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# Enantioselective preparation of 3,4,5-trisubstituted 4,5-dihydroisoxazoles and their stereoselective elaboration of 5-side chain

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**Abstract**—The magnesium ion-induced nitrile oxide cycloaddition to chiral α-silylallyl alcohols was examined. Treatment of chiral allyl alcohol with nitrile oxide in the presence of magnesium cation resulted in the smooth progress of the 1,3-dipolar cycloaddition to give optically active 4,5-dihydroisoxazoles in good yields. The present procedure serves as a good method for the preparation of multi-substituted 4,5-dihydroisoxazoles with high enantiomeric excess. When exposed to tetrabutylammonium fluoride (TBAF), the cycloadducts were converted into 4-substituted-5,6-dihydro-4*H*-[1,2]-oxazines in good yields without loss of optical purity. Acylsilanes, obtained by the oxidation of the cycloadduct, underwent stereoselective allylation reaction induced by Lewis acid to accomplish the elongation of C5-side chain in a stereoselective manner. 

## 1. Introduction

4,5-Dihydroisoxazoles are regarded as a useful synthetic intermediate for constructing carbon-backbones because they are converted to γ-aminoalcohols or β-hydroxyketones in one-step of reductive treatment,[1] and this heterocycle has often been used as key intermediates for the natural product synthesis.[2] Although the recent developments on the 1,3-dipolar cycloaddition provides the preparation of enantiomerically enriched cycloadducts,[3] only limited numbers of methods are available for the enantioselective nitrile oxide cycloaddition (NOC) reaction.[4] Compared with the Diels–Alder reaction, the NOC reaction generally decreased the reaction rate by the presence of Lewis acids and this poses a significant problem for the NOC reaction as a tool for the stereoselective synthesis. We have found the presence of magnesium ion promotes the reaction smoothly and also brings an excellent stereo/regio-selectivity for the reaction.[5] This modification opens a practical aspect of the reaction to prepare multi-substituted 4,5-dihydroisoxazoles that have been regarded as a useful candidate for the construction of acyclic carbon backbones. α-Silylallyl alcohols are readily prepared from allylic alcohols and optically active ones are available by a simple asymmetric reduction with *B*-chlorodiisopinocampheylborane (DIP-Cl).[6] Recently, we have disclosed that chiral 3,4,5-trisubstituted-4,5-dihydroisoxazoles are obtained through magnesium-mediated NOC reaction to non-racemic α-silyl alcohols.[7] In this paper, we report full details of the methodology as well as stereoserective elaboration of C5-side chain of the chiral 4,5-dihydroisoxazoles.

## 2. Results and discussion

Racemic α-silylallyl alcohols **2** were prepared in good yields through the retro-Brock rearrangement of trimethylsilyl ether of allyl alcohol, which was generated in situ by treatment of allyl alcohol **1** with base and TMSCl.[8] To convert racemic-**2** to optically active **2**, the alcohols were oxidized to acylsilane **3**, which were reduced with (−)-DIP-Cl to give (*S*)-(−)-**2** in 85–87% ee (Scheme 1).[6]

The 1,3-dipolar cycloaddition of nitrile oxides with **2** was performed in the presence of magnesium cation (Scheme 2).[5] The results are summarized in Table 1.

Benzonitrile oxide in the presence of magnesium cation underwent the smooth cycloaddition with **2a** to give 4,5-dihydroisoxazole **4a** in 75% yield. The product contained two diastereomers in the ratio of 94:6. The major diastereomer showed positive optical rotation and its

*Keywords*: cycloadditions; asymmetric synthesis; enantioselection; isoxazolines; oxazines.

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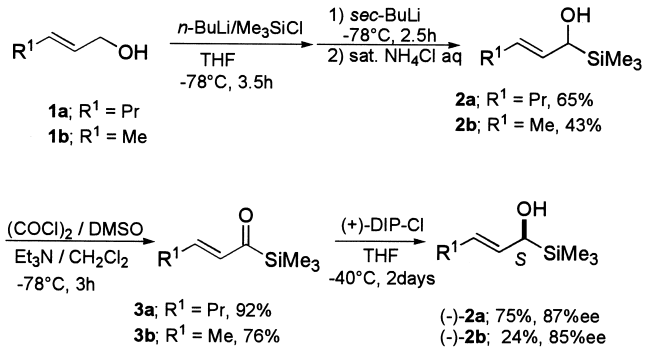
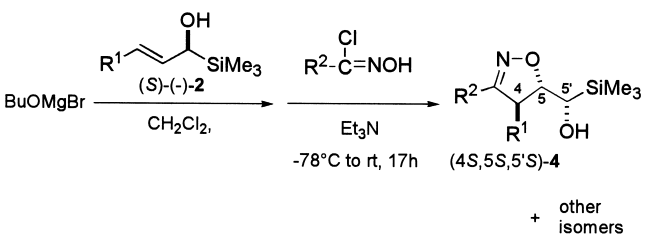



**Scheme 1.**




**Scheme 2.**

**Table 1**. Preparation of chiral 4,5-dihydroisoxazoles **4**

| Entry | $R^1$ | **2** | ee (%) | $R^2$ | Product | Yield (%)[a] | Ratio[b] | ee[b] | $[\alpha]_D$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $C_3H_7-$ | **2a** | 87 | Ph | **4a** | 75 | 94:6 | 82 | +130.4 |
| 2 | $C_3H_7-$ | **2a** | 87 | *p*-Cl–$C_6H_4-$ | **4b** | 52 | 97:3 | 84 | +124.8 |
| 3 | $C_3H_7-$ | **2a** | 87 | *p*-$CF_3$–$C_6H_4-$ | **4c** | 32 | 98:2 | 78 | +124.9 |
| 4 | $C_3H_7-$ | **2a** | 87 | $PhCH_2CH_2-$ | **4d** | 40 | 99:1 | 83 | +91.0 |
| 5 | Me | **2b** | 85 | Ph | **4e** | 59 | 94:6 | 80 | +113.3 |
| 6 | Me | **2b** | 85 | *p*-Cl–$C_6H_4-$ | **4f** | 58 | 95:5 | 80 | +121.9 |
| 7 | Me | **2b** | 81 | *p*-$CF_3$–$C_6H_4-$ | **4g** | 45 | 99:1 | 75 | +99.0 |

[a] Isolated yield.
[b] Determined by HPLC analyses.

