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N-Silyloxaziridines: Synthesis and Use for Electrophilic Amination

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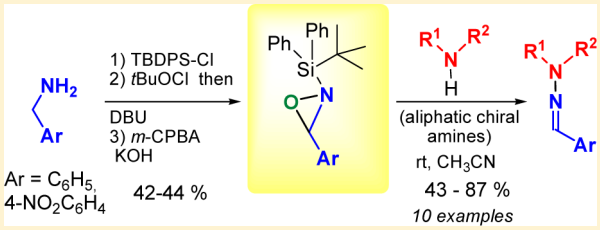
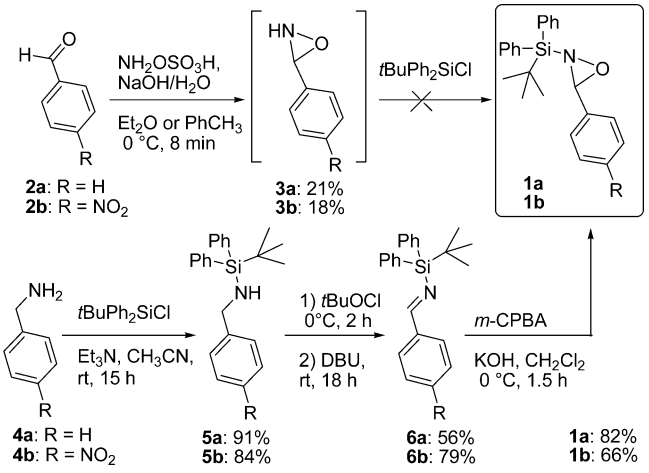
Supporting Information

ABSTRACT: *N*-Silyloxaziridines were synthesized for the first time. Their *tert*-butyldiphenylsilyl (TBDPS) derivatives were stable reagents that were prepared on a multigram scale in three steps and in 44% overall yield from the corresponding benzylamines. They were mild electrophilic aminating reagents that reacted at room temperature with diversely substituted primary and secondary amines to produce *N*-monoalkyl or *N*,*N*-dialkyl benzaldehyde hydrazones in 44−87% yield.



Because of their three-membered strained heterocyclic ring and their weak N−O bond, oxaziridines possess unusual reactivity[1] that has been exploited in photochemical or thermal rearrangements, catalyzed ring-opening,[2] catalyzed asymmetric oxyamination of olefins,[3] and the widely investigated oxidation (oxygen transfer) or amination (nitrogen transfer) of nucleophiles.[1] It has been established that the competition between oxygen or nitrogen transfer depends on the nature of the nucleophile and the substituents on the oxaziridine, especially at the nitrogen atom. *N*-Sulfonyl-,[4,5] *N*-perfluoroalkyl-,[6] *N*-phosphinoyl-,[7] *N*-*tert*-butyl-,[8] and *N*-phosphonioxaziridines[9] have been developed as efficient reagents for oxidation reactions such as epoxidation of olefins, asymmetric enolate hydroxylation, or oxidation of sulfide to sulfoxide. *N*-Chloro-[10] and *N*-methyloxaziridines[8] are attacked at nitrogen by amines to generate, respectively, tetrazines and air-sensitive *N*-methylhydrazines. Electrophilic amination of amines, alcohols, and a wide range of sulfur and carbon nucleophiles is performed by generally unstable *N*-H oxaziridines[11,12] and stable *N*-alkoxycarbonyl-[13−18] and *N*-carboxamidooxaziridines.[19] Since aliphatic hydrazine derivatives are more difficult to prepare than aromatic ones,[20,21] the N−N bond formation from *N*-H or *N*-alkoxycarbonyl oxaziridines and aliphatic amines is particularly interesting. Lastly, calculations of the transition state for aziridination of alkenes by diversely *N*-substituted oxaziridines have shown concerted but highly asynchronous nitrogen transfer and have predicted that hitherto unknown *N*-silyloxaziridines would be the most favorable ones for this reaction.[22] As reagents for electrophilic amination are of great interest in organic synthesis,[23−25] we decided to prepare *N*-silyloxaziridines in order to study their chemical properties. We report here the first synthesis of *N*-silyloxaziridines **1** (Scheme 1) and their reactivity toward amines, thiols, and alkenes. They are stable reagents that react under mild conditions. In contrast with other aminating oxaziridines that transfer their N-substituted group to nucleophiles, benzaldehyde hydrazones **9** or **10** instead of *N*-silylhydrazines are

Scheme 1. Synthesis of *N*-Silyloxaziridines 1



produced in fair to very good yields from diversely substituted primary and secondary amines.

Although silyl derivatives are very popular as protecting groups, their use in amino group protection is mainly limited to the bulky *tert*-butyldiphenylsilyl (TBDPS) group due to the high acid and moisture sensitivity of *N*-silylamines.[26−28] As derivatization at the nitrogen of *N*-H oxaziridines by electrophilic reagents has been reported,[11,29] we attempted to introduce the TBDPS group on the known *N*-H oxaziridines **3**[30] in order to prepare **1**. Oxaziridines **3** were too unstable to be isolated from their solution and were generated from benzaldehyde **2** and hydroxylamine-*O*-sulfonic acid in low yields (18−21%, determined by iodometric titration) (Scheme 1).[11] Unfortunately, treatment of crude **3** by chloro-*tert*-butyldiphenylsilane at room temperature without additives or in the presence of imidazole or DMAP resulted in complex

