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ARTICLE

Thiyl radical-mediated cyclization of ω-alkynyl *O-tert*-butyldiphenylsilyloximes

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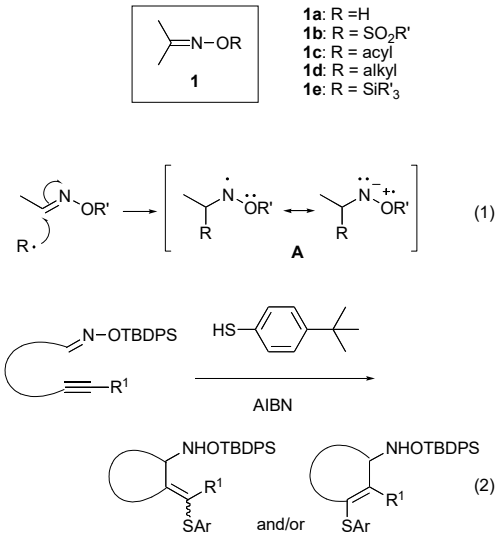
ω-Alkynyl *O-tert*-butyldiphenylsilyloximes, upon treatment with odorless 4-*tert*-butylbenzenethiol in the presence of azobisisobutyronitrile (AIBN) in refluxing benzene, underwent addition of thiyl radical to the alkynyl group followed by radical cyclization of the corresponding vinyl radical onto the *O*-silyloxime moiety to give cyclic *O*-silylhydroxylamines in good yields. The reactivity of *O*-silyloximes in radical cyclization was similar to or even higher than that of *O*-benzyloximes. Facile removal of the silyl group of the cyclization products leading to hydroxylamines and nitrone formation of the hydroxylamines were also demonstrated.

Introduction

Oxime derivatives **1**, which can be classified into oximes **1a**, *O*-sulfonyl oximes **1b**, *O*-acyl oximes **1c**, *O*-alkyl oximes **1d**, and *O*-silyl oximes **1e**, exhibit various reactivities and have been widely utilized in organic synthesis, especially for the synthesis of heterocycles.[1] Among these oximes derivatives, the reactivity of *O*-silyl oximes **1e** has not been extensively investigated, except for *O*-protected oximes,[2] reduction to amines,[3] precursors of nitroso alkenes,[4] and hetero Diels-Alder reaction as 1-siloxyazadienes.[5] In addition, we have reported synthesis of cyclic nitrones[6,7] and both intra- and intermolecular cycloaddition of *N*-boranonitrones.[8] In these reactions, however, *O*-silyl oximes **1e** served only as starting materials for generation of reactive nitrone intermediates. This prompted us to consider the reactivity of *O*-silyl oximes themselves, especially in carbon-carbon bond formation. Taking into account the good radical-accepting ability of *O*-alkyl oximes **1d**, owing to stabilization of the radical intermediate by the electron-donating oxygen atom (eq 1, **A**),[9-12] we anticipated that *O*-silyl oximes could also be used in radical reactions, because silyloxy groups are also strongly electron-donating. To our knowledge, however, there is only one report on radical addition onto *O*-silyl oximes.[13] Therefore, in order to investigate the radical-accepting ability of *O*-silyl oximes, we focused on radical cyclization of ω-alkynyl oximes induced by addition of thiyl radical.[14-16] We have found that the reactivity of *O*-silyl oximes in radical cyclization is equal to or even higher than that of *O*-alkyl oximes (eq 2). We also describe facile removal of silyl groups from the cyclization products and formation of nitrone.



Scheme 1

1. Preparation of the starting oximes

O-Benzyl and *O*-silyl oximes **2** and **3** were prepared as depicted in Scheme 2. *O*-Benzyloximes **2** for comparison with *O*-silyloxime **3** were synthesized from the corresponding aldehydes by treatment with *O*-benzylhydroxylamine hydrochloride and sodium bicarbonate in EtOH-H_2O (Scheme 2, conditions i). *O-tert*-Butyldiphenylsilyl oximes **3** (*O*-TBDPS oximes) were also prepared from aldehydes.

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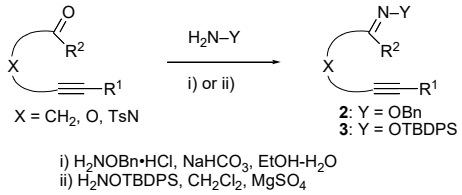
Thus, on treatment of aldehydes with *O*-TBDPS hydroxylamine[17] in the presence of $MgSO_4$ in CH_2Cl_2 (conditions ii), dehydration occurred smoothly to give *O*-TBDPS oximes **3** (Supporting Information).



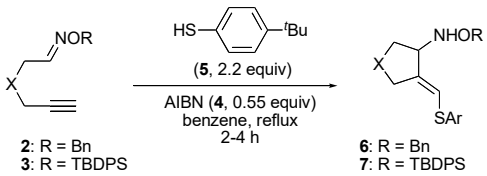
Scheme 2

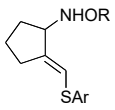
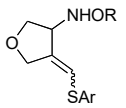
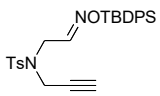
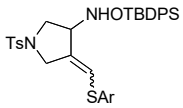
2. Radical cyclization of oximes 2 and 3 with 4-*tert*-butylbenzenethiol

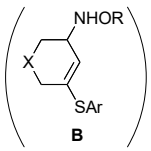
Our investigation of radical cyclization began with a comparison of the reactivity of *O*-benzyl oximes **2** with *O*-silyl oximes **3** in thiyl radical-induced radical cyclization. 4-*tert*-Butylbenzenethiol (**5**)[18] was employed as a thiyl radical precursor in place of conventional benzenethiol (PhSH), because thiol **5** exhibits only a faint smell compared to the offensive odor of PhSH, which makes it undesirable for practical use in radical cyclization. To our knowledge, this is the first report of the use of thiol **5** for radical cyclization as an odorless alternative to PhSH. Heating *O*-benzyl oxime **2a** with 2.2 equiv of 4-*tert*-butylbenzenethiol (**5**) in the presence of 0.55 equiv of azobisisobutyronitrile (AIBN) (**4**) in refluxing benzene induced radical reaction to afford cyclization product **6a** in 54% yield (Table 1, entry 1).[19] Similar treatment of *O*-TBDPS oxime **3a** under the same conditions gave *O*-TBDPS cyclization product **7a** in a similar yield (55%) (entry 2). In contrast, oxime itself (**2a**, R = H) did not react under similar conditions, probably because thiyl radical abstracted oxime hydrogen to give the stable iminoxyl radical (-CH=N-O•), interfering with the radical chain process.[20] A difference in reactivity was observed between **2b** and **3b** as oxygen-tethered starting materials. Radical reaction of *O*-silyl oxime **3b** furnished a much higher yield of cyclization product (81% yield of **7b**) than did the reaction of *O*-benzyl oxime **2b** (44% yield of **6b**) (entries 3 and 4). Radical reaction of nitrogen-tethered *O*-silyl oxime **3c** afforded a good yield (63%) of cyclization product **7c** as a 4:1 mixture of geometrical isomers (entry 5).[21] The data in Table 1 indicate that the reactivity of *O*-silyl oximes **2** is similar to or greater than that of the *O*-benzyl counterparts **3**.

