PhI=NSes: A New Iminoiodinane Reagent for the Copper-Catalyzed Aziridination of Olefins

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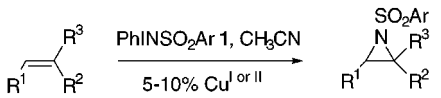
Introduction

In addition to their incorporation in the structures of natural and/or biologically active products, aziridines are of paramount importance in organic synthesis since they are valuable precursors of amino sugars, alkaloids, or substituted α-amino acids.[1] Among the numerous routes to this heterocycle, the copper-catalyzed aziridination of olefins developed by Evans[2] has become a method of choice, allowing the formation of aziridines directly by reaction with a nitrene generated from an iminophenyliodinane (Scheme 1). The value of this process has recently been demonstrated in the total synthesis of natural products and dipeptide isosteres.[3]

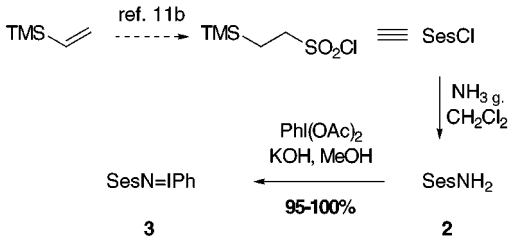
So far, only [*N*-(arenesulfonyl)imino]phenyliodinanes **1** have been used as nitrene sources, leading to *N*-(arenesulfonyl)aziridines.[4] Although several methods of deprotection of sulfonamides have been reported in the literature,[5] their cleavage sometimes proves to be troublesome.[3a,6] Thus, it appeared to us that preparation of *N*-[2-(trimethylsilyl)ethanesulfonyl]aziridines (*N*-(Ses)-aziridines) would provide an interesting alternative to the (arenesulfonyl)aziridines in terms of protection−deprotection strategy.

Until now, no aziridinations using [*N*-(*alkyl*sulfonyl)-imino]phenyliodinanes have been described, probably because the *N*-methylsulfonyl derivative has been claimed to be unstable and explosive.[7] To the best of our knowledge, a single report deals with the attempt to generate a nitrene species from this ylide.[8] Despite this, preliminary experiments with this iodinane have allowed us to

Scheme 1



Scheme 2



prepare in rather modest yields *N*-(methylsulfonyl)-aziridines from olefins[9] but their deprotection would require harsh conditions incompatible with many functional groups.[10]

On the basis of this result, we next turned our attention to the Ses group. This protecting group, originally developed by Weinreb,[11] has found numerous applications in total synthesis.[12] More significantly, *N*-(Ses)aziridines[13a] have been successfully used for the preparation of substituted α-amino acids[13b] and oligosaccharides.[13c] In this context, we report herein the preparation and the synthetic application of the [*N*-((trimethylsilyl)ethanesulfonyl)imino]phenyliodinane *(PhI=NSes)* **3**, *the first [N-(alkyl*sulfonyl)imino]phenyliodinane, *for the copper-catalyzed aziridination of olefins leading to synthetically versatile Ses-protected aziridines*.

Results and Discussion

Following the protocol described for the isolation of the iodinanes PhI=NSO_2Ar,[4,14] the reaction of sulfonamide **2** (prepared from the corresponding sulfonyl chloride according to the recently published procedure)[11b] with iodosobenzene diacetate in the presence of potassium hydroxide gave the reagent **3** (Scheme 2). However, a slight modification of the workup was needed because the nitrene precursor **3** could not be crystallized from the medium. Thus, despite the sensitivity of the phenyliodinanes to water, dilution of the reaction mixture with dichloromethane, followed by an aqueous wash with ice−water, allowed the isolation of PhI=NSes **3** in quantitative yield as a stable yellow solid of analytical purity, which can be stored at −20 °C under argon.

