 252 ($M^+ - C_3H_7$), 212 ($M^+ - C_6H_{11}$). HRMS (EI) calcd for $C_{18}H_{33}NO_2$ (M^+): 295.2511, found: 295.2512.

The minor diastereomer (49.7 mg, 40%): TLC R_f 0.67 (hexane/ethyl acetate 1:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.930 (t, 3H, $J = 7.6$ Hz), 0.934 (t, 3H, $J = 6.9$ Hz), 1.05–1.47 (m, 10H), 1.11 (d, 3H, $J = 6.2$ Hz), 1.51–1.79 (m, 9H), 1.91–1.98 (m, 1H), 2.99–3.07 (m, 1H), 4.08 (dq, 1H, $J = 10.3$ Hz, $J = 6.9$ Hz), 4.17–4.23 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.9, 14.1, 15.5, 18.8, 20.4, 25.9, 26.1, 26.2, 27.6, 29.9, 30.0, 32.7, 34.2, 40.0, 42.2, 56.2, 78.6, 153.5. IR (neat) 2928, 1705, 1489, 1435 cm^{-1}. LRMS (EI) m/z 295 (M^+), 252 ($M^+ - C_3H_7$), 212 ($M^+ - C_6H_{11}$). HRMS (EI) calcd for $C_{18}H_{33}NO_2$ (M^+): 295.2511, found: 295.2511.

3-((*R*)-(−)-1-cyclohexylethyl)-5,6-*cis*-tetramethyleneperhydro-1,3-oxazin-2-one. Prepared from **7** (113.0 mg, 0.416 mmol) and cyclohexene (82.7 mg, 1.007 mmol) by Method A (X = 0 °C): Purified with flash chromatography (hexane/ethyl acetate 3:1) to give two diastereomers (total 48.6 mg, 48%, diastereomer ratio was 1.2:1).

The major diastereomer (26.7 mg, 26%): TLC R_f 0.50 (hexane/ethyl acetate 1:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.91–1.06 (m, 2H), 1.08–1.22 (m, 2H), 1.14 (d, 3H, $J = 7.6$ Hz), 1.31–1.55 (m, 4H), 1.57–1.81 (m, 10H), 1.91–1.96 (m, 1H), 1.96–2.04 (m, 1H), 2.83 (dd, 1H, $J = 2.1$ Hz, $J = 11.7$ Hz), 3.29 (dd, 1H, $J = 4.9$ Hz, $J = 11.7$ Hz), 4.05 (dq, 1H, $J = 9.6$ Hz, $J = 6.9$ Hz), 4.34–4.42 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.8, 19.7, 24.3, 25.1, 25.9, 26.1, 26.2, 29.8, 30.0, 30.1, 32.2, 39.7, 44.5, 56.4, 74.1, 153.6. IR (neat) 2930, 1686, 1485, 1437 cm^{-1}. LRMS (EI) m/z 265 (M^+), 182 ($M^+ - C_6H_{11}$). HRMS (EI) calcd for $C_{16}H_{27}NO_2$ (M^+): 265.2042, found: 265.2040.

The minor diastereomer (21.9 mg, 22%): TLC R_f 0.40 (hexane/ethyl acetate 1:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.88–1.04 (m, 2H), 1.04–1.20 (m, 2H), 1.09 (d, 3H, $J = 6.8$ Hz), 1.26–1.36 (m, 2H), 1.39–1.58 (m, 4H), 1.58–1.78 (m, 8H), 1.87–1.95 (m, 1H), 1.95–2.06 (m, 1H), 2.89 (dd, 1H, $J = 2.0$ Hz, $J = 12.3$ Hz), 3.18 (dd, 1H, $J = 5.5$ Hz, $J = 11.7$ Hz), 4.11 (dq, 1H, $J = 10.2$ Hz, $J = 6.8$ Hz), 4.36–4.42 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.4, 19.5, 24.3, 24.6, 25.9, 26.0, 26.1, 29.94, 29.98, 30.0, 32.0, 39.8, 43.9, 56.0, 74.1, 153.5. IR (neat) 2982, 1667, 1487, 1431 cm^{-1}. LRMS (EI) m/z 265 (M^+), 182 ($M^+ - C_6H_{11}$). HRMS (EI) calcd for $C_{16}H_{27}NO_2$ (M^+): 265.2042, found:

265.2043.

3-Phenyl-4a,5,6,7-tetrahydropyrrolo[1,2-*c*][1,3]oxazin-1-one. Prepared from *N*-methoxycarbonyl-2-trimethylsilylpyrrolidine (10.0 mL, 0.496 mmol) and phenylacetylene (43.7 mg, 0.428 mmol) by Method A (X = 0 °C): Isolated yield 61% (55.8 mg, purified with flash chromatography, hexane/ethyl acetate 3:1): TLC R_f 0.40 (hexane/ethyl acetate 1:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.61–1.73 (m, 1H), 1.83–1.93 (m, 1H), 1.98–2.07 (m, 1H), 2.18–2.27 (m, 1H), 3.52 (ddd, 1H, J = 2.8 Hz, J = 9.6 Hz, J = 12.4 Hz), 3.75 (dt, 1H, J = 11.7 Hz, J = 8.3 Hz), 4.23 (ddd, 1H, J = 2.0 Hz, J = 4.8 Hz, J = 11.0 Hz), 5.67 (d, 1H, J = 2.1 Hz), 7.31–7.39 (m, 3H), 7.63 (dd, 2H, J = 1.4 Hz, J = 7.6 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 22.0, 33.1, 45.7, 56.2, 98.2, 124.8, 128.4, 129.2, 131.7, 148.9, 149.5. IR (neat) 3450, 2975, 1720, 1428 cm^{-1}. LRMS (EI) m/z 215 (M^+). HRMS (EI) calcd for $C_{13}H_{13}NO_2$ (M^+): 215.0946, found: 215.0944.