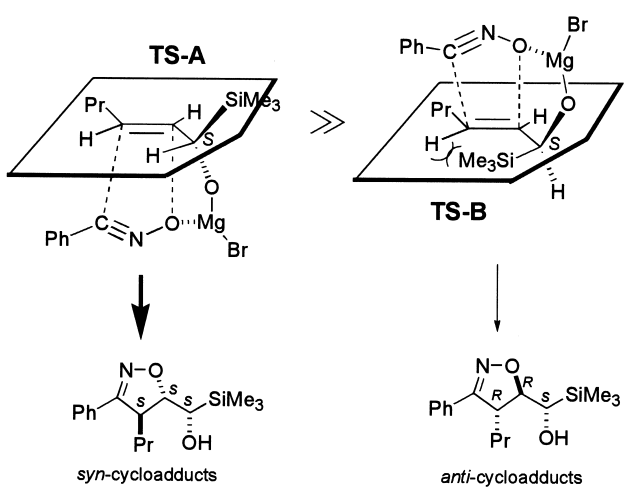
HLPC analysis with ChiralPak AD indicated 82% ee (entry 1). The cycloaddition of other aromatic as well as aliphatic nitrile oxides also gave optically active 4,5-dihydroisoxazoles **4** in good enatiomeric excesses (entry 2–4). All the adducts showed dextrorotatory so that they all were expected to have the same configuration in the three chiral centers. The configuration was confirmed by the X-ray crystallographic analysis performed on compound **4a**, in which newly formed chiral centers at C4 and C5 were both assigned to be *S*.[9]

These stereochemical outcomes are easily understood by comparison with the supposed reaction mechanism of the magnesium-induced cycloaddition reaction (Scheme 3).

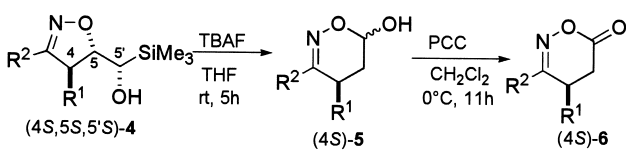
The oxygen atom in the nitrile oxide usually works as a good Lewis base so that it undergoes coordination to magnesium alkoxide under the present reaction conditions. The magnesium alkoxide includes the dipolarophile unit so that the dipole and the dipolarophile are placed close and the reaction rate is enhanced. During the reaction process, there exists the two possible transition states, TS-A and TS-B, but due to the steric interaction between the TMS group and the vinylic proton, TS-B should be disfavored. Thus, the reaction proceeded through TS-A which furnishes *syn*-cycloadducts in an enantioselective manner.[10]

We then examined to remove the TMS group. It is known that α-silyl alcohol is converted to alcohols by treatment with tetrabutylammonium fluoride (TBAF).[11] We assumed that this procedure would be useful to remove the silyl group and examined these conditions to **4** (Scheme 4). The starting cycloadduct **4a** disappeared smoothly by treatment with TBAF but the obtained product was found to be 4-substituted-5,6-dihydro-4*H*-[1,2]-oxazine **5a**,[12] different from the expected 4,5-dihydroisoxazole. The results are summarized in Table 2.

The present conversion of **4** to **5** proceeded in a spot-to-spot manner. The oxazine **5a** contained a pair of diastereomers whose ratio was almost 2:1 due to its hemiacetal structure. To check optical purity of **5a**, PCC oxidation was carried out; [1,2]-oxazin-3-one **6a** was isolated in 67% yield. Compound **6a** showed dextrorotatory and its HPLC analysis with ChiralPak AD revealed that **6a** still maintained 81% ee. Thus, no significant racemization had taken place during




**Scheme 3.**

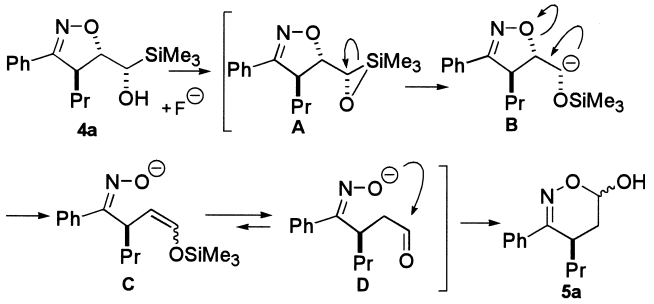



**Scheme 4.**

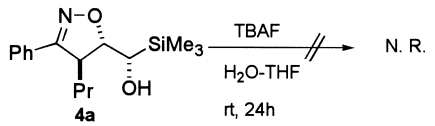
**Table 2**. Conversion of **4** to [1,2]-oxazine **5** and [1,2]-oxazin-3-one **6**

| Entry | $R^1$ | $R^2$ | Yield (%)[a] | | ee[b] | $[\alpha]_D$ |
|---|---|---|---|---|---|---|
| | | | **5** | **6** | | |
| 1 | $C_3H_7-$ | Ph | **5a**; 100 | **6a**; 67 | 81 | +55.1 |
| 2 | $C_3H_7-$ | *p*-Cl–$C_6H_4-$ | **5b**; 92 | **5b**; 80 | 82 | +37.1 |
| 3 | Me | Ph | **5c**; 86 | **6c**; 56 | 73 | +33.7 |
| 4 | Me | *p*-$CF_3$–$C_6H_4-$ | **5d**; 76 | **6d**; 77 | 75 | +18.3 |

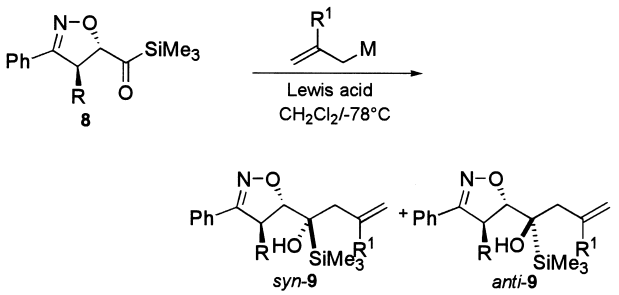
[a] Isolated yield.
[b] Determined by HPLC analyses.




**Scheme 5.**




**Scheme 6.**




**Scheme 7.**

these transformation. Other chiral isoxazoles **4** were converted into **6** by these treatments (entry 2–4).

Supposed mechanism of the conversion of 4,5-dihydroisoxazole **4** to [1,2]-oxazine **5** is depicted in Scheme 5. According to the mechanism reported previously,[11] the first step of the reaction is deprotonation of **4a** by fluoride anion to form an alkoxide, which then attacks the TMS group intramolecularly (intermediate **A**). Through this process the TMS group migrates to the oxygen atom and α-hydroxy-carbanion is then generated (intermediate **B**). $E1_{CB}$-type β-elimination from **B** cleaves C–O bond of the 4,5-dihydroisoxazole to give alkoxide **C**, the oxy-anion of which attacks the formyl unit in **D**, generated from keto–enol tautomerism, to give [1,2]-oxazine structure **5**. It should be remarked that this ring enlargement only occurred under anhydrous conditions; treatment of **4a** with TBAF in wet-THF resulted in no reaction and starting material **4a** was totally recovered (Scheme 6).