In the presence of a catalytic amount of $Cu(OTf)_2$, a slight excess of the iodinane **3** reacted with olefins **4** (the

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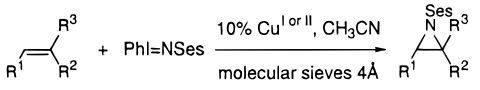
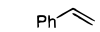
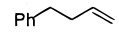
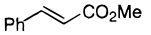
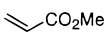
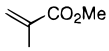
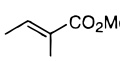
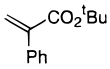
Table 1. Copper-Catalyzed Aziridination of Representative Olefins



4 (1 eq.) 3 (1.2-1.3 eq.) 5

Entry	Substrate	Catalyst	% Yield[a]
1		$Cu(OTf)_2$	**5a** : 58
		CuOTf	**5a** : 68
2		$Cu(OTf)_2$	**5b** : 40
3		$Cu(OTf)_2$	**5c** : 37 (95)[b,c]
		CuOTf	**5c** : 39 (85)[b]
4		$Cu(OTf)_2$	**5d** : 49[d]
5		$Cu(OTf)_2$	**5e** : 52[e]
		CuOTf	**5e** : 60
6		$Cu(OTf)_2$	**5f** : 47[e]
7		$Cu(OTf)_2$	**5g** : 48 (75)[b]
8		$Cu(OTf)_2$	**5h** : 34
9		$Cu(OTf)_2$	**5i** : 55
		CuOTf	**5i** : 67
10		$Cu(OTf)_2$	**5j** : 33
		CuOTf	**5j** : 43

[a] Isolated yield after flash chromatography. [b] Value in parentheses for yield based on consumed starting olefin. [c] 2 equiv of olefin was used. [d] 5 equiv of olefin was used. [e] 63% (entry 5) and 53% (entry 6) of aziridines were, respectively, isolated when 1.7 equiv of PhI=NSes was used.

stoichiometrically limiting component except in entries 3 and 4, Table 1) to form the *N*-(Ses)aziridines **5**. The yields were in the 35−60% range and are comparable to those obtained with PhI=NTs.[2,4,15] Moreover, the yields could be substantially increased by the use of the copper(I) salt, CuOTf, instead of $Cu(OTf)_2$ (Table 1, entries 1, 3, 5, 9, and 10), or by adding a larger quantity of the nitrene precursor (Table 1, entries 5 and 6). The reaction takes place with terminal, electron-rich, or electron-poor olefins. It proceeds in a stereospecific manner with *trans*-olefins since only *trans*-aziridines derived from methyl cinnamate and methyl tiglate were isolated (Table 1, entries 3 and 6). In the case of norbornene, as noted by Evans,[2] the *exo*-aziridine was the sole isomer produced. Finally, as recently described by us for nitrene precursors of type **1**, the 2-substituted acrylates show higher reactivity than methyl acrylate itself (Table 1, entries 5−7 vs entry 4).[15]

As previously demonstrated by Wipf,[13b] *N*-(Ses)aziridines are sufficiently activated to allow ring opening by nucleophiles. Thus, the 3-phenylaziridine derivative **5c** reacted with sodium borohydride/nickel chloride to give exclusively the *N*-Ses-protected phenylalanine **6** in 90% yield, while aziridine **5f** reacted with a soft nucleophile such as *o*-methoxythiophenol under mild conditions to give mainly the C-3 aziridine ring-opened product **7** together with a minor quantity of the product of C-2 attack **8** (Scheme 3).