All the reactions in Table 1 resulted in exclusive formation of five-membered ring products **6** and **7** without any six-membered products **B**. This radical process may involve several equilibriums (Scheme 3).[16a] Reversible addition of thiyl radical **C** to the alkyne moiety[22] provides vinyl radical **D**, which undergoes cyclization to give **6** and **7**. Predominance of (Z)-geometry (X = TsN or O) of the vinyl sulfide group in cyclization products **6** and **7** may be explained in terms of the thermodynamic stabilities of products **6** and **7**. Under radical conditions, vinyl sulfides undergo further radical addition with thiyl radical, resulting in geometrical isomerization.[23] In this case, **E** type products may isomerize to thermodynamically morestable **G** type products by addition-elimination of thiyl radical **C** via radical **F**.

Table 1. Thiyl radical-induced cyclization of oximes **2** and **3** having terminal alkyne moieties.



entry	oxime	products (yield)
1 2	 **2a**: R = Bn **3a**: R = TBDPS	 **6a**: R = Bn (54%) **7a**: R = TBDPS (55%)
3 4	 **2b**: R = Bn **3b**: R = TBDPS	 **6b**: R = Bn (44%) *E* : *Z*= 16:84 **7b**: R = TBDPS (81%) *E* : *Z*= 11:89
5	 **3c**	 **7c** (63%) *E* : *Z*= 20:80



We next examined radical cyclization of *O*-silyl oximes **3** having an internal alkyne moiety (Table 2). Heating oxygen-tethered *O*-benzyl oxime **3d** bearing a methyl group at the alkyne terminus with thiol **5** in the presence of AIBN (**4**) gave six-membered cyclization product **8d** (69%), along with a small amount of five-membered ring product **7d** (7%) (entry 1). In a similar manner, nitrogen-tethered *O*-TBDPS oxime **3e** underwent radical cyclization with thiol **5** to give

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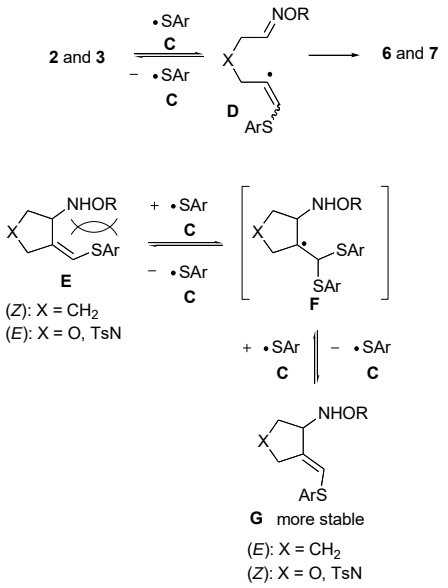
Scheme 3

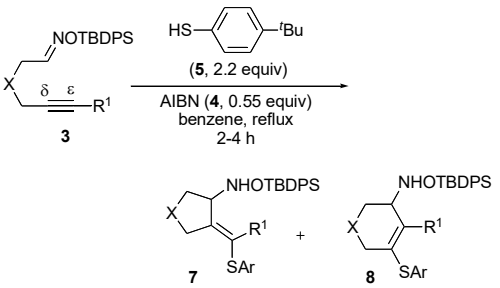


8e and **7e** in 63% and 11% yields, respectively (entry 2). Radical reaction of phenyl-substituted oxime **3f** exhibited clear regio-selectivity and exclusively afforded six-membered cyclization product **8f** in 78% yield (entry 3). Nitrogen-tethered *O*-silyl oxime **3g** also gave **8g** as a sole product in 73% yield (entry 4). Table 2 shows that radical cyclization of oximes **3** having substituents at the alkyne terminus tends to afford six-membered products.

Although the origin of the regio-selectivity remains unclear, one possibility might involve steric interaction in the transition states (Figure 1). Transition state **H** derived from attack at the ε-position of **3** by thiyl radical suffers steric interaction between the oxime group and substituent at the terminal of the alkene moiety, whereas transition state **I** exhibits less steric repulsion. Thus, six-membered cyclization products **8** would be formed predominantly via **I**. In the case of phenyl-substituted substrates, radical intermediate **J** may be strongly stabilized by conjugation with the phenyl group, and hence the reaction would tend to occur via **J** followed by **I** (R' = Ph), resulting in the exclusive formation of six-membered products.

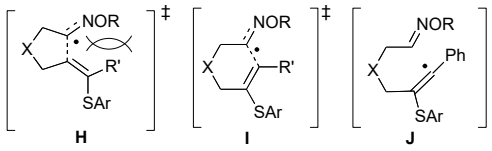
We next examined radical cyclization of homologated substrates (Table 3). *O*-Benzyl oxime **2h**, on treatment with thiol **5** in the presence of AIBN (**4**) in refluxing benzene, underwent radical addition of thiyl radical followed by cyclization to give **9h** in 59% yield (entry 1). Reaction of *O*-silyl counterpart **3h** under the same conditions afforded cyclization product **10h** in a slightly better yield (62%) (entry 2). Radical reaction of nitrogen-tethered *O*-TBDPS oxime **3i** furnished six-membered cyclization product **10i** in a moderate yield (49%) (entry 3). Oxime **3j** having further elongated

Table 2. Thiyl radical-induced cyclization of oximes **2** and **3** having an internal alkyne moiety.



entry	oxime	products (yield)	
1	**3d**: X = O	**7d** (7%)	**8d** (69%)
2	**3e**: X = TsN	**7e** (11%)	**8e** (63%)
3	**3f**: X = O		**8f** (78%)
4	**3g**: X = TsN		**8g** (73%)

Figure 1



tethers, however, afforded thiyl radical-addition product **11j** in 63% yield in place of seven-membered cyclic compound (entry 4). Conformational effects on the present cyclization were also examined (Table 4). Treatment of carbon-tethered ketoxime **3k** under our usual conditions did not give cyclization product **7k** at all, although the corresponding aldoxime **3a** afforded a moderate yield of cyclization product **7a** (Table 4, entry 1 *vs* Table 1, entry 2). Cyclization ability could be recovered by utilizing conformational effects. Thus, tosylamide-tethered ketoxime **3l** underwent thiyl radical addition followed by cyclization to furnish **7l** in 56% yield (entry 2). The tosylamide tether was also effective for phenyl ketoxime **3m**, giving rise to **7m** in 57% yield. Gem-disubstitution effect (Thope-Ingold effect)[24] was found to improve the yield of cyclization product (entries 4 and 5). Malonate-derived aldoxime **3n** afforded the cyclized product in 73% yield, whereas the straight-chain aldoxime **3a** gave only a moderate yield of cyclization product

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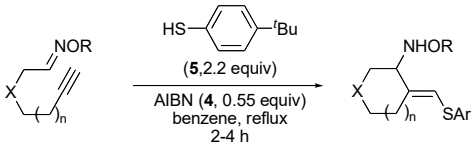
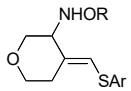
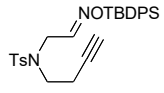
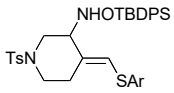
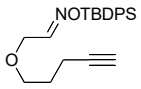
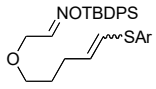
Table 3. Thiyl radical-induced cyclization of homologated oximes **2** and **3**.



2: R = Bn
3: R = TBDPS
n = 1, 2
9: R = Bn
10: R = TBDPS

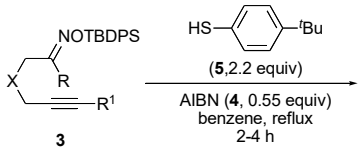
entry	oxime	product (yield)
1 2	 **2h**: R = Bn **3h**: R = TBDPS	 **9h** (59%) **10h** (62%)
3	 **3i**	 **10i** (49%)
4	 **3j**	 **11j** (63%)

7a (Table 4, entry 4 *vs* Table 1, entry 2). The yield of cyclization product **8o** from gem-dimethylated substrate **3o** reached 91% (Table 4, entry 5 *vs* Table 2, entry 3).