We next attempted carbon-chain elaboration reaction at C5 position of the ring. The Swern oxidation converted compounds **4** into acylsilanes **8**, which were regarded as an equivalent of 4,5-dihydroisoxazole-5-carbaldehyde. The nucleophilic addition to the aldehydes provides a useful stereoselective carbon–carbon bond forming methodology if the 4,5-dihydroisoxazole ring offers sufficient steric bias for the stereoselection. With this strategy, the stereoselective carbon-chain elaboration at C3 position was successfully achieved by Wade[13] and our group.[14] 4,5-Dihydroisoxazole-5-carbaldehydes, on the other hand, was very difficult to isolate and purify so that use of them to further transformation was not easy as well as the stereoselection level was moderate.[15] Thus, the acylsilane is regarded as a good candidate for an equivalent of the aldehydes.[11d,16]

The allylation reaction to acylsilane **8** was examined under Lewis acidic conditions (Scheme 7). The results are summarized in Table 3.

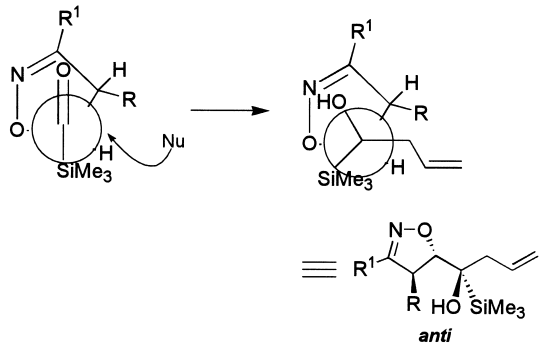
To a solution of **8a** in $CH_2Cl_2$, allyltributyltin and $TiCl_4$ was added at −78°C and allylation product **9a** was isolated in 88% yield (entry 1). The product contained almost a single isomer of compound **9a** and HPLC analysis indicated that its ratio was 4/96. The same isomer of **9a** was formed in the reaction catalyzed by $BF_3{\cdot}OEt_2$, while a diastereomeric mixture of **9a** was obtained from the reaction promoted by $SnCl_4$ (entry 2 and 3). Methacryltin also gave adduct **9b** in good yield. The stereoselectivity was better than the reaction with allyltin (entry 4 and 5). Absence of an alkyl substituent at C4 in 4,5-dihydroisoxazole reduced the selectivity about 1/9–2/8 level (entry 6 and 7).

The configuration at newly formed chiral center was

**Table 3**. Allylation of acylsilane **8**

| Entry | R | $R^1$ | **8** | Lewis acid | Time (h) | **9**; Yield (%)[a] | *syn*/*anti*[b] | $[\alpha]_D$ |
|---|---|---|---|---|---|---|---|---|
| 1 | $C_3H_7-$ | H | **8a** | $TiCl_4$ | 2.5 | **9a**; 88 | 4/96 | +125.8 |
| 2 | $C_3H_7-$ | H | **8a** | $BF_3{\cdot}OEt_2$ | 5 | **9a**; 83 | 7/93 | +119.4 |
| 3 | $C_3H_7-$ | H | **8a** | $SnCl_4$ | 4.5 | **9a**; 84 | 63/37 | +102.7 |
| 4 | $C_3H_7-$ | Me | **8a** | $TiCl_4$ | 3.5 | **9b**; 75 | 1/99 | +105.3 |
| 5 | $C_3H_7-$ | Me | **8a** | $BF_3{\cdot}OEt_2$ | 15.5 | **9b**; 62 | 8/92 | +106.4 |
| 6 | H | H | **8c** | $TiCl_4$ | 2 | **9c**; 79 | 20/80 | [c] |
| 7 | H | H | **8c** | $BF_3{\cdot}OEt_2$ | 2 | **9c**; 92 | 10/90 | [c] |

[a] Isolated yield.
[b] Determined by HPLC analyses.
[c] Starting from racemate.




**Scheme 8.**

determined to be *anti* on the basis of an X-ray crystallographic analysis for compound **9c**.[17] Based on a similar NMR and HPLC behavior, we concluded all of **9** have the same configuration.

It is interesting that the stereoselectivity of the reaction was independent to the sorts of Lewis acid. This is probably due to steric congestion led by trimethylsilyl group at the acylsilane unit that prevents the chelation-type activation. As a result, the reaction should proceed via the Felkin–Ahn type transition state regardless of Lewis acid employed. Scheme 8 shows the likely transition state of the reaction. Nucleophilic attack should occur from the less hindered side (right side of acylsilane unit) to give anti adduct selectively. If C4 substituent, R, is absent, the chelation type activation is now possible for the reaction catalyzed by $TiCl_4$ so the diastereoselectivity decreases (Table 3, entry 6). The observed less selectivity by $SnCl_4$ is likely explained in the same reason (Table 3, entry 3).

In conclusion, we have developed a new facile method to prepare optically active 3,4,5-multisubstituted 4,5-dihydroisoxazoles in a short step. The reaction was well-controlled by the presence of magnesium cation and high enantioselectivity was achieved. Obtained isoxazoles were readily converted into [1,2]-oxazines without loss of optical purity at C4. Elaboration of C5 side chain was also accomplished in a highly selective level. As the 4,5-dihydroisoxazole chemistry is directly connected to the construction of open-chain carbon backbones, this method will provide a useful method in organic synthesis.

## 3. Experimental

### 3.1. General

All $^1H$ and $^{13}C$ NMR spectra were measured in $CDCl_3$ and recorded on JEOL EX-270 (270 MHz for $^1H$ and 67.5 MHz for $^{13}C$) or Brucker Advance 400 (400 MHz for $^1H$ and 100 MHz for $^{13}C$) spectrometer. All the reactions in this paper were performed under nitrogen atmosphere. All of reaction solvents were dried over appropriate drying agents (K for THF and $CaH_2$ for all other solvents) and distilled under nitrogen before use. Allyl alcohols were purified by distillation. Hydroxymoyl chrolides were prepared by literature method.[18] *sec*-BuLi was purchased from Kanto Kagaku and methylmagnesium bromide in ether solution was purchased from Aldrich.