From a synthetic point of view, the *N*-(Ses) protecting group offers the opportunity of mild deprotection of the

Scheme 3

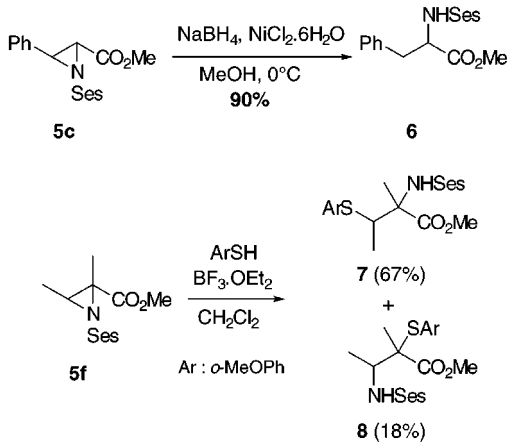
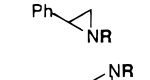
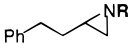


Table 2. Deprotection of the *N*-Ses Derivatives

Compound	Substrate (**R** = Ses)	Conditions[a]	% Yield (**R** = **H**)[b]
7		A	**9** : 95
5a		B	**10** : 62
5b		C	**11** : 60
5i		C	**12** : 60
5j		C	**13** : 68

[a] Key: (A) 3 equiv of CsF, DMF, 90 °C; (B) 4 equiv of TASF, DMF, rt; (C) 4 equiv of TASF, acetonitrile, rt. [b] Isolated yield after flash chromatography.

resulting sulfonamides by use of cesium fluoride in DMF.[11] Thus, under these conditions, compound **6** could be efficiently transformed into the amino derivative **9** in 95% yield (Table 2).

More significantly, *the N-(Ses)aziridines themselves could be deprotected without provoking opening of the aziridine ring*. Except for a few isolated examples, no general procedure exists for this type of transformation.[5c,16,17] While the above conditions (CsF in DMF) applied to aziridines **5** unexpectedly failed to give the corresponding deprotected three-membered ring, it was found that use at room temperature of tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF), a reagent recently found by Roush to cleave silicon protecting groups under mild conditions,[18] provided the NH aziridine products **10**, **11**, **12**, and **13**, respectively, in good yields (nonoptimized, Table 2). To the best of our knowledge, TASF has never been employed before to cleave the Ses protecting group.[19] However, we observed that this procedure failed with the acrylate-derived aziridines **5d**−**f**. Nevertheless, it should be pointed out that the conditions developed by Andersson[17] for deprotection of cyclo-

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hexyl *N*-(tosyl)aziridine-2-carboxylates (i.e., reduction with magnesium in methanol) were recently found to give aziridine ring-opened product when applied to methyl aziridine-2-carboxylates.[20]

In conclusion, PhI=NSes **3** represents the first [(*N*-(alkylsulfonyl)imino]phenyliodinane useful for the copper-catalyzed aziridination of olefins. In comparison to PhI=NTs, its isolation is much easier while their reactivities are comparable. Moreover, this new iodinane allows the formation of *N*-(Ses)aziridines that can, in turn, be opened by nucleophiles under mild conditions and/or deprotected at the nitrogen position without side reactions. In the latter case, use of the hypervalent silicon reagent TASF for deprotection of the Ses group is very convenient. These *N*-(Ses)aziridines are thus of high synthetic interest. Extension of this work to the asymmetric copper-catalyzed aziridination of olefins is currently under investigation.

Experimental Section

General Methods. Melting points are uncorrected. IR spectra of samples were obtained as films (i.e., by application of a $CHCl_3$ solution to an NaCl plate followed by evaporation of the solvent). ^1H and ^{13}C NMR chemical shifts are given as δ values with reference to Me_4Si as internal standard. Thin-layer chromatography was performed on Merck silica gel 60 plates with a fluorescent indicator. The plates were visualized with UV light (254 nm) and with a 3.5% solution of phosphomolybdic acid in ethanol. All column chromatography was conducted on Merck 60 silica gel (230−240 mesh) at medium pressure (200 mbar). All solvents were distilled and stored over 4 Å molecular sieves before use. Elemental analyses were performed at the ICSN, CNRS, Gif-sur-Yvette, France.