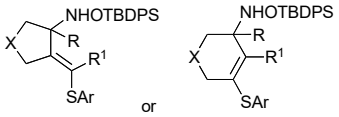
3. Radical cyclization of related substrates

Another kind of radical, such as tin radical, can be used in place of thiyl radical for radical cyclization.[25] Thus, on treatment with Bu_3SnH in the presence of AIBN in refluxing benzene, oxime **3g** having a phenyl group at the alkyne-terminus underwent addition of tributyltin radical followed by radical cyclization of the resulting vinyl radical onto silyl oxime, giving rise to yield six-membered product **12** bearing a vinyl stannyl group in 49%. Since vinyl stannyl compounds are known to be good substrates for Stille coupling, this reaction would be useful in organic synthesis. The present thiyl radical-induced cyclization can be applied to ω-alkenyl *O*-silyl oxime **13**. When oxime **13** was exposed to thiol **5** in the presence of AIBN in refluxing benzene for 3 h, *cis*-cyclized product *cis*-**14** and *trans*-product *trans*-**14** were obtained in 31% and 35% yields, respectively (Scheme 4).

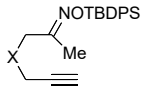
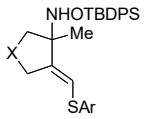
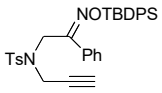
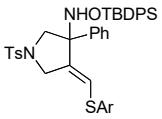
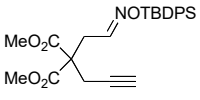
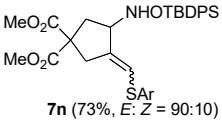
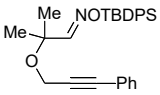
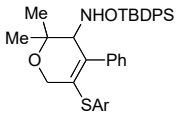
Table 4. Conformational effect in thiyl radical-induced cyclization of *O*-silyl oximes **3**.



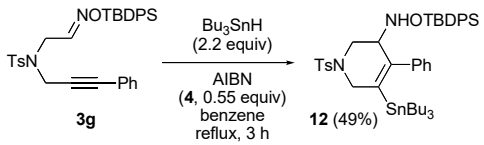
3



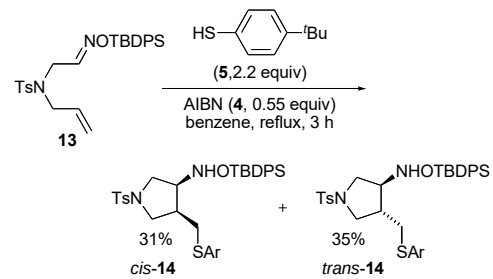
7 or **8**

entry	oxime	product
1 2	 **3k**: X = CH_2 **3l**: X = TsN	 **7k**: X = CH_2 (0%) **7l**: X = TsN (56%)
3	 **3m**	 **7m** (57%)
4	 **3n**	 **7n** (73%, *E*: *Z* = 90:10)
5	 **3o**	 **8o** (91%)

Scheme 4



3g **12** (49%)



13

cis-**14** + *trans*-**14**

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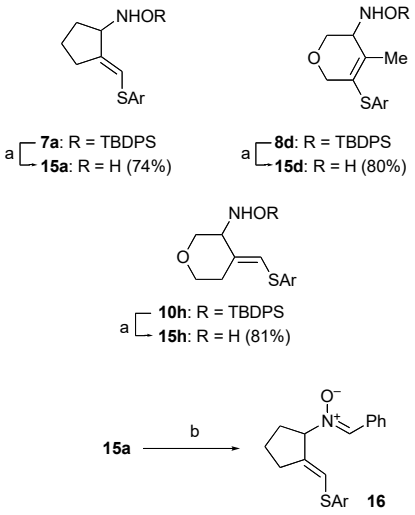
4. Desilylation of the products

Facile cleavage of the oxygen-silicon bond is a characteristic reaction of *O*-silyl compounds, whereas the corresponding cleavage is unavailable with *O*-alkyl compounds. Thus, desilylation of the cyclized products **7a**, **8d** and **10h** was next examined (Scheme 5). When *O*-TBDPS hydroxylamine **7a** was treated with TBAF-AcOH (1:4) in THF at 0 °C, clean desilylation occurred to give hydroxylamine **15a** in 74% yield. Compounds **8d** and **10h** were also exposed to TBAF-AcOH to afford hydroxylamines **15d** and **15h** in 80% and 81% yields, respectively. Since alkyl hydroxylamines are representative precursors for nitrones, which are very useful 1,3-dipolar compounds, nitrone formation was demonstrated by using hydroxylamine **15a**. Thus, hydroxylamine **15a** was condensed with benzaldehyde in the presence of $MgSO_4$ in $(CH_2Cl)_2$ to afford nitrone **16** in 88% yield.

Scheme 5



Conditions: a) TBAF, AcOH, THF, 0 °C; b) PhCHO, $MgSO_4$, $(CH_2Cl)_2$, r.t., 88%

Conclusions

We have demonstrated good radical-accepting ability of *O*-silyloximes by utilizing them for odorless thiol-derived thiyl radical-induced cyclization of ω-alkynyl *O*-*tert*-butyldiphenyloximes. Removal of silyl groups from the cyclization products was readily accomplished to give hydroxylamines. We also showed that one of the hydroxylamines was readily converted to a nitrone. Synthetic applications of the present cyclization and other radical reactions of *O*-silyloximes are under investigation.

Experimental

Melting points were determined with a Yanagimoto micro melting point apparatus and are uncorrected. Infrared spectra (IR) were recorded with a Shimadzu FTIR–8200A. ^{1}H NMR and ^{13}C NMR spectra spectra were recorded on a JEOL JNM–AL300 (300 MHz) spectrometer. Measurements of mass spectra (MS) and high-resolution MS (HRMS) were performed with a JEOL JMS-HX110 mass spectrometer or a JEOL JMS-T100LP. Column chromatography was carried out on silica gel (Silica Gel 60 N, Kanto Chemical Co., Inc. or Silica Gel BW-127ZH, Fuji Silysia Chemical, ltd). Merck precoated thin layer chromatography (TLC) plates (silica gel 60 F254, 0.25 mm, Art 5715) were used for the TLC analysis.

General procedure: To a boiling solution of an oxime **2** or **3** (1 equiv) in benzene (40 mL/ 1 mmol of an oxime) was added dropwise a solution of **5** (2.2 equiv) and AIBN (0.55 equiv) in benzene (5 mL/1 mmol of **5**) via syringe-pump over 2-4 hrs. The mixture was concentrated under reduced pressure, and the residue was chromatographed on silica gel to afford product(s).

(*E*)-*O*-Benzyl-*N*-{2-[(4-*tert*-butylphenylthio)methylene]cyclopentyl}hydroxylamine (6a) (Table 1, entry 1). Following General Procedure, **6a** (35.0 mg, 54%) was obtained from **2a** (35.6 mg, 0.177 mol), **5** (67.1 μL, 0.389 mmol), and **4** (16.0 mg, 97.0 μmol) after purification by column chromatography on silica gel (hexane-AcOEt, 10/1). IR (KBr) 3030, 2963, 2868 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO) δ 1.25 (s, 9H), 1.53-1.67 (m, 2H), 1.75-1.83 (m, 2H), 2.15-2.26 (m, 2H), 3.79-3.89 (m, 1H), 6.34-6.36 (m, 1H), 6.65 (d, *J* = 5.9 Hz, 1H), 7.21-7.33 (m, 9H); ^{13}C-NMR (75 MHz, DMSO) δ 22.6, 30.0, 30.8, 31.0, 34.1, 64.4, 75.5, 116.0, 126.0, 127.4, 127.9, 128.1, 132.3, 138.3, 144.8, 148.8 (one signal overlapped); HRMS (EI) m/z calcd for $C_{23}H_{29}NOS$ 367.1970, found 367.1955.