**3.1.1. Preparation of 1-trimethylsilyl-2-hexen-1-ol [2a].** *General procedure*. To a solution of *trans*-2-hexene-1-ol (6.762 g, 67.5 mmol) in THF (100 mL) was added *n*-BuLi (1.6 M, 45 mL, 72 mmol) at −78°C over 5 min. and the reaction mixture was allowed to stir for 1 h. TMSCl was added to the solution and the reaction mixture was maintained at the same temperature for additional 2.5 h. *sec*-BuLi (0.99 M, 82 mL, 81.2 mmol) was added to the solution at −78°C over 10 min and the resulting mixture was allowed to stir at the same temperature for 2 h. Aqueous $NH_4Cl$ (50 mL) was added to the solution and THF was removed in vacuo. The resulting biphasic mixture was extracted with ether (3×30 mL) and combined organic phase was dried over $Na_2SO_4$. After filtration, ether was removed in vacuo and the residue was subjected to flash chromatography (hexane–ethyl acetate 10:1 then 3:1 v/v) to give 1-trimethylsilyl-2-hexene-1-ol **2a** in 68% yield (7.965 g, 46.2 mmol) as a yellow oil. $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 0.03 (s, 9H), 0.89 (t, $J$=7.3 Hz, 3H), 1.22–1.51 (m, 2H), 2.02 (q, $J$=7.0 Hz, 2H), 3.89 (dd, $J$=0.9, 6.3 Hz, 1H), 5.47 (dd, $J$=6.3, 15.1 Hz, 1H), 5.58 (dt, $J$=6.3, 15.5 Hz, 1H). IR: 3650–3100 $cm^{-1}$.

**3.1.2. 1-Trimethylsilyl-2-buten-1-ol [2b].** Compound **2b** was prepared in a similar way as **2a**. Yellow oil. $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 0.03 (s, 9H), 1.72 (dd, $J$=1.3, 5.9 Hz, 3H), 3.89 (td, $J$=1.3, 6.6 Hz, 1H), 5.42–5.66 (m, 2H). $^{13}C$ NMR (67.5 MHz, $CDCl_3$) $\delta$ −4.2, 17.8, 68.4, 122.4, 132.3. IR: 3650–3100 $cm^{-1}$.

**3.1.3. Oxidation of silyl alcohol 2. Preparation of 1-trimethylsilyl-2-hexen-1-one [3a].** *General procedure*. To a solution of oxalyl chloride (2.4 mL, 27.5 mmol) in $CH_2Cl_2$ (20 mL) was added DMSO (3.7 mL, 52.1 mmol) at −78°C over 10 min. After 1.5 h, a solution of **2a** (3.150 g, 18.3 mmol) in $CH_2Cl_2$ (30 mL) was added to the reaction mixture and the resulting solution was allowed to stir at −78°C for 2 h. $Et_3N$ (13.4 mL, 96.1 mmol) was added to the reaction mixture and the resulting mixture was allowed to warm to 0°C for 2.5 h. The reaction mixture was poured into water (50 mL) and the water phase was extracted with $CH_2Cl_2$ (3×30 mL). The combined organic phase was washed with dil HCl (3×20 mL) and dried over $Na_2SO_4$. After filtration and removal of solvent, crude product was purified through flash chromatography (hexane–ether 15:1 v/v) to give **3a** in 95% yield (2.861 g, 16.8 mmol). Yellow oil. $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 0.26 (s, 9H), 0.90 (t, 3H, $J$=7.3 Hz), 1.55–1.75 (m, 2H), 2.24 (dq, 2H, $J$=1.3, 6.9 Hz), 6.24 (tq, 1H, $J$=1.4, 6.9 Hz), 6.76 (tq, 1H, $J$=6.9, 16.2 Hz). $^{13}C$ NMR (67.5 MHz, $CDCl_3$) $\delta$ −1.5, 14.1, 21.9, 35.2, 137.1, 149.2. IR (neat) $\nu$ 3050–2750, 1640, 1250 $cm^{-1}$.

**3.1.4. 1-Trimethylsilyl-2-buten-1-one [3b].** Compound **3b** was prepared in a similar way as **3a**. Bp 75–90°C/5 mmHg. $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 0.24 (s, 9H), 1.93 (dd, 3H, $J$=1.5, 6.8 Hz), 6.24 (qd, 1H, $J$=1.7, 16.2 Hz), 6.82 (qd, 1H, $J$=6.8, 16.2 Hz). $^{13}C$ NMR (67.5 MHz, $CDCl_3$) $\delta$ −2.0, 18.6, 138.1, 143.8. IR (neat) $\nu$ 3050–2850, 1630, 1240 $cm^{-1}$.

**3.1.5. Asymmetric reduction of 3a. Preparation of *trans*-1-trimethylsilyl-2-hexen-1-ol [(−)-2a].** *General procedure*.

To a solution of (−)-DIP-Cl (3.868 g, 12.1 mmol) in THF (10 mL) at −10°C was added a solution of **3a** (1.288 g, 7.58 mmol) in THF (10 mL) and the reaction mixture was allowed to stir for 20 h at −10°C. The reaction solvent was removed in vacuo, and diethanolamine (3.780 g, 36.0 mmol) in ether (50 mL) was added to the residue. The mixture was allowed to stir for 24 h at room temperature. Precipitate was removed by filtration and the residue was subjected to flash chromatography (hexane–ethyl acetate 15:1 v/v) to give (−)-**2a** in 75% yield (0.972 g, 5.65 mmol). $[\alpha]_D$=−31.0 (*c* 1.07, $CHCl_3$). 87% ee.

*trans*-1-Trimethylsilyl-2-butene-1-ol (−)-**2b** was prepared in a similar way: $[\alpha]_D$=−30.3 (*c* 0.97, $CHCl_3$). 85% ee.

### 3.2. Magnesium ion-induced enantioselective 1,3-dipolar cycloaddition to 2

**3.2.1. (4*S*,5*S*)-5-[(*S*)-Hydroxy(trimethylsilyl)methyl]-3-phenyl-4-propyl-4,5-dihydroisoxazole [(+)-4a].** *General procedure*. Methylmagnesium bromide (3 M in ether, 1.0 mL, 3 mmol) was added to a solution of BuOH (0.227 g, 3.06 mmol) in $CH_2Cl_2$ (10 mL). The reaction solution was cooled to −78°C and (−)-**3a** (0.266 g, 1.55 mmol) was added. Then benzenehydroximoyl chrolide (0.403 g, 2.58 mmol) in $CH_2Cl_2$ (15 mL) and $Et_3N$ (0.276 g, 2.73 mmol) was added in this order. The reaction mixture was allowed to warm to room temperature for 17 h. $NH_4Cl$aq (15 mL) was added and the resulting biphasic mixture was extracted with $CH_2Cl_2$ (3×10 mL). The organic phases were combined and dried over $Na_2SO_4$. After filtration and removal of solvent, the crude product was purified through flash chromatography (hexane–ethyl acetate 15:1 then 1:1 v/v) to give (+)-**4a** in 75% (0.260 g, 0.89 mmol). $[\alpha]_D$=+130.4 (*c* 1.00, $CHCl_3$). 82% ee $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 0.18 (s, 9H), 0.92 (t, 3H, *J*=7.3 Hz), 1.26–1.44 (m, 2H), 1.51–1.68 (m, 2H), 1.71 (d, 1H, *J*=7.9 Hz), 3.26 (dd, 1H, *J*=4.8, 7.8 Hz), 3.67 (td, 1H, *J*=4.3, 8.6 Hz), 4.58 (t, 1H, *J*=4.8 Hz), 7.39–7.42 (m, 3H), 7.63–7.66 (m, 2H). $^{13}$C NMR (67.5 MHz, $CDCl_3$) $\delta$ −3.0, 14.0, 19.9, 33.4, 48.8, 68.0, 88.7, 126.9, 128.8, 129.0, 129.9, 160.6. IR (neat) $\nu$ 3630–3130, 3000–2750, 1590, 1440, 1250 $cm^{-1}$. Anal. calcd for $C_{16}H_{25}NO_2Si$: C, 65.93; H, 8.65; N, 4.81. Found: C, 65.95; H, 8.58; N, 5.02.