[*N*-(2-(Trimethylsilyl)ethanesulfonyl)imino]phenyliodinane (3). To a stirred solution of 2-(trimethylsilyl)ethanesulfonamide (**2**, 1.19 g, 6.56 mmol, 1.00 equiv) and potassium hydroxide pellets (0.92 g, 16.4 mmol, 2.50 equiv) in dry methanol (20 mL) held at 0 °C under argon was added iodosobenzene diacetate (2.12 g, 6.56 mmol, 1.00 equiv). The reaction mixture was kept at 0 °C for 30 min and then allowed to warm to 20 °C. After being stirred for 3 h, the homogeneous yellow solution was cooled before being diluted with dichloromethane (30 mL) and washed with ice−water (20 mL). The organic phase was dried with $MgSO_4$ and then evaporated to dryness to give a pale yellow solid (2.50 g, 6.52 mmol, 99%): mp 84−85.5 °C; IR (film) 2953, 1441, 1330, 1245, 1225, 1165, 1145, 1115, 885, 860, 735 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ −0.06 (s, 9H), 0.92 (m, 2H), 2.84 (m, 2H), 7.40 (t, 2H, J = 7.7 Hz), 7.52 (d, 1H, J = 7.4 Hz), 7.96 (d, 2H, J = 7.9 Hz). Anal. Calcd for $C_{11}H_{18}INO_2SSi$: C, 34.47; H, 4.73; N, 3.65; S, 8.36. Found: C, 34.61; H, 4.74; N, 3.75; S, 8.51.

Typical Aziridination Procedure (unless Otherwise Noted). PhI=NSes **3** (1.3 equiv) was added portionwise, over a period of 3 h, to a mixture held under argon of 4 Å molecular sieves (∼150 mg), $Cu(OTf)_2$ (10 mol %), and olefin (1 equiv) in acetonitrile (1.6 mL). The green reaction mixture was stirred at room temperature for 24 h and then purified directly by flash chromatography on silica gel, affording aziridines **5**.

***N*-(2-(Trimethylsilyl)ethanesulfonyl)-2-phenylaziridine (5a).** Starting from 69 μL (0.6 mmol) of styrene, 0.100 g (0.35 mmol, 58%) of aziridine was isolated as a colorless oil after flash chromatography on silica gel (heptane−ethyl acetate 8:1): ^1H NMR (250 MHz, $CDCl_3$) δ 0.03 (s, 9H), 1.14 (m, 2H), 2.42 (d, 1H, J = 4.4 Hz), 2.98 (d, 1H, J = 7.1 Hz), 3.13 (m, 2H), 3.71 (dd, 1H, J = 4.4, 7.1 Hz), 7.34 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −2.1, 9.7, 35.1, 40.4, 49.1, 126.5, 128.4, 128.7, 135.1; mass spectrum (CI) m/z 284 $(M + H)^+$. Anal. Calcd for $C_{13}H_{21}NO_2SSi$: C, 55.08; H, 7.47; N, 4.94; S, 11.31. Found: C, 54.87; H, 7.27; N, 4.96; S, 11.36.

***N*-(2-(Trimethylsilyl)ethanesulfonyl)-2-(2-phenylethyl)-aziridine (5b).** Starting from 150 μL (1 mmol) of 4-phenyl-1-butene, 0.125 g (0.40 mmol, 40%) of aziridine was isolated as a colorless oil after flash chromatography on silica gel (heptane−ethyl acetate 6:1): ^1H NMR (250 MHz, $CDCl_3$) δ 0.06 (s, 9H), 1.13 (m, 2H), 1.86 (m, 2H), 2.06 (d, 1H, J = 4.6 Hz), 2.57 (d, 1H, J = 7 Hz), 2.78 (m, 3H), 3.05 (m, 2H), 7.19−7.29 (m, 5H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ −1.9, 9.8, 33.1, 33.4, 33.8, 38.3, 48.9, 126.3, 128.4, 128.7; mass spectrum (CI) m/z 312 $(M + H)^+$. Anal. Calcd for $C_{15}H_{25}NO_2SSi\cdot 0.25H_2O$: C, 57.01; H, 8.13; N, 4.43; S, 10.14. Found: C, 57.03; H, 7.97; N, 4.29; S, 10.21.