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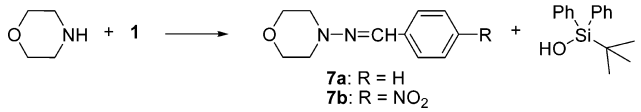
Table 1. Amination of Morpholine by *N*-Silyloxaziridines 1



entry	oxaziridine	solvent	reaction progress at rt[a] (%), reaction time (h)	temp (°C)	time (h)	product	yield (%)
1	**1a**	$CHCl_3$	55, 21	20 then 45	30	**7a**	56
2	**1b**	$CHCl_3$	68, 4	20	15	**7b**	89
3	**1b**	CH_3CN	88, 4	20	15	**7b**	82

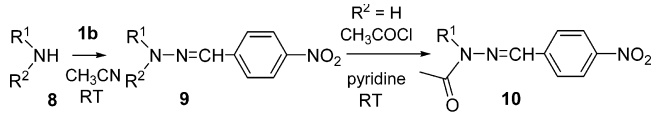
[a]Determined by ^{1}H NMR integration of the morpholino signals in the reaction mixture (c = 0.5 mol L^{-1}) at indicated reaction time.

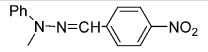
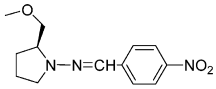
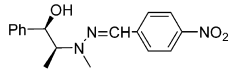
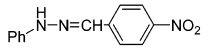
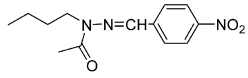
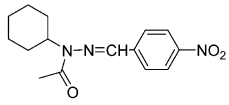
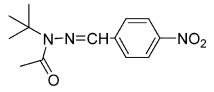
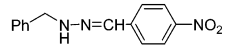
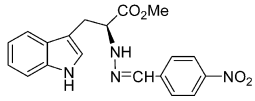
mixtures. Subsequently, the synthesis of *N*-silyloxaziridines **1** was successful starting from *N*-TBDPS amines **5**,[31] which were prepared in very good yields from the corresponding amines **4** (Scheme 1). According to Colvin's method,[32] *N*-chlorination of *N*-TBDPS amines **5** by *tert*-butyl hypochlorite followed by treatment with DBU afforded in 56−79% yields *N*-TBDPS imines **6**, which were moisture sensitive. Attempts to oxidize imine **6a** by anhydrous Li-*m*-CPBA, which was very efficient in the synthesis of *N*-alkoxycarbonyl oxaziridines,[13] did not supply the desired oxaziridine **1a**. Modification of Ruano's conditions[33] using a dry solution of *m*-CPBA in the presence of solid KOH led within 1.5 h at 0 °C to oxaziridines **1a**,**b** from *N*-TBDPS imines **6**. Purification of **1** by chromatography over silica gel resulted in extensive decomposition, even in the presence of triethylamine. We found that pretreatment of silica by chlorotrimethylsilane followed by heating at 190 °C under vacuum, minimized decomposition during flash chromatography and so allowed purification of **1**. Oxaziridines **1** were obtained as solids on a multigram scale and in 66−82% yield from **6**. They were stable for several months when kept at 4 °C. Their NMR spectra showed one characteristic heterocyclic CH signal at ca 4.6 ppm (^{1}H NMR) and ca. 75 ppm (^{13}C NMR), indicating the sole presence of the *trans* diasteromer due to the bulky TBDPS substituent. The carbons of the TBDPS diastereotopic phenyl groups displayed distinct signals in the ^{13}C NMR spectrum. Oxaziridine **1b** was quite stable in the presence of moisture since ^{1}H NMR monitoring of a mixture of **1b** (c = 0.1 mol l^{-1}) and water (3.5 equiv) in $CDCl_3/CD_3CN$ (5:2) showed only 10% decomposition after 14 days at room temperature.

Next, we studied the reactivity of oxaziridines **1** toward morpholine as a model for amines (Table 1). The reaction was monitored by ^{1}H NMR using integration of the morpholino signals. With oxaziridine **1a**, the reaction was slow at room temperature (55% progress after 21 h at room temperature) and produced hydrazone **7a** (56% isolated yield) and *tert*-butyldiphenylsilanol[34] (Table 1, entry 1). Moderate heating was needed in order to complete the reaction. Reaction of oxaziridine **1b** was faster in similar conditions (Table 1, entry 2). The yield of hydrazone **7b** was also higher (89%). An increase in the rate of morpholine amination with an electron-withdrawing substituent of the 3-phenyl group was also observed in the case of *N*-alkoxycarbonyloxaziridines.[13] The use of a polar solvent such as acetonitrile increased the reaction rate and had little influence on the yield in **7b** (Table 1, entry 3).

Reaction of aliphatic or aromatic amines **8** with the more reactive oxaziridine **1b** was then investigated and supplied hydrazones **9** or **10**, except in the case of the less basic diphenylamine or imidazole which gave no reaction after extended heating at 45 °C (Table 2). Acetonitrile was

Table 2. Amination of Amines 8 by *N*-Silyloxaziridine 1b



entry	**8**	Isolated product structure	**9**, yield (%)	**10**, yield (%)
1	**8a**[a]		**9a**, 76	-
2	**8b**		**9b**, 45	-
3	**8c**		**9c**, 63	-
4	**8d**[a]		**9d**, 44	-
5	**8e**		-	**10e**, 43
6	**8f**		-	**10f**, 70
7	**8g**		-	**10g**, 44
8	**8h**		**9h**, 87	-
9	**8i**		**9i**, 63	-

[a]Reaction was run at 45 °C for 72 h.