Other cycloaddition reactions were carried out in a similar manner.

**3.2.2. (4*S*,5*S*)-3-(4-Chlorophenyl)-5-[(*S*)-hydroxy(trimethylsilyl)methyl]-4-propyl-4,5-dihydroisoxazole [(+)-4b].** $[\alpha]_D$=+124.8 (*c* 1.06, $CHCl_3$). 84% ee. $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 0.18 (s, 9H), 0.92 (t, 3H, *J*=7.3 Hz), 1.26–1.43 (m, 2H), 1.50–1.69 (m, 2H), 1.65 (d, 1H, *J*=7.6 Hz), 3.25 (dd, 1H, *J*=4.3, 7.9 Hz), 3.65 (ddd, 1H, *J*=4.0, 5.0, 8.6 Hz), 4.58 (t, 1H, *J*=4.8 Hz), 7.37 (m, 2H), 7.57 (m, 2H). $^{13}$C NMR (67.5 MHz, $CDCl_3$) $\delta$ −3.0, 14.0, 19.8, 33.4, 48.7, 68.1, 89.0, 127.5, 128.1, 129.0, 135.7, 159.6. IR (neat) $\nu$ 3600–3100, 3000–2700, 1590, 1250 $cm^{-1}$. HRMS (FAB) calcd for (M+H) $C_{16}H_{25}ClNO_2Si$: 326.1343, found 326.1333.

**3.2.3. (4*S*,5*S*)-5-[(*S*)-Hydroxy(trimethylsilyl)methyl]-4-propyl-3-[4-(trifluoromethyl)phenyl]-4,5-dihydroisoxazole [(+)-4c].** $[\alpha]_D$=+124.9 (*c* 0.54, $CHCl_3$). 78% ee. $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 0.19 (s, 9H), 0.93 (t, 3H, *J*=7.0 Hz), 1.26–1.43 (m, 2H), 1.51–1.75 (m, 3H), 3.24–3.27 (br, 1H), 3.73 (ddd, 1H, *J*=3.6, 4.9, 8.6 Hz), 4.62 (dd, 1H, *J*=4.3, 4.9 Hz), 7.66 (m, 2H), 7.76 (m, 2H). $^{13}$C NMR (67.5 MHz, $CDCl_3$) $\delta$ −3.0, 14.0, 19.8, 33.4, 48.4, 68.3, 89.5, 121.8, 125.6, 127.1, 131.3, 132.6, 159.5. IR (neat) $\nu$ 3640–3100, 3000–2700, 1610, 1320, 1130 $cm^{-1}$. HRMS (FAB) calcd for (M+H) $C_{17}H_{25}F_3NO_2Si$: 360.1604, found 360.1609.

**3.2.4. (4*S*,5*S*)-5-[(*S*)-Hydroxy(trimethylsilyl)methyl]-3-(2-phenylethyl)-4-propyl-4,5-dihydroisoxazole [(+)-4d].** $[\alpha]_D$=+91.0 (*c* 1.15, $CHCl_3$). 83% ee. $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 0.18 (s, 9H), 0.99 (t, 3H, *J*=7.1 Hz), 1.27–1.72 (m, 4H), 2.56 (q, 2H, *J*=7.6 Hz), 2.74 (dq, 2H, *J*=7.0, 9.2 Hz), 2.91–3.07 (m, 3H), 3.15–3.24 (m, 3H), 3.69 (s, 1H), 4.38 (dd, 1H, *J*=4.0, 7.0 Hz), 7.24–7.38 (m, 5H). $^{13}$C NMR (67.5 MHz, $CDCl_3$) $\delta$ −3.2, 14.1, 19.9, 28.2, 32.2, 33.5, 50.4, 67.1, 87.2, 126.2, 128.2, 128.4, 140.7, 162.0. IR (neat) $\nu$ 3600–3100, 3000–2700, 1600, 1240 $cm^{-1}$. HRMS (EI) calcd for ($M^+$) $C_{18}H_{29}NO_2Si$: 319.1966, found 319.1969.

**3.2.5. (4*S*,5*S*)-5-[(*S*)-Hydroxy(trimethylsilyl)methyl]-4-methyl-3-phenyl-4,5-dihydroisoxazole [(+)-4e].** $[\alpha]_D$=+113.3 (*c* 1.03, $CHCl_3$), 80% ee. $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 0.18 (s, 9H), 1.32 (d, 3H, *J*=6.9 Hz), 1.65 (d, 1H, *J*=6.6 Hz), 3.32 (t, 1H, *J*=6.0 Hz), 3.69 (quint, 1H, *J*=6.9 Hz), 4.44 (t, 1H, *J*=5.6 Hz), 7.38–7.45 (m, 3H), 7.73–7.68 (m, 2H). $^{13}$C NMR (67.5 MHz, $CDCl_3$) $\delta$ −3.1, 17.3, 43.3, 66.3, 91.0, 126.9, 128.7, 129.8, 161.5. IR (neat) $\nu$ 3650–3150, 3030–2700, 1600, 1250 $cm^{-1}$. Anal. calcd for $C_{14}H_{21}NO_2Si$: C, 63.84; H, 8.04; N, 5.32. Found: C, 63.83; H, 8.25; N, 5.11.

**3.2.6. (4*S*,5*S*)-3-(4-Chlorophenyl)-5-[(*S*)-hydroxy(trimethylsilyl)methyl]-4-methyl-4,5-dihydro-isoxazole [(+)-4f].** $[\alpha]_D$=+121.9 (*c* 0.86, $CHCl_3$). 80% ee. $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 0.18 (s, 9H), 1.31 (d, 3H, *J*=7.3 Hz), 1.80–2.03 (br, 1H), 3.31 (d, 1H, *J*=5.0 Hz), 3.68 (quint, 1H, *J*=7.1 Hz), 4.45 (dd, 1H, *J*=5.0, 6.0 Hz), 7.38 (m, 2H), 7.58 (m, 2H). $^{13}$C NMR (67.5 MHz, $CDCl_3$) $\delta$ −3.2, 17.10, 42.8, 66.2, 91.2, 127.1, 127.9, 128.7, 135.4, 160.3. IR (neat) $\nu$ 3650–3150, 3030–2700, 1590, 1240 $cm^{-1}$. Anal. calcd for: $C_{14}H_{20}ClNO_2Si$: C, 56.45; H, 6.77; N, 4.70. Found: C, 56.18; H, 6.93; N, 4.60.