(*E*)-*N*-{2-[(4-*tert*-Butylphenylthio)methylene]cyclopentyl}-*O*-(*tert*-butyldiphenylsilyl)hydroxylamine (7a) (Table 1, entry 2). Following General Procedure, **7a** (45.5 mg, 55%) was obtained from **2a** (60.9 mg, 0.174 mol), **5** (66.1 μL, 0.383 mmol), and **4** (14.9 mg, 90.5 μmol) after purification by column chromatography on silica gel (hexane-AcOEt, 25/1). IR (KBr) 3072, 2963, 2858 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.09 (s, 9H), 1.31 (s, 9H), 1.62-2.23 (m, 6H), 3.80 (s, 1H), 4.98 (d, *J* = 7.0 Hz, 1H), 6.29 (s, 1H), 7.20-7.70 (m, 14H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 19.2, 23.0, 27.1, 27.4, 30.2, 31.3, 31.4, 34.4, 67.0, 118.4, 126.0, 127.4, 127.5, 128.6, 129.5, 132.9, 134.0, 135.5, 135.8, 135.9, 144.0, 149.3; HRMS (EI) m/z calcd for $C_{32}H_{41}NOSSi$ 515.2678, found 515.2687.

***O*-Benzyl-*N*-{4-[(4-*tert*-butylphenylthio)methylene]tetrahydrofuran-3-yl}hydroxylamine (6b) (Table 1, entry 3).** Following General Procedure, **6b** (28.0 mg, 44%, *E*/*Z* = 16/84) was obtained from **2b** (33.7 mg, 0.166 mol), **5** (63.0 μL, 0.365 mmol), and **4** (14.9 mg, 90.5 μmol) after purification by column chromatography on silica gel (hexane-AcOEt, 5/1). IR

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(KBr) 3030, 2962, 2866, 1716 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.24 (s, 9H), 3.78-3.83 (m, 1H), 3.90-3.95 (m, 1H), 4.01-4.07(m, 1H), 4.18-4.25 (m, 1H), 4.35-4.42 (m, 1H), 4.67 (s, 2H x 0.16), 4.71 (br s, 2H x 0.84), 6.19-6.21 (m, 1H x 0.16), 6.33-6.35 (m, 1H x 0.84), 7.19-7.27 (m, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 31.0, 34.3, 64.1, 69.5, 71.9, 76.3, 119.0, 126.0, 127.7, 128.21, 128.28, 128.3, 129.2, 137.3, 138.6, 150.1 (several signals overlapped); HRMS (FAB) *m/z* calcd for $C_{21}H_{26}NO_2Si$ $[M+H]^+$ 370.1762, found 370.1782.

***N*-{4-[(4-*tert*-Butylphenylthio)methylene]tetrahydrofuran-3-yl}-*O*-(*tert*-butyldiphenylsilyl)hydroxylamine (7b). (Table 1, entry 4).** Following General Procedure, **7b** (67.0 mg, 81%, *E*/*Z* = 11/89) was obtained from **2b** (57.5 mg, 0.159 mol), **5** (60.4 μL, 0.350 mmol), and **4** (13.0 mg, 79.5 μmol) after purification by column chromatography on silica gel (hexane-AcOEt, 25/1). All data were described without distinction of the two diastereomers. IR (KBr) 3072, 2961, 2932, 2856 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.10 (s, 9H x 0.89), 1.12 (s, 9H x 0.11), 1.30 (s, 9H x 0.11), 1.31 (s, 9H x 0.89), 3.73-3.81 (m, 1H + 2H x 0.89), 4.05-4.40 (m, 2H x 0.11 + 2H x 0.89 + 2H x 0.11), 5.17 (br, 1H x 0.89), 5.48 (br, 1H x 0.11), 6.24 (s, 1H x 0.11), 6.29 (s, 1H x 0.89), 7.21-7.41 (m, 14H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 19.0, 19.2, 26.6, 27.4, 29.7, 31.3, 34.5, 64.5, 65.8, 69.7, 71.2, 71.4, 71.6, 119.2, 119.4, 126.1, 127.5, 127.7, 129.1, 129.2, 129.6, 131.8, 133.7, 135.7, 135.9, 138.5, 150.1; HRMS (FAB) m/z calcd for $C_{31}H_{39}NO_2SSi$ $[M+H]^+$ 517.2471, found 517.2567.

***N*-{4-[(4-*tert*-Butylphenylthio)methylene]-1-tosylpyrrolidin-3-yl}-*O*-(*tert*-butyldiphenylsilyl)hydroxylamine (7c) (Table 1, entry 5).** Following General Procedure, **7c** (70.3 mg, 63%, *E*/*Z* = 20/80) was obtained from **3c** (84.4 mg, 0.167 mol), **5** (63.5 μL, 0.368 mmol), and **4** (46.6 mg, 0.284 mmol) after purification by column chromatography on silica gel (hexane-CH_2Cl_2, 1/2 then hexane-AcOEt, 25/1). IR (KBr) 2963, 2858, 2349 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.04 (s, 9H x 0.2), 1.06 (s, 9H x 0.8), 1.29 (s, 9H x 0.2), 1.31 (s, 9H x 0.8), 2.41 (s, 3H x 0.2), 2.43 (s, 3H x 0.8), 3.12-3.28 (m, 1H x 0.8, 1H x 0.2), 3.56-3.88 (m, 1H x 0.8 x 3, 1H x 0.2 x 3, 1H x 0.8), 4.16 (br, 1H x 0.2), 5.00 (d, *J* = 10.9 Hz, 1H x 0.8), 5.33 (d, *J* = 8.1 Hz, 1H x 0.2), 6.12 (s, 1H x 0.8), 6.29 (s, 1H x 0.2), 7.13-7.72 (m, 18H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 19.1, 21.5, 27.2, 27.3, 31.2, 34.5, 50.2, 50.9, 51.5, 52.4, 63.1, 64.5, 122.4, 122.7, 126.1, 126.2, 127.5, 127.6, 127.7, 127.9, 129.3, 129.6, 129.7, 131.1, 131.7, 132.2, 133.2, 133.4, 133.5, 134.9, 135.4, 135.7, 135.9, 143.7, 143.8, 150.3, 150.4; HRMS (EI) m/z calcd for $C_{38}H_{46}N_2O_3S_2Si$ 670.2719, found 670.2711.

***N*-{4-[1-(4-*tert*-Butylphenylthio)ethylidene]tetrahydrofuran-3-yl}-*O*-(*tert*-butyldiphenylsilyl)hydroxylamine (7d) and**

***N*-[5-(4-*tert*-Butylphenylthio)-4-methyl-3,6-dihydro-2*H*-pyran-3-yl]-*O*-(*tert*-butyldiphenylsilyl)hydroxylamine (8d) (Table 2, entry 1).**

Following General Procedure, **7d** (6.3 mg, 7%) and **8d** (61.0 mg, 69%) were obtained from **3d** (60.7 mg, 0.166 mmol), **5** (63.0 μL, 0.365 mmol), and **4** (14.9 mg, 91.3 μmol) after purification by column chromatography on silica gel (hexane-AcOEt, 10/1).