3-Phenyl-5,6,7,8-tetrahydro-4a*H*-pyrido[1,2-*c*][1,3]oxazin-1-one. Prepared from *N*-methoxycarbonylpiperidine (10.0 mL, 0.498 mmol) and phenylacetylene (32.6 mg, 0.319 mmol) by Method A (X = 0 °C): Isolated yield 36% (26.7 mg, purified with flash chromatography, hexane/ethyl acetate 10:1): TLC R_f 0.60 (hexane/ethyl acetate 1:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.38–1.63 (m, 3H), 1.67–1.77 (m, 1H), 1.77–1.84 (m, 1H), 1.88–1.96 (m, 1H), 2.75 (dt, 1H, J = 2.8 Hz, J = 13.0 Hz), 3.99 (dt, 1H, J = 11.7 Hz, J = 2.7 Hz), 4.50 (dt, 1H, J = 13.1 Hz, J = 2.0 Hz), 5.42 (d, 1H, J = 3.5 Hz), 7.31–7.42 (m, 3H), 7.61 (dd, 2H, J = 2.0 Hz, J = 8.2 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 24.2, 25.0, 33.9, 45.2, 55.3, 98.7, 124.5, 128.4, 129.1, 131.7, 147.2, 149.6. IR (neat) 3400, 2938, 1719, 1449 cm^{-1}. LRMS (EI) m/z 229 (M^+). HRMS (EI) calcd for $C_{14}H_{15}NO_2$ (M^+): 229.1103, found: 229.1103.

3-Ethyl-4-methyl-6-phenyl-3,4-dihydro-2*H*-1,3-oxazin-2-one. Prepared from *N*-methoxycarbonyldiethylamine (10.0 mL, 0.498 mmol) and phenylacetylene (42.7 mg, 0.418 mmol) by Method A (X = 0 °C): Isolated yield 59% (53.6 mg, purified with flash chromatography, hexane/ethyl acetate 3:1): TLC R_f 0.57 (hexane/ethyl acetate 1:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.25 (t, 3H, J = 7.6 Hz), 1.36 (d, 3H, J = 6.2 Hz), 3.26 (dq, 1H, J = 14.4 Hz, J = 6.9 Hz), 3.67 (dq, 1H, J = 13.7 Hz, J = 7.6 Hz), 4.11 (dq, 1H, J = 6.2 Hz, J = 4.8 Hz), 5.55 (d, 1H, J = 4.8 Hz), 7.30–7.38 (m, 3H), 7.62 (dd, 2H, J = 1.4 Hz, J = 8.2 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 12.7, 22.0, 41.6, 51.0, 100.4, 124.5, 128.4, 129.1, 131.7, 147.7, 150.2. IR (neat) 3088, 2977, 1717, 1451 cm^{-1}. LRMS (EI) m/z 217 (M^+), 202 ($M^+ - CH_3$), 188 ($M^+ - C_2H_5$). HRMS (EI) calcd for $C_{13}H_{15}NO_2$ (M^+): 217.1103, found: 217.1103.

3-Butyl-*trans*-5,6-diphenylperhydro-1,3-oxazine (9). To a cation pool (**2**, 5 mL, cooled at −78 °C) generated from **1** (0.250 mmol) was added a solution of (*E*)-1,2-diphenylethene (0.209 mmol) in CH_2Cl_2 (5 mL, cooled at −78 °C) by syringe pump (flow rate, 5.0 mL/min). The reaction mixture was immediately warmed to 0 °C. After being stirred for 10 min, this mixture was added to a solution of $NaBH_4$ (1.08 mmol) in MeOH (10 mL). The reaction mixture was stirred for 3 h at room temperature, and then water (2 mL) and Et_3N (1 mL) were added. The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (10 cm) of silica gel to remove Bu_4NBF_4. The silica gel was washed with ether (300 mL). The combined filtrate was concentrated to give a crude product, which was purified by flash chromatography (hexane/ethyl acetate 5:1) to obtain the title compound (47.9 mg, 78%): TLC R_f 0.73 (hexane/ethyl acetate 1:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.98 (t, 3H, J = 7.6 Hz), 1.43 (tq, 2H, J = 7.6 Hz, J = 7.6 Hz), 1.51–1.63 (m, 2H), 2.79–2.87 (m, 1H), 2.92–2.99 (m, 1H), 3.13–3.29 (m, 3H), 4.53 (d, 1H, J = 10.3 Hz), 4.60 (d, 1H, J = 9.6 Hz), 4.78 (d, 1H, J = 10.3 Hz), 7.01 (d, 1H, J = 8.2 Hz), 7.08–7.23 (m, 8H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 20.5, 30.2, 44.6, 51.3, 57.1, 84.6, 85.0, 126.6, 126.9, 127.5, 127.8, 128.22, 128.24, 139.6, 140.2. IR (neat) 2963, 1690, 1482, 1238 cm^{-1}. IR (neat) 3031, 2957, 1453, 1364 cm^{-1}. LRMS (FAB) m/z 296 (MH^+) HRMS (FAB) calcd for $C_{20}H_{26}NO$ (MH^+): 296.2014, found: 296.2014.

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Supporting Information

Atomic coordinates of DFT calculation and X-ray crystallographic analysis. These materials are available free of charge on the Web at: http//www.csj/journals/bcsj/.

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