**3.2.7. (4*S*,5*S*)-5-[(*S*)-Hydroxy(trimethylsilyl)methyl]-4-methyl-3-[4-(trifluoromethyl)phenyl]-4,5-dihydroisoxazole [(+)-4g].** $[\alpha]_D$=+99.0 (*c* 0.90, $CHCl_3$). 75% ee. $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 0.19 (s, 9H), 1.6–1.8 (br, 1H), 1.33 (d, 3H, *J*=6.9 Hz), 3.33 (br, 1H), 3.75 (quint, 1H, *J*=6.9 Hz), 4.49 (dd, 1H, *J*=4.6, 6.3 Hz), 7.66 (m, 2H), 7.76 (m, 2H). $^{13}$C NMR (67.5 MHz, $CDCl_3$) $\delta$ −3.1, 17.2, 43.0, 66.7, 91.8, 125.7, 127.2, 130.4, 132.4, 160.5. IR (neat) $\nu$ 3650–3130, 3130–2750, 1610, 1240 $cm^{-1}$. HRMS (FAB) calcd for (M+H) $C_{15}H_{21}F_3NO_2Si$: 332.1294, found 332.1293.

**3.2.8. Cleavage of the isoxazole ring by TBAF. Preparation of (4*S*)-3-phenyl-4-propyl-5,6-dihydro-4*H*-[1,2]oxazin-6-ol [(+)-5a].** *General procedure*. To a solution of (+)-**4a** (0.726 g, 2.51 mmol) in THF (10 mL)

was added TBAF (1.0 M, 2.7 mL, 2.7 mmol) and the resulting solution was allowed to stir at room temperature for 40 h. Solvent was removed in vacuo and the residue was subjected to flash chromatography (hexane–ethyl acetate 3:1 then 1:1 v/v) to give **5a** in 100% yield (0.547 g, 2.50 mmol). Pale yellow oil. $[\alpha]_D$=+38.8 (*c* 1.29, $CHCl_3$). $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 0.80 (t, 3H, *J*=7.1 Hz), 1.17–1.66 (m, 4H), 1.87–2.16 (m, 2H), 2.83–2.89 (m, 1H, 4-H minor isomer), 3.02 (m, 1H, 4-H major isomer), 3.10–3.40 (br, 1H), 5.47 (dd, 1H, *J*=3.0, 5.6 Hz, minor isomer), 5.52 (dd, 1H, *J*=3.3, 4.3 Hz, major isomer), 7.36–7.51 (m, 3H), 7.51–7.56 (m, 2H). $^{13}C$ NMR (67.5 MHz, $CDCl_3$) $\delta$ major; 13.7, 19.4, 28.3, 29.5, 34.3, 91.1, 126..6, 128.3, 129.1, 135.1, 162.0. Minor, 13.3, 19.6, 29.3, 29.7, 34.2, 92.4, 126.7, 128.4, 129.2,.135.1, 161.9. IR (neat) $\nu$: 3700–3100, 3000–2700, 1590, 1430, 1270 $cm^{-1}$. Anal. calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.18; N, 6.39. Found: C, 70.77; H, 7.91; N, 6.34.

Other oxazines were prepared in a similar manner.

**3.2.9. (4*S*)-3-(4-Chlorophenyl)-4-propyl-5,6-dihydro-4*H*-[1,2]oxazin-6-ol [(+)-5b].** Pale yellow oil. $[\alpha]_D$ +34.9 (*c* 0.63, $CHCl_3$). $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 0.81–0.93 (m, 3H), 1.21–1.92 (m, 4H), 1.92–1.97 (m, 1H), 2.07–2.18 (m, 1H), 2.77–2.81 (m, 1H, minor isomer), 2.93–3.02 (m, 1H, major isomer), 5.45 (dd, 1H, *J*=3.0, 4.6 Hz, minor isomer), 5.51 (dd, 1H, *J*=3.6, 7.3 Hz, major isomer), 7.35–7.51 (m, 4H). $^{13}C$ NMR (67.5 MHz, $CDCl_3$) $\delta$ major; 13.1, 19.3, 28.1, 29.6, 34.4, 91.1, 128.0, 128.0, 128.6, 133.5, 135.1, 160.9. Minor; 15.1, 19.5, 29.1, 30.6, 34.0, 92.4, 127.1, 128.4, 128.6, 133.5, 135.2, 160.8. IR (neat) $\nu$ 3700–3000, 3000–2750, 1590, 1220 $cm^{-1}$. HRMS (EI) calcd for ($M^+$) $C_{13}H_{16}ClNO_2$: 253.0869, found 253.0870.

**3.2.10. (4*S*)-4-Methyl-3-phenyl-5,6-dihydro-4*H*-[1,2]oxazin-6-ol [(+)-5c].** Pale yellow oil. $[\alpha]_D$=+36.2 (*c* 1.00, $CHCl_3$). $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 1.10 (d, 3H, *J*=7.3 Hz, major isomer), 1.24 (d, 3H, *J*=7.3 Hz, minor isomer), 1.82–2.05 (m, 2H), 2.95 (m, 1H, minor isomer), 3.13 (m, 1H, *J*=7.3 Hz, major isomer), 3.4–3.8 (br, 1H), 5.50–5.55 (m, 1H), 7.37–7.41 (m, 3H), 7.51–7.60 (m, 2H). $^{13}C$ NMR (67.5 MHz, $CDCl_3$) $\delta$ major; 18.8, 23.3, 32.5, 91.0, 126.8, 128.4, 129.2, 161.8. Minor; 19.7, 24.1, 31.4, 91.3, 126.6, 128.5, 129.4, 161.8. IR (neat) $\nu$ 3650–3050, 3000–2750, 1590, 1440 $cm^{-1}$. HRMS (EI) calcd for ($M^+$) $C_{11}H_{13}NO_2$: 191.0946, found 191.0946.