7d: IR (KBr) 3072, 2962, 2858 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.08 (s, 9H), 1.29 (s, 9H), 1.56 (s, 3H), 3.66 (dd, *J* = 9.9 and 3.9 Hz, 1H), 3.90 (br, 1H), 4.21 (dd, *J* = 14.1 and 2.1 Hz, 1H), 4.44-4.55 (m, 2H), 5.15 (br, 1H), 7.13-7.70 (m, 14H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 19.1, 20.3, 27.3, 31.2, 34.5, 64.7, 70.8, 71.1, 125.9, 127.4, 127.5, 129.4, 129.5, 131.3, 133.9, 135.70, 135.73, 150.4 (several signals overlapped); HRMS (EI) *m/z* calcd for $C_{32}H_{42}NO_2SSi$ 531.2627, found 531.2608

8d: IR (KBr) 3072, 2961, 2856 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.10 (s, 9H), 12.8 (s, 9H), 1.65 (s, 3H), 3.06 (d, *J* = 9.3 Hz, 1H), 3.39 (dd, *J* = 11.4 and 2.1 Hz, 1H), 3.91 (s, 1H), 4.50 (d, *J* = 11.4 Hz, 1H), 5.49 (d, *J* = 10.2 Hz, 1H), 7.09-7.76 (m, 14H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 18.7, 19.2, 27.4, 31.2, 34.4, 61.0, 64.2, 68.7, 126.1, 127.4, 127.5, 128.5, 129.46, 129.49, 129.6, 130.1, 133.9, 135.2, 135.4, 135.7, 135.9, 149.8; HRMS (FAB) *m/z* calcd for $C_{32}H_{40}NO_2SSi$ $[M+H]^+$ 532.2706, found 532.2656

***N*-{4-[(*E*)-1-(4-*tert*-Buthylphenylthio)ethylidene]-1-tosylpyrrolidin-3-yl}-*O*-(*tert*-buthyldiphenylsilyl)hydroxylamine (7e) and**

***N*-[5-(4-*tert*-Butylphenylthio)-4-methyl-1-tosyl-1,2,3,6-tetrahydropyridin-3-yl]-*O*-(*tert*-butyldiphenylsilyl)hydroxylamine (8e) (Table 2, entry 2).**

Following General Procedure, **7e** (12.7 mg, 11%) and **8e** (70.4 mg, 63%) were obtained from **3e** (84.5 mg, 0.163 mmol), **5** (61.8 μL, 0.358 mmol), and **4** (14.7 mg, 89.5 μmol) after purification by column chromatography on silica gel (hexane-CH_2Cl_2, 1/2 then hexane-AcOEt, 5/1).

7e: IR (KBr) 2961, 2858 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.07 (s, 9H), 1.29 (s, 9H, 3H), 2.44 (s, 3H), 2.90 (dd, *J* = 5.1 and 10.3 Hz, 1H), 3.58 (d, *J* = 14.7 Hz, 1H), 3.80 (br, 1H), 4.05 (d, *J* = 14.7 Hz, 1H), 4.22 (d, *J* = 10.3 Hz, 1H), 4.96 (br, 1H), 7.08-7.77 (m, 18H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 19.2, 19.4, 21.6, 27.0, 27.3, 31.2, 50.9, 51.4, 63.4, 126.0, 127.5, 127.6, 127.7, 128.1, 128.6, 129.6, 129.7, 131.8, 132.1, 133.4, 134.8, 135.5, 135.7, 135.8, 143.7 (several signals overlapped); HRMS (EI) m/z calcd for $C_{39}H_{48}N_2O_3S_2Si$ 684.2876, found 684.2875.

8e: IR (KBr) 2961, 2856, cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.12 (s, 9H), 1.29 (s, 9H), 1.60 (s, 3H), 2.39 (s, 3H), 2.41 (d, *J* = 11.0 Hz, 1H), 3.10 (d, *J* = 16.1 Hz, 1H), 3.25 (d, *J* = 9.5 Hz, 1H), 3.86 (d, *J* = 16.1 Hz, 1H), 4.39 (d, *J* = 11.7 Hz, 1H), 5.35 (d, *J* = 10.6 Hz, 1H), 7.03-7.77 (m, 18H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 18.9, 19.2, 21.5, 27.3, 31.2, 34.5, 43.5, 48.9, 61.9, 126.0, 126.2, 127.4, 127.6, 127.7, 129.4, 129.6, 133.5, 133.6, 133.7, 135.7, 135.9, 136.0, 143.7, 150.0; HRMS (EI) m/z calcd for $C_{39}H_{48}N_2O_3S_2Si$ 684.2876, found 684.2890.

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_N_-[5-(4-_tert_-Butylphenylthio)-4-phenyl-3,6-dihydro-2_H_-pyran-3-yl]-_O_-(_tert_-butyldiphenylsilyl)hydroxylamine (8f) (Table 2, entry 3).

Following General Procedure, **8f** (76.9 mg, 78%) was obtained from **3f** (70.9 mg, 0.166 mmol), **5** (63.0 µL, 0.365 mmol), and **4** (14.9 mg, 91.3 µmol) after purification by column chromatography on silica gel (hexane-AcOEt, 20/1). IR (KBr) 2962, 2856 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.00 (s, 9H), 1.29 (s, 9H), 3.57-3.64 (m, 2H), 4.01 (dd, *J* = 16.2 and 1.8 Hz, 1H) 4.11 (d, *J* = 16.5 Hz, 1H), 4.56 (d, *J* = 9.6 Hz, 1H), 5.50 (br, 1H), 7.16-7.58 (m, 19H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 19.1, 27.2, 31.1, 34.4, 60.9, 64.8, 68.5, 126.0, 127.2, 127.27, 127.33, 127.7, 127.8, 128.5, 129.3, 131.0, 132.3, 133.6, 133.7, 135.3, 135.55, 135.61, 136.9, 138.8, 150.4; HRMS (FAB) *m/z* calcd for $C_{37}H_{44}NO_2SSi$ $[M+H]^+$ 594.2862, found.594.2876

_N_-[5-(4-_tert_-Butylphenylthio)-4-phenyl-1-tosyl-1,2,3,6-tetrahydropyridin-3-yl]-_O_-(_tert_-butyldiphenylsilyl)hydroxylamine (8g) (Table 2, entry 4).

Following General Procedure, **8g** (87.2 mg, 73%) was obtained from **3g** (92.5 mg, 0.159 mmol), **5** (60.4 µL, 0.350 mmol), and **4** (14.4 mg, 87.5 µmol) after purification by column chromatography on silica gel (hexane-AcOEt, 6/1). IR (KBr) 2963, 2858 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.98 (s, 9H), 1.31 (s, 9H), 2.42 (s, 3H), 2.69 (d, *J* = 11.7 Hz, 1H), 3.23 (d, *J* = 16.5 Hz, 1H), 3.77 (d, *J* = 9.9 Hz, 1H), 3.89 (d, *J* = 16.5 Hz, 1H), 4.32 (d, *J* = 11.7 Hz, 1H), 5.40 (d, *J* = 10.3 Hz, 1H), 7.01-7.61 (m, 23H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 19.2, 21.5, 27.2, 31.2, 34.6, 44.1, 48.8, 62.0, 126.2, 127.4, 127.5, 127.8, 127.9, 128.6, 128.8, 129.4, 129.7, 129.9, 131.3, 133.3, 133.5, 133.6, 135.6, 135.7, 137.7, 138.8, 143.8, 150.9 (several signals overlapped); HRMS (EI) m/z calcd for $C_{44}H_{50}N_2O_3S_2Si$ 746.3032, found 746.3101.