***N*-(2-(Trimethylsilyl)ethanesulfonyl)-2-(methoxycarbonyl)-3-phenylaziridine (5c).** Starting from 146 mg (0.9 mmol) of *trans*-methyl cinnamate and in the presence of 50 mg of $(CuOTf)_2\cdot C_6H_6$, 120 mg (0.35 mmol, 39%) of aziridine together with 65 mg (0.39 mmol, 44%) of unreacted cinnamate were isolated as a colorless oil after flash chromatography on silica gel (heptane−ethyl acetate 9:1 then 8/1): ^1H NMR (250 MHz, $CDCl_3$) δ 0.04 (s, 9H), 1.12 (m, 2H), 3.18 (m, 2H), 3.45 (d, 1H, J = 3.8 Hz), 3.87 (s, 3H), 4.40 (d, 1H, J = 3.8 Hz), 7.36 (m, 5H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ −2.0, 9.9, 47.0, 47.2, 52.0, 53.2, 127.0, 128.8, 129.1, 133.3, 166.3; mass spectrum (CI) m/z 342 $(M + H)^+$. Anal. Calcd for $C_{15}H_{23}NO_4SSi\cdot 0.25H_2O$: C, 52.07; H, 6.85; N, 4.05. Found: C, 51.73; H, 6.66; N, 4.22.

***N*-(2-(Trimethylsilyl)ethanesulfonyl)-2-(methoxycarbonyl)aziridine (5d).** Starting from 360 μL (4.0 mmol) of methyl acrylate dissolved in acetonitrile (2 mL) and 310 mg (0.8 mmol) of PhI=NSes, 0.105 g (0.395 mmol, 49%) of aziridine was isolated as a colorless oil after flash chromatography on silica gel (heptane−ethyl acetate 4:1): ^1H NMR (300 MHz, $CDCl_3$) δ 0.07 (s, 9H), 1.13 (m, 2H), 2.60 (d, 1H, J = 4.1 Hz), 2.75 (d, 1H, J = 7.0 Hz), 3.16 (m, 2H), 3.30 (dd, 1H, J = 4.1, 7.0 Hz), 3.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −2.0, 9.5, 31.6, 34.8, 49.3, 53.0, 167.5; mass spectrum (CI) m/z 266 $(M + H)^+$. Anal. Calcd for $C_9H_{19}NO_4SSi$: C, 40.73; H, 7.22; N, 5.28; S, 12.08. Found: C, 40.81; H, 7.04; N, 5.21; S, 11.89.

***N*-(2-(Trimethylsilyl)ethanesulfonyl)-2-(methoxycarbonyl)-2-methylaziridine (5e).** Starting from 128 μL (1.2 mmol) of methyl methacrylate, 0.175 g (0.63 mmol, 52%) of aziridine was isolated as a colorless oil after flash chromatography on silica gel (heptane−ethyl acetate 4:1): ^1H NMR (250 MHz, $CDCl_3$) δ 0.07 (s, 9H), 1.12 (m, 2H), 1.84 (s, 3H), 2.65 (s, 1H), 2.86 (s, 1H), 3.14 (m, 2H), 3.77 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ −1.9, 9.7, 15.7, 39.2, 45.2, 51.5, 53.1, 169.1; mass spectrum (CI) m/z 280 $(M + H)^+$. Anal. Calcd for $C_{10}H_{21}NO_4SSi$: C, 42.98; H, 7.58; N, 5.01; S, 11.47. Found: C, 42.93; H, 7.43; N, 4.87; S, 11.51.