preferably chosen as the solvent, and the reaction was run overnight at room temperature, except in the case of aniline derivatives **8a** and **8d** which needed heating (entries 1 and 4). In many cases (entries 1, 4, 8, and 9) hydrazones **9a**, **9d**, **9h**, and **9i** were isolated as solids after crystallization in the appropriate solvent. Extensive decomposition of hydrazone **9** was generally observed during purification by silica gel chromatography and was minimized using basic alumina in

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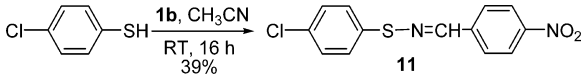
the case of *N*,*N*-disubstituted hydrazones **9b**,**c** (entries 2 and 3). Instability of hydrazones **9e**−**g** required further acylation of the monosubstituted nitrogen (R^2 = H) in order to isolate the stable products **10e**−**g** (entries 5−7). As the reaction did not involve asymmetric centers, it provided access to chiral enantiopure hydrazones **9b**, **9c**, and **9i** (entries 2, 3, and 9) from enantiopure amines **8b**, **8c**, and **8i**. Yields in 4-nitrobenzaldehyde hydrazones **9** or **10** were higher than that of the corresponding cyclohexanone hydrazones obtained from the unstable 3,3-pentamethyleneoxaziridine, which generally reacted at higher temperature.[11]

Reaction of oxaziridine **1b** with some other nucleophiles was also studied. 4-Chlorothiophenol was aminated in mild conditions to afford 4-nitrobenzylidene sulfenamide **11** in fair yield due to decomposition during silica gel purification (Scheme 2). We also tested the reaction of stilbene or

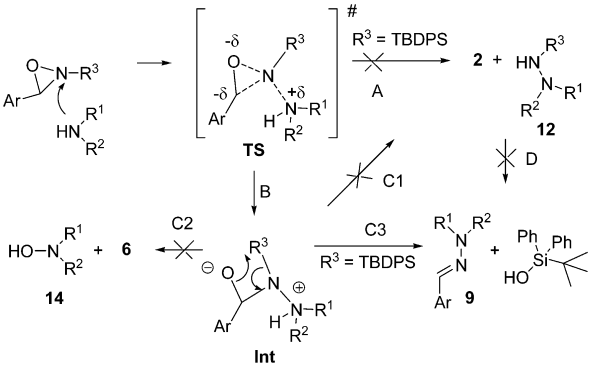
Scheme 2. Amination of 4-Chlorothiophenol by 1b



dimethylmaleate with *N*-TBDPS oxaziridine **1b** because calculations have predicted that *N*-(trimethylsilyl)oxaziridines would be good targets for alkene aziridination.[22] Unfortunately, no reaction occurred after 72 h at 50 °C (neat reagents), perhaps because of the steric hindrance of the bulky TBDPS group.

An N−N bond is created during reaction of **1** with amines, but unlike the other *N*-substituted aminating oxaziridines,[13] the transfer of the silylated nitrogen of **1** to amines producing *N*-TBDPS hydrazine **12** (R^3 = TBDPS) was not observed (Scheme 3, reaction A). As *N*-TBDPS hydrazine **12** might react

Scheme 3. Plausible Mechanism for Amination of Amines with Oxaziridines



with the electrophilic benzaldehyde **2** to give hydrazone **9** (Scheme 3, reaction D), an authentic sample of *tert*-butyldimethylsilylamino morpholine **13** was prepared[32] in order to check this hypothesis. The reaction of **13** at room temperature with 1 equiv of **2b** in anhydrous $CDCl_3$ (c = 1 mol L^{-1}) was monitored by ^{1}H NMR. As only 8% of **13** was transformed after 8 days, the intermediary formation of *N*-TBDPS hydrazine **12** during the reaction of amine and **1** was ruled out.

In the case of *N*-(alkoxycarbonyl)oxaziridines, we formerly proposed a mechanism postulating transition state **TS** or intermediate **Int** (R^3 = alkoxycarbonyl) and reactions A, B, and C1 for the transfer of the *N*-(alkoxycarbonyl) group to amines producing **12** and **2** (Scheme 3).[13] When R^3 = TBDPS, the increase of the reaction rate in a polar solvent or in the presence of the aryl electron-withdrawing group of **1b** (Table 1) still supports the proposal for **TS** or **Int**. As *N*-TBDPS hydrazine **12** is not produced, concerted fragmentation of transition state **TS** (reaction A) can be excluded. So, pathway B conducting to intermediate **Int** can be examined. Intermediate **Int** may be considered as an aza-analogue of the β-hydroxysilane intermediate formed in the Peterson olefination[35] (reaction from an α-silyl organometallic reagent and a ketone). Its fragmentation follows a new pathway (C3) producing hydrazone **9** because of the affinity of oxygen for silicon,[35] instead of pathway C1 postulated with *N*-(alkoxycarbonyl)-[13] or *N*-methyloxaziridines[8] (hydrazine formation, R^3 = alkoxycarbonyl or methyl) or pathway C2 producing hydroxyl amine **14** which is obtained in the case of *N*-sulfonyloxaziridines (R^3 = sulfonyl).[36]

In conclusion, the first preparation of *N*-silyloxaziridine is described in an efficient way. *N*-TBDPS oxaziridines **1a**,**b** are stable and mild aminating reagents that react at room temperature with diversely substituted primary and secondary amines to produce hydrazones **9** or **10** in 44−87% yield. This new access to *N*-monoalkyl or *N*,*N*-dialkyl hydrazones **9** and especially to enantiopure chiral ones, may stimulate development of their very diverse reactivity.[37,38] For instance, hydrazones **9** may find applications in the synthesis of chiral pyrazolidinones,[39] may improve chemical diversity in the reaction of 1,1-dialkylhydrazones with arynes[40,41] or may be used in the synthesis of 1,3,4-trisubstituted pyrazoles.[42]

EXPERIMENTAL SECTION

4-Nitrobenzenemethanamine (4b). Prepared according to the literature:[43] mp 134−136 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.42 (brs, 2H), 3.92 (s, 2H), 7.42 (d, 2H, J = 8.6 Hz), 8.11 (d, 2H, J = 8.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.7 (CH2), 123.7 (CH), 127.7 (CH), 146.9 (C), 150.5 (C).