***O*-Benzyl-*N*-{4-[(*E*)-(4-*tert*-butylphenylthio)methylene]tetrahydro-2*H*-pyran-3-yl}hydroxylamine (9h) (Table 3, entry 1).**

Following General Procedure, **9h** (40.3 mg, 59%) was obtained from **2h** (36.1 mg, 0.166 mmol), **5** (63.0 µL, 0.365 mmol), and **4** (14.9 mg, 91.3 µmol) after purification by column chromatography on silica gel (hexane-AcOEt, 10/1). IR (KBr) 2962, 2904 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.30 (s, 9H), 2.52-2.55 (m, 2H), 3.44-3.53 (m, 3H), 3.63 (dd, *J* = 11.7 and 3.0 Hz, 1H), 3.90-3.98 (m, 2H), 4.70 (d, *J* = 11.4 Hz, 1H), 4.76 (d, *J* = 11.4 Hz, 1H), 5.50-5.90 (very br, 1H), 6.19 (s, 1H), 7.23-7.65 (m, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 28.1, 31.2, 34.5, 62.8, 68.1, 69.8, 76.5 120.8, 126.1, 127.8, 128.3, 128.5, 129.0, 132.3, 136.2, 137.6, 149.7; HRMS (FAB) *m/z* calcd for $C_{23}H_{30}NO_2S$ $[M+H]^+$ 384.1997, found 384.1968.

***N*-{4-[(*E*)-(4-*tert*-Butylphenylthio)methylene]tetrahydro-2*H*-pyran-3-yl}-*O*-(*tert*-butyldiphenylsilyl)hydroxylamine (10h) (Table 3, entry 2).**

Following General Procedure, **10h** (56.4 mg, 62%) was obtained from **3h** (60.7 mg, 0.166 mmol), **5** (63.0 µL, 0.365 mmol), and **4** (14.9 mg, 91.3 µmol) after purification by column chromatography on silica gel (hexane-AcOEt, 15/1). IR (KBr) 3072, 2962, 2856 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.10 (s, 9H), 1.31 (s, 9H), 2.31-2.41 (m, 1H), 2.48-2.54 (m, 1H), 3.41 (td, *J* = 10.8 and 3.3 Hz, 1H), 3.50 (dd, *J* = 12.0 and 3.0 Hz, 1H), 3.86-3.93 (m, 1H), 3.97-4.01 (m, 1H), 5.60 (br, 1H), 5.98 (s, 1H), 7.22-7.72 (m, 14H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 19.2, 27.1, 27.4, 27.9, 31.3, 34.4, 64.1, 68.1, 69.3, 120.8, 126.0, 127.5, 127.7, 128.8, 129.5, 132.4, 133.8, 135.3, 135.8, 135.9, 136.1, 149.5; HRMS (FAB) *m/z* calcd for $C_{32}H_{42}NO_2SSi$ $[M+H]^+$ 532.2706, found 532.2711.

***N*-{4-[(*E*)-(4-*tert*-Butylphenylthio)methylene]-1-tosylpiperidin-3-yl}-*O*-(*tert*-butyldiphenylsilyl)hydroxylamine (10i) (Table 3, entry 3).**

Following General Procedure, **10i** (59.7 mg, 49%) was obtained from **3i** (92.3 mg, 0.178 mmol), **5** (67.5 µL, 0.391 mmol), and **4** (16.1 mg, 97.9 µmol) after purification by column chromatography on silica gel (hexane-AcOEt, 5/1). IR (KBr) 2963, 2858 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.10 (s, 9H), 1.30 (s, 9H), 2.25-2.36 (m, 1H), 2.40 (s, 3H), 2.47-2.55 (m, 2H) 2.66 (dd, *J* = 8.4 and 3.3 Hz, 1H), 3.27 (d, *J* = 10.3 Hz, 1H), 3.49-3.53 (m, 1H), 3.69 (d, *J* = 11.0 Hz, 1H), 5.51 (d, *J* = 10.6 Hz, 1H), 5.86 (s, 1H), 7.14-7.71 (m, 18H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 19.2, 21.5, 26.5, 27.4, 31.2, 34.5, 46.2, 48.4, 62.9, 122.6, 126.0, 127.5, 127.7, 129.1, 129.6, 129.7, 131.8, 133.3, 133.7, 133.9, 135.8, 135.9, 143.6, 149.9 (several signals overlapped); HRMS (EI) m/z calcd for $C_{39}H_{48}N_2O_3S_2Si$ 684.2876 found 684.2891.

2-[5-(4-_tert_-Butylphenylthio)pentyloxy]acetaldehyde _O_-(_tert_-butyldiphenylsilyl)oxime (11j) (Table 3, entry 4).

Following General Procedure, **11j** (58.6 mg, 63%, *E/Z* = 1:1) was obtained from **3j** (63.0 mg, 0.166 mmol), **5** (63.0 µL, 0.365 mmol), and **4** (14.9 mg, 91.3 µ mol) after purification by column chromatography on silica gel (hexane-AcOEt, 20/1). All data were described without distinction of the diastereomers.

IR (KBr) 3072, 2960, 2858 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.10 (s, 9H) 1.30 (s, 9H), 1.64-1.74 (m, 2H), 2.15-2.33 (m, 2H), 3.37-3.57 (m, 2H), 4.06-4.09 (m, 1H), 4.50-4.53 (m, 1H), 5.68-5.80 (m, 1H x 0.5), 5.84-5.97, (m, 1H x 0.5), 6.10-6.23 (m, 1H), 7.13-7.16 (m, 1H x 0.5), 7.66-7.69 (m, 1H x 0.5), 7.25-7.41 (m, 14H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 19.2, 25.7, 27.0, 28.9, 29.5, 31.3, 67.4, 69.7, 122.5, 124.4, 126.0, 127.6, 129.0, 129.6, 131.2, 133.3, 134.7, 135.5, 153.3 (several signals overlapped); HRMS (FAB) *m/z* calcd for $C_{33}H_{44}NO_2SSi$ $[M+H]^+$ 546.2862, found 546.2812.

***N*-{4-[(*E*)-(4-*tert*-Butylphenylthio)methylene]-3-methyl-1-tosylpyrrolidin-3-yl}-*O*-(*tert*-butyldiphenylsilyl)hydroxylamine (7l) (Table 4, entry 2).**

Following General Procedure, **7l** (66.8 mg, 56%) was obtained from **3l** (92.2 mg, 0.178 mmol), **5** (67.4 µL, 0.391 mmol), and **4** (16.0

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mg, 97.7 μmol) after purification by column chromatography on silica gel (hexane-CH_2Cl_2, 1/5, 1/3 then hexane-AcOEt, 8/1).

IR (KBr) 3072, 2963, 2932, 2858 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.05-1.08 (m, 12H), 1.29 (s, 9H), 2.42 (s, 3H), 2.86 (d, *J* = 9.7 Hz, 1H), 3.65 (d, *J* = 9.7 Hz, 1H), 3.74 (dd, *J* = 12.6 and 2.0 Hz, 1H), 3.86 (dd, *J* = 12.6 and 2.0 Hz, 1H), 5.06 (br s, 1H), 6.11 (br s, 1H), 7.15-7.78 (m, 18H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 19.2, 21.4, 21.5, 27.1, 27.2, 31.2, 34.5, 50.9, 56.4, 67.6, 120.1, 126.2, 127.5, 128.0, 129.3, 129.7, 131.4, 133.1, 133.3, 135.4, 135.8, 136.1, 138.6, 143.7, 150.3 (several signals overlapped); HRMS (EI) m/z calcd for $C_{39}H_{48}N_2O_3S_2Si$ 684.2876, found 684.2859.