***N*-(2-(Trimethylsilyl)ethanesulfonyl)-2-(methoxycarbonyl)-2,3-dimethylaziridine (5f).** Starting from 96 μL (0.8 mmol) of methyl tiglate, 0.110 g (0.37 mmol, 47%) of aziridine was isolated as a colorless oil after flash chromatography on silica gel (heptane−ethyl acetate 5:1): ^1H NMR (250 MHz, $CDCl_3$) δ 0.04 (s, 9H), 1.08 (m, 2H), 1.31 (d, 3H, J = 5.8 Hz), 1.48 (s, 3H), 3.08 (m, 2H), 3.63 (q, 1H, J = 5.8 Hz), 3.75 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ −2.0, 9.7, 12.8, 15.3, 43.6, 51.1, 53.0, 168.8; mass spectrum (CI) m/z 294 $(M + H)^+$. Anal. Calcd for $C_{11}H_{23}NO_4SSi\cdot 0.03C_7H_{16}$: C, 45.42; H, 7.98; N, 4.72; S, 10.81. Found: C, 45.46; H, 7.71; N, 4.67; S, 11.02.

***N*-(2-(Trimethylsilyl)ethanesulfonyl)-2-(*tert*-butoxycarbonyl)-2-phenylaziridine (5g).** Starting from 184 mg (0.9 mmol) of *tert*-butyl atropate, 165 mg (0.43 mmol, 48%) of aziridine together with 50 mg (0.24 mmol, 27%) of unreacted starting material were isolated as a colorless oil after flash chromatography on silica gel (heptane−ethyl acetate 8:1): ^1H NMR (300 MHz, $CDCl_3$) δ 0.07 (s, 9H), 1.23 (m, 2H), 1.46 (s, 9H), 2.56 (s, 1H), 3.28 (m, 2H), 3.43 (s, 3H), 7.35−7.44 (m, 5H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ −2.0, 9.7, 27.6, 37.6, 50.1, 53.8, 83.6, 127.2, 128.5, 128.7, 135.1, 165.2; mass spectrum (CI) m/z 384 $(M + H)^+$. Anal. Calcd for $C_{18}H_{29}NO_4SSi$: C, 56.36; H, 7.62; N, 3.65; S, 8.36. Found: C, 56.58; H, 7.62; N, 3.63; S, 8.32.

***N*-(2-(Trimethylsilyl)ethanesulfonyl)-7-azabicyclo[4.1.0]-heptane (5h).** Starting from 81 μL (0.8 mmol) of cyclohexene, 72 mg (0.275 mmol, 34%) of aziridine was isolated as a white solid after flash chromatography on silica gel (heptane−ethyl acetate 6:1): mp 57−58 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 0.06

(19) This could be an interesting alternative to the classical reagent (i.e., CsF in DMF) since cases have been reported in which the *N*-(Ses) protecting group could not be removed under the standard conditions. For example, see: Ward, D. E.; Gai, Y.; Kaller, B. F. *J. Org. Chem.* **1996**, *61*, 5498.

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(s, 9H), 1.08−1.15 (m, 2H), 1.23−1.35 (m, 2H), 1.39−1.51 (m, 2H), 1.89 (m, 4H), 2.95 (m, 2H), 3.00−3.07 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −2.0, 9.8, 19.5, 23.0, 39.1, 49.0; mass spectrum (CI) *m*/*z* 262 $(M + H)^+$. Anal. Calcd for $C_{11}H_{23}NO_2SSi$: C, 50.53; H, 8.87; N, 5.36; S, 12.26. Found: C, 50.62; H, 8.61; N, 5.15; S, 12.26.

***N*-(2-(Trimethylsilyl)ethanesulfonyl)-3-azatricyclo[3.2.1.0.^{2,4exo}]octane (5i).** Starting from 94 mg (1.0 mmol) of norbornene, 0.150 g (0.55 mmol, 55%) of aziridine was isolated as a white solid after flash chromatography on silica gel (heptane−ethyl acetate 5:1): mp 59.5−61 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.06 (s, 9H), 0.81 (d, 1H, J = 10 Hz), 1.06−1.14 (m, 2H), 1.26−1.30 (m, 2H), 1.47−1.54 (m, 3H), 2.52 (s, 2H), 2.90 (s, 2H), 2.99−3.06 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ −2.0, 9.8, 25.7, 28.3, 35.9, 41.0, 49.2; mass spectrum (CI) *m*/*z* 274 $(M + H)^+$. Anal. Calcd for $C_{12}H_{23}NO_2SSi$: C, 52.71; H, 8.48; N, 5.12; S, 11.72. Found: C, 52.43; H, 8.16; N, 5.02; S, 11.65.