***N*-[(1,1-Dimethylethyl)diphenylsilyl]benzenemethanamine (5a).** Prepared according to the literature:[31] ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22 (s, 9H), 1.39 (br s, 1H), 4.12 (d, 2H, J = 7.7 Hz), 7.33−7.53 (m, 11H), 7.90 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.6 (C), 27.5 (CH_3), 46.7 (CH_2), 126.5 (CH), 127.0 (CH), 127.6 (CH), 128.3 (CH), 129.2 (CH), 135.1 (C), 135.8 (CH), 143.7 (C).

***N*-[(1,1-Dimethylethyl)diphenylsilyl]-4-nitrobenzenemethanamine (5b).** 4-Nitrobenzenemethanamine (**4b**) (4.38 g, 28.7 mmol) in anhydrous acetonitrile (50 mL) was reacted under nitrogen with triethylamine (6.1 mL, 43.4 mmol) and *tert*-butylchlorodiphenylsilane (7.92 g, 28.8 mmol). After 15 h at room temperature and filtration through Celite, the solution was concentrated. The resulting solid was dissolved in a 4:1 mixture of *n*-pentane/AcOEt (200 mL) and the organic phase was washed with aqueous 1 M $NaHCO_3$, water, then was dried over $MgSO_4$, filtered, and concentrated. After crystallization in *n*-hexane, *N*-[(1,1-dimethylethyl)diphenylsilyl]-4-nitrobenzenemethanamine (**5b**) was obtained as a yellow solid (9.46 g, 84% yield): mp 74−76 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.00 (s, 9H), 1.30 (brs, 1H), 3.98 (s, 2H), 7.26−7.33 (m, 8H,), 7.59−7.63 (m, 4H), 8.05 (d, 2H, J = 8.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.7 (C), 27.5 (CH3), 46.3 (CH2), 123.6 (CH), 127.5 (CH), 127.7 (CH), 129.5 (CH), 134.5 (C), 135.8 (CH), 146.7 (C), 151.4 (C). HRMS (ESI) for $C_{23}H_{26}N_2O_2SiNa$ $[M + Na]^+$ calcd 413.1661, found 413.1640.

***N*-[(1,1-Dimethylethyl)diphenylsilyl]benzaldimine (6a).** Under argon and at 0 °C, a solution of *tert*-butyl hypochlorite[44] (2.0 g, 20 mmol) in anhydrous THF (5 mL) was added dropwise to *N*-[(1,1-dimethylethyl)diphenylsilyl]benzenemethanamine (**5a**) (6.3 g, 18 mmol) in anhydrous THF (30 mL). After 2 h at 0 °C, the mixture

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was concentrated. The residue was dissolved in anhydrous ether (30 mL). Then, DBU (2.7 g, 18 mmol) in ether (3 mL) was added at 0 °C under argon. The mixture was left at room temperature overnight, filtered through anhydrous Celite, and concentrated. After Kugelrohr distillation *N*-[(1,1-dimethylethyl)diphenylsilyl]benzaldimine (**6a**) (3.52 g, 56% yield) was obtained as a pale yellow oil, which solidified on standing: mp 52−56 °C; Eb = 135−140 °C (p = 0.1 mbar); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08 (s, 9H), 7.28−7.41 (m, 10H), 7.57−7.61 (m, 3H), 7.78−7.82 (m, 2H), 8.78 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.9 (C), 27.3 (CH_3), 127.6 (CH), 128.5 (CH), 128.7 (CH), 129.4 (CH), 131.5 (CH), 133.7 (C), 136.0 (CH), 138.9 (C), 171.3 (CH); HRMS (ESI) for $C_{23}H_{25}NSiNa$ $[M + Na]^+$ calcd 366.1654, found 366.1655.

***N*-[(1,1-Dimethylethyl)diphenylsilyl]-4-nitrobenzaldimine (6b).** Under argon and at 0 °C, a solution of *tert*-butylhypochlorite[44] (2.72 g, 25.1 mmol) in anhydrous $CHCl_3$ (4 mL) was added dropwise to *N*-[(1,1-dimethylethyl)diphenylsilyl]-4-nitrobenzenemethanamine (**5b**) (6.50 g, 16.6 mmol) in anhydrous $CHCl_3$ (25 mL). After 3 h at 0 °C, the mixture was concentrated. The residue was dissolved in anhydrous ether (30 mL) and reacted at 0 °C with DBU (3.2 mL, 21.4 mmol) under argon. The mixture was left at room temperature overnight, filtered, and concentrated. The resulting residue was recrystallized under argon from anhydrous boiling cyclohexane to afford *N*-[(1,1-dimethylethyl)diphenylsilyl]-4-nitrobenzaldimine (**6b**) (5.11 g, 79% yield) as a yellow solid: mp 96−97 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10 (s, 9H), 7.30−7.38 (m, 6H), 7.55−7.58 (m, 4H), 7.94 (d, 2H, J = 8.8 Hz), 8.23 (d, 2H, J = 8.8 Hz), 8.81 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.9 (C), 27.3 (CH_3), 123.9 (CH), 127.8 (CH), 129.3 (CH), 129.8 (CH), 132.8 (C), 136.0 (CH), 143.2 (C), 149.5 (C), 168.8 (CH); HRMS (EI) for $C_{19}H_{15}N_2O_2Si$ $[M - t\text{-}Bu]^+$ calcd 331.0903, found 331.0930.

