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Note

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Direct *N*-H/*N*-Me Aziridination of Unactivated Olefins Using *O*-(Sulfonyl)hydroxylamines as Aminating Agents

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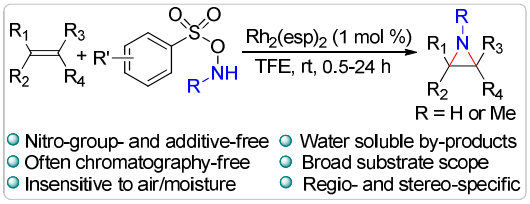
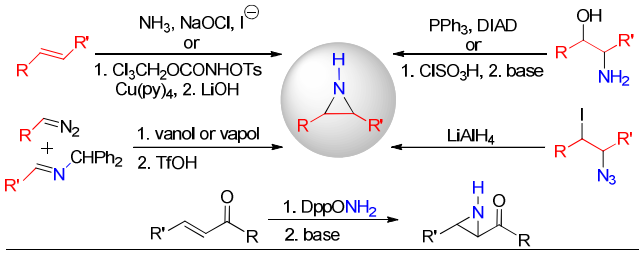
Supporting Information Placeholders



ABSTRACT: Unactivated aziridines are the core substructures in a plethora of bioactive natural products, and serve as building blocks in organic synthesis. Despite this, very limited methods are available to access them directly from olefins, as most of the known methods are devoted to their activated counterparts. Herein, we have developed a highly efficient Rh(II)-catalyzed method for the direct preparation of unactivated aziridines from olefins using *O*-(sulfonyl)hydroxylamines as the aminating agent. The reactions proceed with a high stereospecificity.

The unactivated aziridines (*N*-H/*N*-Me) are in high demand because of their presence in many natural, semi-synthetic and synthetic bioactive molecules.[1] They also serve as important building blocks in organic synthesis because of their remarkable reactivity *via* ring-opening as well as ring-expansion, and rearrangements.[2] The regio- and stereo-specific ring opening of unprotected (unactivated) aziridines with different nucleophiles (*N*, *O*, *S*, *C*) offers various functionalized unprotected scaffolds like amino-alcohols, diamines, thio-amines, halo-amines, etc.[3] Whereas the methods for activated aziridines (e. g., *N*-Ts, *N*-Ns, *N*-acyl) preparation from alkenes are well established, the direct method for accessing non-activated aziridines are less explored, and most of these methods are multi-steps (Scheme 1).[4,5] In 2014, Falck, Kurti, Ess and Co-workers (including the corresponding author of this manuscript) reported the first direct method for the preparation of *N*-H and *N*-Me aziridines from alkenes using 2,4-dinitrophenyl hydroxylamine (DPH) as the aminating agent in the presence of a rhodium catalyst (Du Bois catalyst) (**A**, Figure 1).[6] This elegant method requires DPH in stoichiometric amount that has several intrinsic drawbacks. For instance, the by-product, 2,4-dinitrophenol (DNP), interferes *via* undesired ring opening reaction, both DPH and DNP are relatively unstable/explosive in nature due to a high NO_2/C ratio, DNP occasionally co-elutes along with the product during column-chromatography, etc. Improving their previous method, Kurti et al. demonstrated another protocol using hydroxylamine-*O*-sulfonic acid (HOSA), instead of DPH, as the aminating reagent in the presence of 1.2 equivalent of pyridine

Scheme 1. General Methods to Access Unprotected Aziridines



Vanol = 3,3′-Diphenyl-2,2′-bi-1-naphthalol. Vapol = 2,2′-Diphenyl-(4-biphenanthrol. $DppONH_2$ = O-(Diphenylphosphinyl)hydroxylamine.

and the same rhodium catalyst (**B**, Figure 1).[7] This modification could overcome the drawbacks of their previous method to a great extent, but: (i) necessitated the use of 1.2 equivalent of pyridine, (ii) column chromatography was still necessary, and (iii) the use of a relatively costly hexafluoroisopropanol (HFIP) as the solvent.

We were interested to develop an atom-economical, additive/base-free and possibly a column chromatography-free method, as the strained aziridine rings frequently open during silica-gel purification. To achieve these objectives, the aminating reagent desirably should: (i) exists in a non zwitter-ionic form, (ii) be stable and readily available, and (iii) essentially generate a non-interfering by-product that can be easily

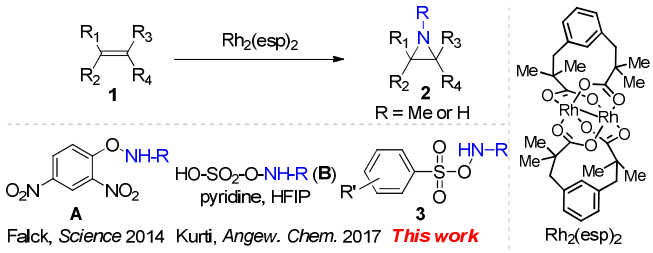
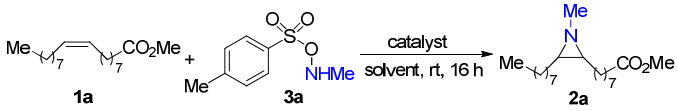