***N*-(2-(Trimethylsilyl)ethanesulfonyl)-2-nonylaziridine (5j).** Starting from 205 μL (1.0 mmol) of 1-undecene, 0.110 g (0.33 mmol, 33%) of aziridine was isolated as a colorless oil after flash chromatography on silica gel (heptane−ethyl acetate 15:1): ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.07 (s, 9H), 0.88 (t, 3H, J = 6.9 Hz), 1.11−1.19 (m, 2H), 1.23−1.57 (m, 16H), 2.08 (d, 1H, J = 4.6 Hz), 2.59 (d, 1H, J = 7.0 Hz), 2.70 (m, 1H), 3.03−3.10 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ −1.9, 9.8, 14.1, 22.7, 26.9, 29.3, 29.4, 29.6, 31.6, 32.0, 33.4, 39.3, 48.9; mass spectrum (EI) *m*/*z* 333 $(M)^+$. Anal. Calcd for $C_{16}H_{35}NO_2SSi$: C, 57.61; H, 10.57; N, 4.20; S, 9.61. Found: C, 57.38; H, 10.48; N, 4.11; S, 9.76.

Reductive Ring Opening of the *N*-(Ses)aziridine 5c. A solution of the *N*-(Ses)aziridine **5c** (80 mg, 0.234 mmol) in methanol (4 mL) was treated at 0 °C under argon with nickel chloride hexahydrate (55 mg, 0.234 mmol), and after the mixture had stirred for 5 min, sodium borohydride (88 mg, 2.34 mmol) was added in small portions. The reaction mixture was stirred for 1 h at 0 °C before saturated aqueous NH_4Cl (5 mL) was added. The mixture was extracted with dichloromethane (3 × 10 mL), the combined organic phases were dried over $MgSO_4$, and the solvents were evaporated under vacuum. The residue was purified by column chromatography on silica gel (ethyl acetate−heptane 1:3), providing *N*-(Ses)-phenylalanine methyl ester **6** (72 mg, 80%) as a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.07 (s, 9H), 0.92 (m, 2H), 2.67−2.84 (m, 2H), 3.08 (dd, 1H, J = 7.9, 13.8 Hz), 3.26 (dd, 1H, J = 5.1, 13.8 Hz), 3.88 (s, 3H), 4.44 (ddd, 1H, J = 9.4 Hz), 7.30−7.42 (m, 5H); mass spectrum (CI) *m*/*z* 344 $(M + H)^+$.

Acid-Catalyzed Ring Opening of the *N*-(Ses)aziridine 5f. To a solution of the *N*-(Ses)aziridine **5f** (76 mg, 0.260 mmol) and 2-methoxythiophenol (95 μL, 0.780 mmol) in CH_2Cl_2 (1.2 mL) was added at −20 °C under argon boron trifluoride etherate (64 μL, 0.520 mmol). The reaction mixture was then allowed to come to 0 °C and stirred for 2 h before saturated aqueous $NaHCO_3$ (2 mL) was added. The mixture was extracted with ethyl acetate (2 × 5 mL), the combined organic phases were dried over $MgSO_4$, and the solvents were evaporated under vacuum. Elution of the chromatography column with ethyl acetate−heptane (1:5) first gave compound **7** (75 mg, 67%) as a colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.04 (s, 9H), 1.04−1.12 (m, 2H), 1.33 (d, 3H, J = 7.1 Hz), 1.72 (s, 3H), 2.95−3.08 (m, 2H), 3.32 (q, 1H, J = 7.1 Hz), 3.72 (s, 3H), 3.92 (s, 3H), 5.73 (s, 1H), 6.92 (2d, 2H, J = 7.9 Hz), 7.33 (dd, 1H), 7.45 (dd, 1H); mass spectrum (CI) *m*/*z* 434 $(M + H)^+$.