**3.2.11. (4*S*)-4-Methyl-3-[4-(trifluoromethyl)phenyl]-5,6-dihydro-4*H*-[1,2]oxazin-6-ol [(+)-5d].** Pale yellow oil. $[\alpha]_D$=+33.2 (*c* 1.06, $CHCl_3$). $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 1.10 (d, 3H, *J*=7.3 Hz, major isomer), 1.26 (t, 3H, *J*=7.3 Hz, minor isomer), 1.83–2.06 (m, 2H), 2.17–2.32 (m, 1H), 2.95 (dq, 1H, *J*=4.5, 7.8 Hz, minor isomer), 3.13 (m, 1H, *J*=7.3 Hz, major isomer), 5.55 (dd, 1H, *J*=2.6, 4.0 Hz, major isomer), 5.59 (t, 1H, *J*=3.3, minor isomer), 7.67 (m, 4H). $^{13}C$ NMR (67.5 MHz, $CDCl_3$) $\delta$ major; 18.5, 23.3, 32.3, 91.2, 125.3, 125.3, 127.1, 131.0, 138.4, 160.7. Minor; 20.6, 24.7, 31.6, 91.7, 121.9, 125.9, 138.4, 160.4. IR (neat) $\nu$ 3650–3050, 3000–2750, 1260 $cm^{-1}$. HRMS (EI) calcd for ($M^+$) $C_{12}H_{12}F_3NO_2$: 259.0830, found 259.0817.

**3.2.12. Oxidation to oxazinone 6. Preparation of (4*S*)-3-phenyl-4-propyl-4,5-dihydro-[1,2]oxazin-6-one [(+)-6a].** *General procedure*. To a suspension of PCC (0.112 g, 0.52 mmol) in $CH_2Cl_2$ was added (+)-**5a** (0.158 g, 0.72 mmol) in $CH_2Cl_2$ (10 mL) and the reaction mixture was allowed to stir at 0°C for 1.5 h. The supernatant of the reaction mixture was directly put through chromatography (hexane–ethyl acetate 3:1 then 1:1) and desired **6a** was isolated in 67% yield (0.104 g, 0.48 mmol). Red oil. $[\alpha]_D$=+55.1 (*c* 1.02, $CHCl_3$). 81% ee. $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 0.91 (t, 3H, *J*=7.1 Hz,), 1.14–1.73 (m, 4H), 2.69 (dd, 1H, *J*=5.9, 16.5 Hz), 2.85 (dd, 1H, *J*=1.8, 16.5 Hz), 3.28 (m, 1H), 7.44–7.55 (m, 3H), 7.74–7.78 (m, 2H). $^{13}C$ NMR (67.5 MHz, $CDCl_3$) $\delta$ 13.6, 19.8, 29.9, 32.6,33.8, 126.7, 128.9, 131.3, 131.6, 164.6, 169.1. IR (neat) $\nu$ 3000–2750, 1770, 1600, 1440, 1160 $cm^{-1}$. HRMS (EI) calcd for ($M^+$) $C_{13}H_{15}NO_2$: 217.1087, found 217.1107.

Other oxazinones **6** were prepared in a similar manner.

**3.2.13. (4*S*)-3-(4-Chlorophenyl)-4-propyl-4,5-dihydro-[1,2]oxazin-6-one [(+)-6b].** Oil. $[\alpha]_D$=+37.1 (*c* 0.99, $CHCl_3$). 82% ee. $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 0.91 (t, 3H, *J*=7.1 Hz,), 1.19–1.39 (m, 1H), 1.40–1.70 (m, 3H), 2.69 (dd, 1H, *J*=5.9, 16.5 Hz), 2.85 (dd, 1H, *J*=1.8, 16.5 Hz), 3.28 (dtd, 1H, *J*=1.8, 6.3, 10.6 Hz), 7.45 (m, 2H), 7.70 (m, 2H). $^{13}C$ NMR (67.5 MHz, $CDCl_3$) $\delta$ 13.6, 19.8, 29.8, 32.5,33.7, 128.0, 129.2, 130.1, 137.5, 163.6, 168.7. IR (neat) $\nu$: 1780, 1260 $cm^{-1}$. Anal. calcd for $C_{13}H_{14}ClNO_3$: C, 62.03; H, 5.61; N, 5.56. Found: C, 62.41; H, 5.88; N, 5.14.

**3.2.14. (4*S*)-4-Methyl-3-phenyl-4,5-dihydro-[1,2]oxazin-6-one [(+)-6c].** Oil. $[\alpha]_D$=+33.7 (*c* 1.04, $CHCl_3$). 74% ee. $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 1.33 (d, 3H, *J*=7.2 Hz), 2.71 (dd, 1H, *J*=3.0, 16.5 Hz), 2.79 (dd, 1H, *J*=5.4, 16.8 Hz), 3.43 (ddq, 1H, *J*=2.6, 5.4, 7.2 Hz), 7.44–7.55 (m, 3H), 7.75–7.79 (m, 2H). $^{13}C$ NMR (67.5 MHz, $CDCl_3$) $\delta$ 16.9, 29.5, 32.6, 127.0, 129.3, 131.7, 165.1, 169.2. IR (neat) $\nu$ 1780, 1440, 1260 $cm^{-1}$. HRMS (EI) calcd for ($M^+$) $C_{11}H_{11}NO_2$: 189.0804, found 189.0786.

**3.2.15. (4*S*)-4-Methyl-3-[4-(trifluoromethyl)phenyl]-4,5-dihydro-[1,2]oxazin-6-one [(+)-6d].** White solid. $[\alpha]_D$= +18.3 (*c* 1.23, $CHCl_3$). 74% ee. $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 1.35 (d, 3H, *J*=7.6 Hz), 2.74 (dd, 1H, *J*=3.0, 16.5 Hz), 2.82 (dd, 1H, *J*=5.0, 17.2 Hz), 3.43 (ddq, 1H, *J*=3.0, 5.0, 7.6 Hz), 7.44 (m, 2H), 7.90 (m, 2H). $^{13}C$ NMR (67.5 MHz, $CDCl_3$) $\delta$ 16.5, 29.1, 32.0, 125.9, 125.9, 127.1, 134.8, 163.5, 168.3. IR (neat) $\nu$ 1760, 1440, 1260 $cm^{-1}$. HRMS (EI) calcd for ($M^+$) $C_{12}H_{10}F_3NO_2$: 257.0658, found 257.0666.

**3.2.16. Preparation of (3-phenyl-4-propyl-4,5-dihydroisoxazol-5-yl)-trimethylsilanylmethanone [(+)-8a].** This preparation was carried out in a similar manner to the oreparation of **3**. Pale yellow oil. $[\alpha]_D$=+114.7 (*c* 1.31, $CHCl_3$). $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 0.27 (s, 9H), 0.92 (t, 3H, *J*=7.3 Hz), 1.32–1.41 (m, 2H), 1.50–1.69 (m, 2H), 3.85 (td, 1H, *J*=3.6, 8.6 Hz), 4.65 (d, 1H, *J*=3.6 Hz), 7.40–7.43 (m, 3H), 7.64–7.78 (m, 2H). $^{13}C$ NMR (67.5 MHz, $CDCl_3$) $\delta$ −2.8, 13.6, 19.8, 33.0, 48.6, 94.4, 127.1, 128.2, 128.8, 130.1, 160.6. IR (neat) $\nu$ 3000–2700, 1720, 1630, 1430, 1240 $cm^{-1}$. Anal. calcd for $C_{16}H_{23}NO_2Si$: C, 66.39; H, 8.01; N, 4.48. Found: C, 66.27; H, 7.98; N, 4.77.