***N*-[(1,1-Dimethylethyl)diphenylsilyl]-3(4-nitrophenyl)-oxaziridine (1b).** To a freshly prepared *m*-CPBA solution in CH_2Cl_2 (0.45 M, 27 mL, 12.1 mmol, dried over $MgSO_4$ and then filtered)[13] under argon were added at 0 °C KOH (2.16 g, 38.5 mmol) and a solution of *N*-[(1,1-dimethylethyl)diphenylsilyl]-4-nitrobenzaldimine (**6b**) (4.28 g, 11.02 mmol) in anhydrous CH_2Cl_2 (5 mL). The slurry was stirred for 1.5 h at 0 °C and then filtered through Celite. After concentration in vacuo, the residue was divided in four fractions. Before chromatography, silica gel (25 g) in petroleum ether (50 mL) was reacted with TMSCl (2.7 g) for 30 min. The solvent was removed in vacuo, and the silanized silica was heated at 190 °C for 2 h under vacuum (0.1 mbar). Each fraction was purified by flash chromatography under nitrogen over silanized silica gel (25 g, anhydrous CH_2Cl_2/*n*-pentane = 2:3). *N*-[(1,1-Dimethylethyl)diphenylsilyl]-3(4-nitrophenyl)oxaziridine (**1b**) (2.92 g, 66% yield) was obtained as a pale yellow solid: mp 79−80 °C; R_f (2:3 CH_2Cl_2/*n*-pentane) 0.40; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.15 (s, 9H), 4.57 (s, 1H), 7.37−7.53 (m, 6H), 7.62−7.67 (m, 4H), 7.74 (d, 2H, J = 8.1 Hz), 8.23 (d, 2H, J = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.4 (C), 27.5 (CH_3), 74.4 (CH), 123.6 (CH), 127.8 and 128.0 (CH), 128.8 (CH), 129.9 and 130.2 (C), 130.4 and 130.5 (CH), 136.1 and 136.2 (CH), 143.3 (C), 149.0 (C); HRMS (ESI) for $C_{23}H_{24}N_2O_3SiNa$ $[M + Na]^+$ calcd 427.1454, found 427.1456. Anal. Calcd for $C_{23}H_{24}N_2O_3Si$: C, 68.29; H, 5.98. Found: C, 68.50; H, 6.12.

***N*-[(1,1-Dimethylethyl)diphenylsilyl]-3-phenyloxaziridine (1a).** The same procedure as used for **1b** afforded expected oxaziridine **1a** (0.361 g, 82% yield) from *N*-[(1,1-dimethylethyl)diphenylsilyl]-benzaldimine (**6a**) (0.419 g, 1.22 mmol): mp 74−77 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.28 (s, 9H), 4.67 (s, 1H), 7.40−7.55 (m, 11H), 7.72 (m, 2H), 7.80 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.4 (C), 27.5 (CH_3), 75.9 (CH), 127.8 and 127.9 (CH), 128.4 (CH), 129.8 (CH), 130.1 and 130.2 (CH), 130.4 and 130.8 (C), 135.5 (CH), 136.0 (C), 136.2 and 136.3 (CH); HRMS (ESI) for $C_{23}H_{25}NOSiNa$ $[M + Na]^+$ calcd 382.1603, found 382.1604.

General Procedure for Amination of Amines by Oxaziridine 1b. To a solution of oxaziridine **1b** (101 mg, 0.25 mmol) in anhydrous acetonitrile (0.5 mL) was added the amine (0.25 mmol). The mixture was stirred overnight at room temperature and concentrated before purification or acylation. The crude product was acylated at 0 °C in CH_2Cl_2 (0.5 mL) by acetyl chloride (19 μL, 0.26 mmol) and anhydrous pyridine (22 μL, 0.26 mmol). After 1 h at 0 °C and 3 h at room temperature, the mixture was diluted by CH_2Cl_2 (5 mL), washed by 10% aqueous citric acid and by water, dried over Na_2SO_4, filtered, concentrated, and purified.

***N*-(Benzylidene amino)morpholine (7a).** From morpholine (45 μL, 0.51 mmol) and oxaziridine **1a** (375 mg, 0.58 mmol) in CH_2Cl_2 (1 mL) at 45 °C for 30 h, the general procedure afforded hydrazone **7a** as an orange solid (51.1 mg, 56% yield) after chromatography over silica gel (ether/*n*-pentane = 1:4): mp 91−92 °C (lit.[11] mp 88−89 °C, lit.[40] mp 90−91 °C); R_f (1:4 ether/ *n*-pentane) 0.13; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.11 (t, 4H, J = 4.9 Hz), 3.83 (t, 4H, J = 4.9 Hz), 7.21−7.31 (m, 3H), 7.52−7.55 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 51.9 (CH_2), 66.5 (CH_2), 126.2 (CH), 128.4 (CH), 128.6 (CH), 135.9 (C), 136.3 (CH).