Continued elution of the column with ethyl acetate−heptane (1:4) gave compound **8** (20 mg, 18%) as a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.01 (s, 9H), 1.04−1.15 (m, 2H), 1.22 (s, 3H), 1.38 (d, 3H, J = 6.6 Hz), 2.98−3.20 (m, 2H), 3.73 (s, 3H), 3.78 (m, 1H), 3.84 (s, 3H), 5.25 (d, 1H, J = 8.9 Hz), 6.92 (m, 2H), 7.31−7.48 (m, 2H); mass spectrum (CI) *m*/*z* 434 $(M + H)^+$.

Typical Procedure for the Deprotection of the *N*-(Ses)-aziridines. Method B: 2-Phenylaziridine (10). A solution of the *N*-(Ses)aziridine **5a** (58 mg, 0.205 mmol) and TASF (225 mg, 4 equiv) in DMF (0.7 mL) was stirred at room temperature. After completion of the reaction as indicated by TLC, the mixture was purified by flash chromatography on silica gel (heptane−ethyl acetate 1:2), affording the deprotected aziridine **10** (15 mg, 0.126 mmol, 62%) as a yellow oil whose spectroscopic data were identical to those previously reported:[17] ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.15 (br s, 1H), 1.80 (d, 1H, J = 3.4 Hz), 2.21 (d, 1H, J = 6.0 Hz), 3.02 (dd, 1H, J = 3.4 and 6.0 Hz), 7.22−7.34 (m, 5H); mass spectrum (CI) *m*/*z* 120 $(M + H)^+$.

Method C: 3-Azatricyclo[3.2.1.0.^{2,4exo}]octane (12). A solution of the *N*-(Ses)aziridine **5i** (74 mg, 0.270 mmol) and TASF (230 mg, 3 equiv) in acetonitrile (1 mL) was stirred at room temperature. After completion of the reaction as indicated by TLC, the mixture was purified by flash chromatography on silica gel (dichloromethane−ethanol 9:1), affording the deprotected aziridine **12** (18 mg, 0.164 mmol, 60%) as a colorless oil whose spectroscopic data were identical to those previously reported:[21] ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.70 (d, 1H, J = 10.7 Hz), 0.99 (br s, 1H), 1.11−1.17 (m, 1H), 1.23−1.29 (m, 2H), 1.46−1.50 (m, 2H), 1.98 (s, 2H), 2.34 (s, 2H); mass spectrum (CI) *m*/*z* 110 $(M + H)^+$.

2-Phenylethylaziridine (11). Starting from 80 mg (0.257 mmol) of *N*-(Ses)aziridine **5b**, 23 mg (0.156 mmol, 60%) of the deprotected aziridine **11** was isolated as a yellow oil after flash chromatography on silica gel (dichloromethane−ethanol 9:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25 (br s, 1H), 1.35 (d, 1H, J = 3.5 Hz), 1.69−1.78 (m, 3H), 1.94 (m, 1H), 2.77 (m, 2H), 7.17−7.28 (m, 5H); mass spectrum (CI) *m*/*z* 148 $(M + H)^+$.

2-Nonylaziridine (13). Starting from 110 mg (0.33 mmol) of *N*-(Ses)aziridine **5j**, 38 mg (0.224 mmol, 68%) of the deprotected aziridine **13** was isolated as a yellow oil after flash chromatography on silica gel (dichloromethane−ethanol 9:1): ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.88 (t, 3H, J = 6.9 Hz), 1.19−1.50 (m, 18H), 1.77 (d, 1H), 1.95 (m, 1H); mass spectrum (CI) *m*/*z* 170 $(M + H)^+$.

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