_N_-{4-[(_E_)-(4-_tert_-Butylphenylthio)methylene]-3-phenyl-1-tosylpyrrolidin-3-yl}-_O_-(_tert_-butyldiphenylsilyl)hydroxylamine (7m) (Table 4, entry 3).

Following General Procedure, **7m** (68.7 mg, 57%) was obtained from **3m** (93.2 mg, 0.160 mmol), **5** (60.9 μL, 0.353 mmol), and **4** (14.5 mg, 88.3 μmol) after purification by column chromatography on silica gel (hexane-CH_2Cl_2, 1/5).

IR (KBr) 2963, 2858 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.97 (s, 9H), 1.26 (s, 9H), 2.40 (s, 3H), 3.43 (d, *J* = 9.9 Hz, 1H), 3.62 (d, *J* = 9.9 Hz, 1H), 3.88 (d, *J* = 14.6 Hz, 1H), 4.04 (d, *J* = 14.6 Hz, 1H), 5.34 (s, 1H), 6.05 (s, 1H), 7.11-7.65 (m, 23H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 19.0, 21.4, 21.5, 27.1, 31.2, 34.4, 51.3, 56.7, 73.9, 121.4, 126.1, 127.2, 127.6, 127.8, 127.9, 128.2, 129.2, 129.7, 129.8, 129.9, 131.5, 132.6, 132.9, 135.8, 136.0, 137.8, 140.0, 143.6, 150.1. One signal was orverlapped.; HRMS (EI) m/z calcd for $C_{44}H_{50}N_2O_3S_2Si$ 746.3032, found 746.3033.

Dimethyl 3-[(4-_tert_-butylphenylthio)methylene]-4-(_tert_-butyldiphenylsilyloxyamino)cyclopentane-1,1-dicarboxylate (7n) (Table 4, entry 4).

Following General Procedure, **7n** (72.6 mg, 73%, *E*/*Z* = 90/10) was obtained from **3n** (77.3 mg, 0.166 mmol), **5** (63.0 μL, 0.365 mmol), and **4** (14.9 mg, 91.3 μ mol) after purification by column chromatography on silica gel (hexane-AcOEt, 8/1). All data were described without distinction of the two diastereomers.

IR (KBr) 2957, 2858, 1736 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.08 (s, 9H x 0.9), 1.10 (s, 9H x 0.1), 1.30 (s, 9H x 0.1), 1.31 (s, 9H x 0.9), 2.28-2.34 (m, 1H), 2.53-2.60 (m, 1H), 2.92-2.97 (m, 1H), 3.61-3.72 (m, 6H), 3.91-3.95 (br, 1H), 5.23 (br, 1H), 6.22 (br s, 1H x 0.1), 6.23 (br s, 1H x 0.9), 7.18-7.70 (m, 14H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 19.2, 27.3, 31.3, 34.5, 37.9, 52.9, 58.1, 65.4, 76.6, 120.6, 126.0, 127.46, 127.53, 128.7, 129.5, 132.3, 133.7, 135.7, 135.8, 172.1 (several signals overlapped); HRMS (EI) *m/z* calcd for $C_{36}H_{45}NO_5SSi$ $[M]^+$631.2788, found.631.2809

_N_-[5-(4-_tert_-Butylphenylthio)-2,2-dimethyl-4-phenyl-3,6-dihydro-2_H_-pyran-3-yl]-_O_-(_tert_-butyldiphenylsilyl)hydroxylamine (8o) (Table 4, entry 5).

Following General Procedure, **8o** (93.5 mg, 91%) was obtained from **3o** (75.6 mg, 0.166 mmol), **5** (63.0 μL, 0.365 mmol), and **4** (14.9 mg, 91.3 μmol) after purification by column chromatography on silica gel (hexane-AcOEt, 20/1).

IR (neat) 2962, 2858 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.92 (s, 9H), 1.27-1.28 (m, 12H), 1.54 (s, 3H), 3.53 (d, *J* = 6.6 Hz, 1H), 3.96 (dd, *J* = 17.4 and 1.5 Hz, 1H), 4.07 (d, *J* = 17.4 Hz, 1H), 5.46 (br, 1H), 7.15-7.48 (m, 14H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 18.6, 24.0, 25.4, 27.2, 31.20, 31.24, 34.5, 64.4, 67.9, 73.8, 126.0, 127.0, 127.3, 127.4, 127.8, 128.7, 129.1, 129.3, 129.4, 129.8, 130.8, 133.6, 133.7, 135.75, 135.84,139.6, 140.2, 150.3 (several signals overlapped); HRMS (ESI) *m/z* calcd for $C_{39}H_{48}NO_2SSi$ 622.3175 $[M+H]^+$, found 622.3166

***O*-(*tert*-Butyldiphenylsilyl)-*N*-{4-phenyl-1-tosyl-5-(tributylstannyl)-1,2,3,6-tetrahydropyridin-3-yl}hydroxylamine (12) (Scheme 4).**

To a boiling solution of an oxime **3g** (96.5 mg, 0.166 mmol) in benzene (6.3 mL) was added dropwise a solution of Bu_3SnH (95.8 mL, 0.365 mmol) and AIBN (15.0 mg, 91.3μmol) in benzene (2.0 mL) via syringe-pump over 2 hrs and the resulting mixture was heated at reflux further for 3 hrs. The mixture was concentrated under reduced pressure, and the residue was chromatographed on silica gel (K_2CO_3 10 w/w%, hexane-AcOEt, 5/1) to afford **12** (71.6 mg, 49%) as a colorless oil.

IR (KBr) 2957, 2928, 2855 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.44-0.60 (m, 6H), 0.770-0.87 (m, 9H), 0.96 (s, 9H), 1.01-1.26 (m, 12H), 2.42 (s, 3H), 2.56 (d, *J* = 9.2 Hz, 1H), 3.35 (d, *J* = 16.8 Hz, 1H), 3.70 (d, *J* = 10.6 Hz, 1H), 4.10 (d, *J* = 16.8 Hz, 1H), 4.42 (d, *J* = 10.6 Hz, 1H), 5.44 (d, *J* = 11.0 Hz, 1H), 6.88 (br d, *J* = 6.6 Hz, 2H), 7.10-7.60 (m, 15H), 7.75 (d, *J* = 8.1 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 10.3, 13.5, 19.1, 21.5, 27.2, 28.9, 43.9, 51.1, 62.1, 127.1, 127.3, 127.4, 127.8, 127.9, 128.4, 129.2, 129.3, 129.6, 129.7, 133.5, 133.8, 133.9, 135.6, 135.7, 140.2, 143.6, 143.9, 147.9; HRMS (FAB) m/z calcd for $C_{46}H_{64}N_2O_3SSiSn$ $[M+H]^+$ 872.3429, found 872.3519.

_N_-[{3_R_*,3_S_*-4-(4-_tert_-Butylphenylthio)methyl}-1-tosylpyrrolidin-3-yl]-_O_-(_tert_-butyldiphenylsilyl)hydroxylamine (_cis_-14) and its (3_R_*,4_R_*)-isomer (_trans_-14) (Scheme 4).

Following General Procedure, ***cis*-14** (33.4 mg, 31%) and ***trans*-14** (38.4 mg, 35%) were obtained from **13** (82.1 mg, 0.162 mmol), **5** (61.5 mmL, 0.356 mmol), and **4** (14.6 mg, 89.1 mmol) after purification by column chromatography on silica gel (hexane-CH_2Cl_2, 1/2 then hexane-AcOEt, 5/1).