***N*-(4-Nitrobenzylideneamino)morpholine 7b.** From morpholine (23 μL, 0.26 mmol) and oxaziridine **1b** (107 mg, 0.27 mmol) in $CHCl_3$, the general procedure afforded hydrazone **7b** as an orange solid (55.3 mg, 89% yield) after chromatography over silica gel (CH_2Cl_2/*n*-pentane = 2:3): mp 150−152 °C (lit.[45] mp 149−151 °C); R_f (2:3 CH_2Cl_2/*n*-pentane) 0.07; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.20 (t, 4H, J = 5.0 Hz), 3.83 (t, 4H, J = 5.0 Hz), 7.46 (s, 1H), 7.64 (d, 2H, J = 9.0 Hz), 8.23 (d, 2H, J = 9.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 51.3 (CH_2), 66.3 (CH_2), 124.0 (CH), 126.2 (CH), 131.6 (CH) 142.4 (C) 147.0 (C). Anal. Calcd for $C_{11}H_{13}N_3O_3$: C, 56.16; H, 5.57; N, 17.86. Found: C, 56.10; H, 5.56; N, 17.62.

4-Nitrobenzaldehyde *N*-Methyl-*N*-phenylhydrazone (9a). From *N*-methylaniline (27 μL, 0.25 mmol) and oxaziridine **1b** (101 mg, 0.25 mmol) at 45 °C for 3 days, the general procedure afforded hydrazone **9a** as an orange solid (48.6 mg, 76% yield) after crystallization in ether/*n*-pentane: mp 132−133 °C (lit.[46] mp 133−134 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.50 (s, 3H), 7.03 (t, 1H, J = 6.7 Hz),7.35−7.43 (m, 4H), 7.48 (s, 1H), 7.80 (d, 2H, J = 8.9 Hz), 8.23 (d, 2H, J = 8.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 33.7 (CH_3), 116.0 (CH), 122.0 (CH), 124.1 (CH), 126.0 (CH), 128.7 (CH), 129.2 (CH), 143.2 (C), 146.5 (C), 147.2 (C). Anal. Calcd for $C_{14}H_{13}N_3O_2$, 0.25 H_2O: C, 64.73; H, 5.24; N, 16.18. Found: C, 64.44; H, 5.12; N, 16.17.

***(2S)*-*N*-(4-Nitrobenzylideneamino)-2-methoxymethylpyrrolidine (9b).** From 2(*S*)-(methoxymethyl)pyrrolidine (45 μL, 0.36 mmol) and oxaziridine **1b** (158 mg, 0.39 mmol) in CH_3CN, general procedure afforded hydrazone **9b** as an orange solid (42.73 mg, 45% yield) after chromatography over basic alumina (CH_2Cl_2/*n*-pentane = 15:85): mp 78−79 °C; R_f (3:7 CH_2Cl_2/*n*-pentane) 0.17; $[\alpha]^{23}_D$ = −231 (c = 0.6, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.91−2.13 (m, 4H), 3.16−3.23 (m, 1H), 3.41 (s, 3H), 3.41−3.43 (m, 1H), 3.48 (dd, J = 6.3 Hz, J = 9.3 Hz, 1H), 3.58 (dd, J = 3.6 Hz, J = 9.3 Hz, 1H), 3.75 (m, 1H), 7.09 (s, 1H), 7.61 (d, 2H, J = 8.9 Hz), 8.15 (d, 2H, J = 8.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.3 (CH_2), 26.9 (CH_2), 48.3 (CH_2), 59.3 and 63.0 (CH or CH_3), 74.3 (CH_2), 124.1 (CH), 124.9 (CH), 127.4 (CH), 144.1 (C), 145.7 (C); HRMS (EI) for $C_{13}H_{17}N_3O_3$ $[M]^+$ calcd 263.1270, found 263.1253.

***(1R-2S)*-*N*-(4-Nitrobenzylideneamino)ephedrine (9c).** From (1*R*,2*S*)-ephedrine (57.8 mg, 0.35 mmol) and oxaziridine **1b** (150 mg, 0.36 mmol) in CH_3CN at rt overnight, the general procedure afforded hydrazone **9c** as a viscous oil after chromatography over basic alumina (CH_2Cl_2/*n*-pentane = 1:1) (69.06 mg, 63% yield): R_f (1:1 CH_2Cl_2/*n*-pentane) 0.20; $[\alpha]^{23}_D$ = −165 (c = 0.5, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.14 (d, 3H, J = 6.9 Hz, CH_3), 2.86 (s, 3H), 3.51 (qd, 1H, J = 6.9 Hz, J = 3.7 Hz), 3.67 (brs, 1H), 5.08 (d, 1H, J = 3.7 Hz), 7.04 (s, 1H), 7.16−7.32 (m, 5H), 7.50 (d, 2H, J = 8.9 Hz), 8.09 (d, 2H, J = 8.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.8 (CH_3), 37.6 (CH_3), 68.2 (CH), 76.7 (CH), 124.2 (CH), 125.2 (CH), 126.2 (CH), 127.2 (CH), 127.5 (CH), 128.3 (CH), 141.7 (C),143.2 (C), 146.0 (C); HRMS (ESI) for $C_{17}H_{19}N_3O_3Na$ $[M + Na]^+$) calcd 336.1324, found 336.1321.