**3.2.17. Allylation reaction of 8. Preparation of (4*S*,5*S*)-5-[(1*R*)-1-hydroxy-1-trimethylsilyl-3-butenyl]-3-phenyl-4-propyl-4,5-dihydroisoxazole [(+)-9a].** *General procedure*. To a solution of (+)-**8a** (0.801 g, 2.77 mmol) in $CH_2Cl_2$ (10 mL) at −78°C, ally tributyltin (1.816 g, 5.49 mmol) and $TiCl_4$ (0.31 mL, 2.82 mmol) were added. The reaction mixture was allowed to warm to room temperature over 18 h. dil HCl (5 mL) was added to the mixture and the resulting biphasic solution was extracted with $CH_2Cl_2$ (3×20 mL). The organic phase was combined and dried over $Na_2SO_4$. After filtration and removal of solvent. The crude product was purified through flash chromatography (hexane–ethyl acetate 15:1) to give **9a** in 88% yield (0.811 g, 2.44 mmol). Colorless oil. $[\alpha]_D$=+125.8 (*c* 0.93, $CHCl_3$). $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 0.19 (s, 9H), 0.87 (t, 3H, *J*=7.1 Hz), 1.17–1.74 (m, 5H), 2.36 (dd, 1H, *J*=8.0, 14.5 Hz), 2.45 (dd, 1H, *J*=6.8, 14.5 Hz), 3.90 (td, 1H, *J*=4.0, 6.9 Hz), 4.63 (d, 1H, *J*=4.0 Hz), 5.17 (dd, 1H, *J*=1.6, 15.8 Hz), 5.16 (dd, 1H, *J*=1.2, 12.5 Hz), 5.78–5.93 (m, 1H), 7.39–7.41 (m, 3H), 7.65–7.69 (m, 2H). $^{13}$C NMR (67.5 MHz, $CDCl_3$) $\delta$ −2.1, 14.1, 19.2, 33.4, 39.2, 46.1, 70.8, 91.2, 118.9, 127.0, 128.7, 128.9, 129.8, 133.1, 160.5. IR (neat) $\nu$ 3640–3200, 3000–2750, 1640, 1590, 1440, 1240 cm$^{-1}$. Anal. calcd for $C_{19}H_{29}NO_2Si$: C, 68.54; H, 8.82; N, 4.22. Found: C, 68.44; H, 9.12; N, 4.24.

Other compounds **9** were prepared in a similar manner.

**3.2.18. (4*S*,5*S*)-5-[(1*R*)-1-Hydroxy-3-methyl-1-trimethylsilyl-3-butenyl]-3-phenyl-4-propyl-4,5-dihydroisoxazole [(+)-9b].** Colorless oil. $[\alpha]_D$=+105.3 (*c* 1.01, $CHCl_3$). $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 0.14 (s, 9H), 0.87 (t, 3H, *J*=7.3 Hz), 1.24–1.68 (m, 5H), 1.93 (s, 3H), 2.39 (d, 1H, *J*=13.5 Hz), 2.44 (d, 1H, *J*=14.2 Hz), 3.81 (q, 1H, *J*=5.3 Hz), 4.51 (d, 1H, *J*=4.3 Hz), 4,81 (s, 1H), 4.98 (t, 1H, *J*=2.0 Hz), 7.39–7.44 (m, 3H), 7.65–7.69 (m, 2H). $^{13}$C NMR (67.5 MHz, $CDCl_3$) $\delta$ −2.1, 13.9, 18.9, 25.4, 34.1, 41.8, 47.8, 70.4, 91.1, 115.3, 126.8, 128.7, 129.0, 129.7, 142.5, 160.1. IR (neat) $\nu$ 3640–3200, 3000–2750, 1640, 1590, 1440, 1240 cm$^{-1}$. HRMS (FAB) calcd for (M+H) $C_{20}H_{32}NO_2Si$: 346.2202, found 346.2203.

**3.2.19. (5*S* *)-5-[(1*R* *)-1-Hydroxy-1-trimethylsilyl-3-butenyl]-3-phenyl-4,5-dihydroisoxazole [9c].** White solid. $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 0.10 (s, 9H), 1.50 (s, 1H), 2.15 (dd, 1H, *J*=8.3, 13.9 Hz), 2.42 (dd, 1H, *J*=6.9, 13.9 Hz), 3.03 (dd, 1H, *J*=10.6, 16.5 Hz), 3.39 (dd, 1H, *J*=10.6, 16.5 Hz), 4.74 (dd, 1H, *J*=6.6, 9.6 Hz), 5.01 (dd, 1H, *J*=2.0, 9.3 Hz), 5.05 (dd, 1H, *J*=1.3, 13.5 Hz), 5.63–5.82 (m, 1H), 7.27–7.31 (m, 3H), 7.56–7.58 (m, 2H). $^{13}$C NMR (67.5 MHz, $CDCl_3$) $\delta$ −2.4, 33.4, 40.5, 68.3, 87.0, 118.4, 126.6, 128.6, 129.6, 130.0, 133.1, 157.6. IR (neat) $\nu$ 3640–3200, 3000–2750, 1640, 1590, 1440, 1240 cm$^{-1}$. HRMS (FAB) calcd for (M+H) $C_{16}H_{24}NO_2Si$: 290.1570, found 290.1579.

### 3.3. X-Ray structural analysis for (4*S*,5*S*)-5-[(*S*)-hydroxy(trimethylsilyl)methyl]-3-phenyl-4-propyl-4,5-dihydroisoxazole [(+)-4a]

*Crystal data*. $C_{16}H_{25}NO_2Si$, *M*=291.46, monoclinic, *a*=11.790(3), *b*=24.800(4), *c*=5.720(5) Å, $\beta$=91.79°(3), *V*=1672(1) Å$^3$, space group $P2_1/n$, *Z*=4. 4122 of reflections were collected and 1851 unique reflections were used. Final *R* value was 0.0586. Details are available from Cambridge Crystalographic Data Centre on request.[9]

### 3.4. X-Ray structural analysis for (5*S* *)-5-[(1*R* *)-1-hydroxy-1-trimethylsilyl-3-butenyl]-3-phenyl-4,5-dihydroisoxazole [9c]

*Crystal data*. $C_{16}H_{23}NO_2Si$, *M*=289.45, monoclinic, *a*=6.938(5), *b*=20.694(5), *c*=11.863(4) Å, $\beta$=94.27°(4), *V*=1699(1) Å$^3$, space group $P2_1/a$, *Z*=4. 4324 of reflections were collected and 1466 unique reflections were used. Final *R* value was 0.0776. Details are available from Cambridge Crystalographic Data Centre on request.[17]

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