***cis*-14**: IR (KBr) 3854, 2856 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.04 (s, 9H), 1.29 (s, 9H), 2.16-2.28 (m, 1H), 2.40-2.49 (m, 4H), 2.80 (dd, *J* =

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7.3 and 5.9 Hz, 1H), 2.99 (t, *J* = 9.5 Hz, 1H), 3.22 (dd, *J* = 10.6 and 5.5 Hz, 1H), 3.30 (br, 1H), 3.47 (t, *J* = 9.5 Hz, 1H), 3.59 (d, *J* = 10.6 Hz, 1H), 4.87 (d, *J* = 9.2 Hz, 1H), 7.09-7.71 (m, 18H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 19.0, 21.5, 27.2, 31.2, 31.9, 34.4, 40.6, 50.7, 51.1, 62.8, 126.0, 127.5, 127.6, 129.7, 129.8, 131.4, 133.2, 133.6, 135.6, 135.8, 143.5, 149.8; HRMS (EI) m/z calcd for $C_{38}H_{48}N_2O_3S_2Si$ 672.2876, found 672.2862.

***trans*-14**: IR (KBr) 3855, 3747, 3738, 3715, 3678, 3672, 3651, 2392, 2349 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) 1.01 (s, 9H), 1.28 (s, 9H), 2.13 (br, 1H), 2.40-2.47 (m, 4H), 2.71-2.77 (m, 1H), 2.85-2.90 (m, 1H), 3.15-3.26 (m, 4H), 4.97 (br, 1H), 7.11-7.64 (m, 18H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 19.0, 21.5, 27.2, 31.2, 34.4, 36.4, 40.4, 50.5, 51.5, 66.1, 126.0, 127.4, 127.5, 127.7, 129.6, 129.7, 131.3, 132.5, 133.1, 133.2, 135.6, 135.8, 143.5, 149.7; HRMS (EI) m/z calcd for $C_{38}H_{48}N_2O_3S_2Si$ 672.2876, found 672.2872.

(*E*)-*N*-{2-[4-(*tert*-butylphenylthio)methylene]cyclopentyl}hydroxylamine (15a) (Scheme 5).

To a stirred solution of **7a** (100 mg, 0.194 mmol) in THF (1.9 mL) was added a solution of TBAF (ca. 0.29 mmol) and acetic acid (67 μL, 1.2 mmol) in THF (2.2 mL) at 0 °C, and the mixture was stirred at the same temperature for 2 h. After addition of H_2O, the resulting mixture was extracted with AcOEt (x 3). The organic layer was washed with sat. $NaHCO_3$ aq. (x 1), brine (x 1), dried (Na_2SO_4) and concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane-AcOEt, 2/1) and purified by PTLC (hexane-AcOEt, 1/1) to afford **15a** (40.0 mg, 74%).

IR (KBr) 2963, 2905, 2870 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.30 (s, 9H), 1.79-2.37 (m, 6H), 3.90 (s, 1H), 4.81 (br, 1H), 6.34 (s, 1H) 7.26-7.31 (m, 4H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 23.2, 30.2, 31.1, 31.3, 34.5, 66.8, 118.9, 126.1, 129.1, 132.6, 143.5, 149.7; HRMS (EI) m/z calcd for $C_{16}H_{23}NOS$ 277.1500, found 277.1488.

***N*-[5-(4-*tert*-butylphenylthio)-4-methyl-3,6-dihydro-2*H*-pyran-3-yl]hydroxylamine (15d) (Scheme 5).**

To a stirred solution of **8d** (34.7 mg, 0.0652 mmol) in THF (0.65 mL) was added a solution of TBAF (ca. 0.10 mmol) and acetic acid (22 μL, 0.38 mmol) in THF (0.75 mL) at 0 °C, and the mixture was stirred at the same temperature for 2.5 h. After addition of H_2O, the same work-up for **15a** gave a crude material, which was chromatographed on silica gel (hexane-AcOEt, 2/1) followed by (hexane-AcOEt, 1/1) to afford **15d** (15.2 mg, 80%) as colorless oil. IR (neat) 3384, 3250, 2963 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.29 (s, 9H), 2.09 (t, *J* = 2.1 Hz, 3H), 3.36 (br s, 1H), 3.53 (dd, *J* = 11.7 and 2.4 Hz, 1H), 3.98 (br s, 2H), 4.32 (dd, *J* = 11.7 and 1.8 Hz, 1H), 6.20 (br s, 1H), 7.13-7.23 (m, 2H), 7.23-7.35 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 19.0, 31.2, 34.5, 61.4, 64.9, 68.7, 126.2, 129.5, 129.6, 129.9, 134.3, 150.0; HRMS (EI) m/z calcd for $C_{16}H_{23}NO_2S$ 293.1449, found 293.1439.

(*E*)-*N*-{4-[4-(*tert*-butylphenylthio)methylene]tetrahydro-2*H*-pyran-3-yl}hydroxylamine (15h) (Scheme 5).

To a stirred solution of TBDPS ether **10h** (36.4 mg, 0.0684 mmol) in THF (0.7 mL) was added a solution of TBAF (ca. 0.10 mmol) and acetic acid (23 μL, 0.40 mmol) in THF (0.8 mL) at 0 °C, and the mixture was stirred at the same temperature for 2 h. After addition of H_2O, the same work-up for **15a** gave a crude material, which was purified by PTLC (hexane-AcOEt, 1/1) to afford **15h** (16.3 mg, 81%) as colorless oil. IR (neat) 3364, 3252, 2961 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.31 (s, 9H), 2.38-2.63 (m, 2H), 3.48-3.56 (m, 2H), 3.59 (dd, *J* = 11.7 and 2.7 Hz, 1H), 3.90-4.08 (m, 1H), 4.15 (dd, *J* = 11.7 and 1.8 Hz, 1H), 6.28 (s, 1H), 7.27-7.38 (m, 4H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 28.0, 31.2, 34.5, 64.1, 68.0, 69.0, 122.6, 126.2, 129.4, 131.9, 134.5, 150.1; HRMS (EI) m/z calcd for $C_{16}H_{23}NO_2S$ 293.1449, found 293.1447.

(*Z*)-*N*-[(*E*)-2-{4-(*tert*-butylphenylthio)methylene}cyclopentyl]-1-phenylmethanimine oxide (16) (Scheme 5).

To a stirred suspension of hydroxylamine **15a** (53.7 mg, 0.194 mmol) and $MgSO_4$ (35.0 mg, 0.291 mmol) in 1,2-dichloroethane (0.19 mL) was added benzaldehyde (60 μL, 0.59 mmol) at 0 °C, and the mixture was stirred at room temperature for 30 min. The resulting mixture was concentrated under reduced pressure. The residue was purified by PTLC (hexane-AcOEt, 1/1) to afford **16** (62.2 mg, 88%) as pale yellow oil. IR (neat) 2963, 1489 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.29 (s, 9H), 1.76-1.95 (m, 1H), 1.97-2.23 (m, 2H), 2.41-2.69 (m, 3H), 4.84 (dd, *J* = 6.3 and 4.5 Hz, 1H), 6.48 (dd, *J* = 3.6 and 2.4 Hz, 1H), 7.25-7.35 (m, 4H), 7.37-7.45 (m, 3H), 7.46 (s, 1H), 8.18-8.32 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 23.6, 30.4, 31.1, 32.3, 34.4, 79.9, 123.4, 126.1, 128.4, 128.6, 129.6, 130.2, 130.4, 131.6, 132.9, 139.3, 150.2; HRMS (FAB) m/z calcd for $C_{23}H_{27}NOS$ $[M+H]^+$ 366.1881, found 366.1899.

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The acknowledgements come at the end of an article after the conclusions and before the notes and references.

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