4-Nitrobenzaldehyde *N*-Phenylhydrazone (9d). From aniline (23 μL, 0.25 mmol) and oxaziridine **1b** (104 mg, 0.26 mmol) in CH_3CN at 50 °C for 3 days, general procedure afforded hydrazone **9d** as a solid after crystallization in *n*-pentane/isopropyl oxide (17.8 mg,

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44% yield): mp 148−151 °C (lit.[47] mp 156−158 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.96 (t, 1H, J = 7.3 Hz),7.16 (d, 2H, J = 8.6 Hz), 7.33 (t, 2H, J = 8.5 Hz), 7.71 (s, 1H), 7.78 (d, 2H, J = 8.9 Hz), 7.99 (brs, 1H), 8.23 (d, 2H, J = 8.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 113.1 (CH), 121.2 (CH), 124.1 (CH), 126.2 (CH), 129.4(CH), 133.8 (CH), 141.7 (C), 143.6 (C), 146.9 (C).

4-Nitrobenzaldehyde *N*-Acetyl-*N*-butylhydrazone (10e). From *n*-butylamine (35 μL, 0.35 mmol) and oxaziridine **1b** (149 mg, 0.37 mmol) in CH_3CN at rt overnight and subsequent acetylation with acetyl chloride (26 μL, 0.36 mmol) and pyridine (29 μL, 0.36 mmol), the general procedure afforded hydrazone **10e** as a yellow solid (40.5 mg, 43% yield) after chromatography over silica gel (CH_2Cl_2/*n*-pentane = 1:1): mp 110−111 °C; R_f (1:1 CH_2Cl_2/*n*-pentane) 0.20; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, 3H, J = 7.2 Hz), 1.27−1.39 (m, 2H), 1.44−1.56 (m, 2H), 2.40 (s, 3H), 3.93 (t, 2H, J = 7.5 Hz, CH_2), 7.63 (s), 7.75 (d, 2H, J = 8.9 Hz), 8.21 (d, 2H, J = 8.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8 (CH_3), 20.2 (CH_2), 21.8 (CH_3), 27.5 (CH_2), 40.1 (CH_2), 124.1 (CH), 127.6 (CH), 135.0 (CH), 141.0 (C), 148.0 (C), 172.9 (C); HRMS (ESI) for $C_{13}H_{17}N_3O_3Na$ $[M + Na]^+$: calcd 286.1168, found 286.1168.

4-Nitrobenzaldehyde *N*-Acetyl-*N*-cyclohexylhydrazone (10f). From cyclohexylamine (40 μL, 0.35 mmol) and oxaziridine **1b** (152 mg, 0.37 mmol) in CH_3CN at rt overnight and subsequent acetylation with acetyl chloride (26 μL, 0.36 mmol) and pyridine (29 μL, 0.36 mmol), the general procedure afforded hydrazone **10f** as a yellow solid (70.9 mg, 70% yield) after chromatography over silica gel (CH_2Cl_2): mp 149−150 °C; *Rf* (CH_2Cl_2) 0.1; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11−1.39 (m, 3H), 1.65−1.69 (m, 3H), 1.81−1.85 (m, 2H), 2.13−2.27 (m, 2H), 2.35 (s, 3H), 4.22 (brs, 1H), 7.74 (d, 2H, J = 8.9 Hz), 7.95 (brs, 1H), 8.19 (d, 2H, J = 8.9 Hz, Ar); ^{1}H NMR (300 MHz, DMSO, 45 °C) δ 1.19−1.46 (m, 3 H), 1.42−1.46 (m, 3H), 1.63−1.67 (m, 2H), 2.18−2.22 (m, 2H), 2.23 (s, 3H), 4.30 (m, 1H), 7.99 (d, 2H, J = 8.9 Hz), 8.28 (d, 2H, J = 8.9 Hz), 8.39 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.4 (CH_3), 25.4 (CH_2), 26.4 (CH_2), 30.0 (CH_2), 55.6 (br, CH), 124.1 (CH), 127.3 (CH), 135.3 (br, CH), 141.4 (C), 148.0 (C), 173.1 (br, C); HRMS (ESI) for $C_{15}H_{19}N_3O_3Na$ $[M + Na]^+$ calcd 312.1324, found 312.1323. Anal. Calcd for $C_{15}H_{19}N_3O_3$: C, 62.27; H, 6.62. Found: C, 62.07; H, 6.62.

4-Nitrobenzaldehyde *N*-Acetyl-*N*-*tert*-butylhydrazone (10g). From *tert*-butylamine (37 μL, 0.35 mmol) and oxaziridine **1b** (151 mg, 0.37 mmol) in CH_3CN at rt overnight and subsequent acetylation with acetylchloride (26 μL, 0.36 mmol) and pyridine (29 μL, 0.36 mmol), the general procedure afforded hydrazone **10g** as a yellow solid (40.5 mg, 44% yield) after chromatography over silica gel (CH_2Cl_2/*n*-pentane = 1:1 then CH_2Cl_2): mp 112−113 °C; R_f (CH_2Cl_2) 0.1; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.43 (s, 9H), 1.91 (s, 3H), 7.89 (d, 2H, J = 8.8 Hz), 8.21 (s, 1H), 8.25 (d, 2H, J = 8.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.1 (CH_3), 28.8 (CH_3), 61.5 (C), 124.2 (CH), 129.0 (CH), 138.6 (C), 149.6 (C), 162.2 (CH), 168.8 (C); HRMS (ESI) for $C_{13}H_{17}N_3O_3Na$ $[M + Na]^+$ calcd 286.1168, found 286.1167.

4-Nitrobenzaldehyde *N*-Benzylhydrazone (9h). From benzylamine (39 μL, 0.25 mmol) and oxaziridine **1b** (151 mg, 0.36 mmol) in CH_3CN at rt overnight, the general procedure afforded hydrazone **9h** as an orange solid (34.7 mg) after filtration. Concentration of the filtrate and crystallization in *n*-pentane afforded a second crop (44.2 mg, 87% total yield): mp 124−126 °C (lit.[48] mp 131 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.51 (d, J = 4.9 Hz, 2H), 6.17 (br t, 1H), 7.34−7.40 (m, 5H), 7.56 (s, 1H), 7.67 (d, 2H, J = 8.9 Hz), 8.20 (d, 2H, J = 8.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.9 (CH_2), 124.0 (CH), 125.8 (CH), 127.9 (CH), 128.1 (CH), 128.9 (CH), 132.1 (CH), 137.1 (C), 142.6 (C), 146.6 (C); HRMS (EI) for $C_{14}H_{13}N_3O_2$ $[M]^+$ calcd 255.1008, found 255.1033. Anal. Calcd for $C_{14}H_{13}N_3O_2$: C, 65.87; H, 5.13. Found: C, 66.18; H, 5.24.

***N*-(4-Nitrobenzylidene-amino)-L-tryptophane, Methyl Ester (9i).** From tryptophane, methyl ester (75 mg, 0.34 mmol, prepared by extraction with CH_2Cl_2 of a mixture of HCl, Trp-OMe and aqueous K_2CO_3) and oxaziridine **1b** (149 mg, 0.37 mmol) in CH_3CN at rt overnight, the general procedure afforded hydrazone **9i** as a yellow solid (80.1 mg, 63% yield) after concentration and crystallization in CH_2Cl_2/*n*-pentane: mp 140−141 °C; $[\alpha]^{23}_D$ = +80.8 (c = 1, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.35−3.40 (m, 2H), 3.72 (s, 3H), 4.57−4.59 (q, 1H, J = 8 Hz), 6.17 (d, 1H, J = 8 Hz), 7.06 (d, 1H, J = 2.5 Hz), 7.14 (t, 1H, J = 8 Hz), 7.23 (t, 1H, J = 8 Hz), 7.38 (d, 1H, J = 8 Hz), 7.58−7.64 (m, 3H), 8.08 (br s, 1H), 8.17 (d, 2H, (d, 1H, J = 8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.5 (CH_2), 52.3 and 62.3 (CH or CH_3), 110.3 (C), 111.3 (CH), 118.6 (CH), 119.7 (CH), 122.3 (CH), 122.9 (CH), 123.9 (CH), 126.2 (CH), 127.5 (C), 136.2 (C), 136.3 (CH), 141.7 (C), 147.0 (C), 173.3 (C); Anal. Calcd for $C_{19}H_{18}N_4O_4$, 0.25 H_2O: C, 61.53; H, 5.03; N, 15.11. Found: C, 61.68; H, 4.99; N, 14.71. HRMS (ESI) for $C_{19}H_{18}N_4O_4Na$ $[M + Na]^+$ calcd 389.1226, found 389.1224.

***N*-(4-Nitrobenzylidene)-4-chlorobenzenesulfenamide (11).** 4-Chlorothiophenol (50.45 mg, 0.3495 mmol) and oxaziridine **1b** (151.1 mg, 0.374 mmol) were reacted overnight at room temperature in anhydrous acetonitrile (0.8 mL). After chromatography over silica gel (petroleum ether/CH_2Cl_2 = 4:1 to 0:1) *N*-(4-nitrobenzylidene)-4-chlorobenzenesulfenamide (**11**) was afforded as a yellow solid (40.1 mg, 39% yield): mp 135−136 °C; R_f (petroleum ether/CH_2Cl_2 3:2) 0.41; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, 2H, J = 8.7 Hz), 7.54 (d, 2H, J = 8.7 Hz), 7.84 (d, 2H, J = 8.7 Hz), 8.29 (d, 2H, J = 8.7 Hz), 8.53 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 124.1 (CH), 127.8 (CH), 128.6 (CH), 129.5 (CH), 133.8 (C), 134.7 (C), 141.1 (C), 148.5 (C), 154.0 (CH); HRMS (ESI) for $C_{13}H_{10}{}^{35}ClN_2O_2S$ $[M + H]^+$ calcd 293.01515, found 293.0155.

***N*-(*tert*-Butyldimethylsilyl)aminomorpholine (13).** According to the literature procedure,[32] a solution of *N*-aminomorpholine (1.02 g, 10 mmol), triethylamine (1.53 mL, 11 mmol), and DMAP (24.4 mg, 0.2 mmol) in anhydrous ether (7 mL) was reacted at 0 °C with *tert*-butylchlorodimethylsilane (1.658 g, 11 mmol) in ether (5 mL). The resulting mixture was stirred for 48 h at room temperature and then filtered through anhydrous Celite. After distillation under vacuum, *N*-(*tert*-butyldimethylsilyl)aminomorpholine (**13**) (1.43 g, 66% yield) was afforded as a colorless liquid: Eb = 56−57 °C (p = 0.1 mbar); ^{1}H NMR (200 MHz, $CDCl_3$) δ − 0.03 (s, 3H), 0.87 (s, 9H), 2.10 (br s, 1H), 2.47 (t, 4H, J = 5.4 Hz), 3.65 (t, 4H, J = 5.4 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ − 5.2 (CH_3), 17.5 (C), 26.5 (CH_3), 61.2 (CH_2), 67.1 (CH_2).

■ ASSOCIATED CONTENT

Supporting Information

General experimental methods and copies of ^{1}H and ^{13}C NMR spectra for all prepared compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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