Figure 1. Aminating Agents Used for *N*-H and *N*-Me Aziridination of alkenes

removed just by an aqueous work-up. In this regard, *O*-sulfonylhydroxylamines (**3**, Figure 1) attracted our attention. This class of reagents have been mainly explored for α-oxytosylation of carbonyl compounds, and $C(Sp^2)$-H as well as $C(Sp^3)$-H amination.[8] We herein report a rhodium-catalyzed synthesis of *N*-Me and *N*-H aziridines from alkenes using *N*-Methyl-*O*-tosylhydroxylamine[8] (**3a**) and 2,4,6-$Me_3C_6H_2S(O)_2ONH_2$ (**3b**) as the aminating reagents,[9] respectively.

Our study for *N*-Me aziridination began using methyl oleate **1a** as the model substrate in the presence of **3a** as the aminating reagent in 2,2,2-trifluoroethanol (TFE) (Table 1). Under this condition, both Fe(II)- and Fe(III)-based catalysts did not produce the desired product (entries 1 and 2). Whereas CuBr was found ineffective, $Cu(OAc)_2$ and $Cu(acac)_2$ could catalyze the reaction to produce **2a** in 20-35% yield (entries 3-5). The yield improved significantly to 52% with $FeSO_4.7H_2O$ (entry 6). Switching to various Rh-based catalysts further improved the yield of the reaction, eventually giving the desired product in excellent yield (96%) with $Rh_2(esp)_2$ in 30 min (entry 9). The lowering of the catalyst loading from 5 mol % to 1 mol % did

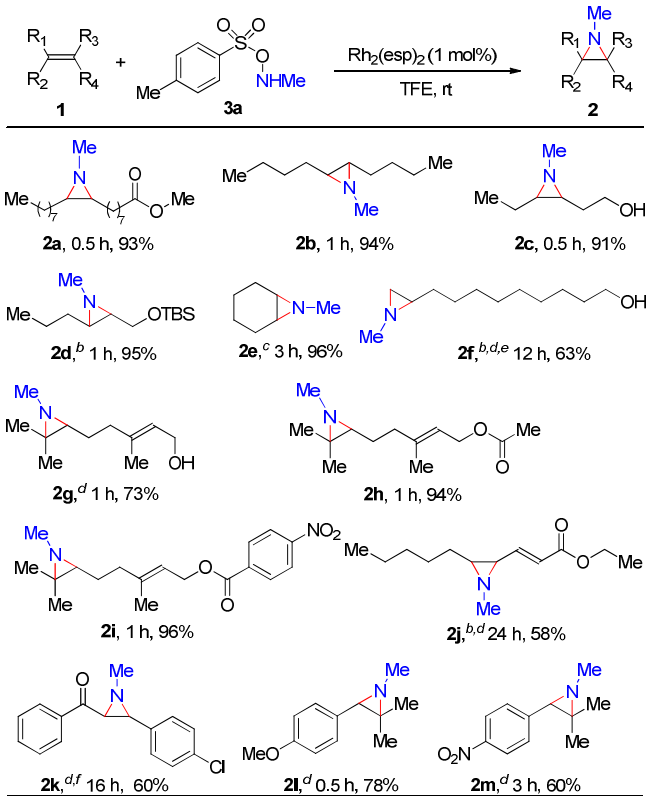
Table 1. Reaction Condition Optimization[a]



Entry	Catalyst	Solvent	Yield (%)[b]
1	$FeCl_2$ (5 mol %)	TFE	-
2	$FeCl_3$ (5 mol %)	TFE	-
3	CuBr (5 mol %)	TFE	trace
4	$Cu(OAc)_2$ (5 mol %)	TFE	20
5	$Cu(acac)_2$ (5 mol %)	TFE	35
6	$FeSO_4.7H_2O$ (5 mol %)	TFE	52
7	$Rh_2(OAc)_2$ (5 mol %)	TFE	65
8	$Rh_2(TFA)_2$ (5 mol %)	TFE	-
9	$Rh_2(esp)_2$ (5 mol %)	TFE	96[c]
10	$Rh_2(esp)_2$ (1 mol %)	TFE	93[c]
11	$Rh_2(esp)_2$ (1 mol %)	EtOH	trace
12	$Rh_2(esp)_2$ (1 mol %)	THF	-
13	$Rh_2(esp)_2$ (1 mol %)	CH_3CN	trace
14	$Rh_2(esp)_2$ (1 mol %)	DMF	-
15	$Rh_2(esp)_2$ (1 mol %)	CH_2Cl_2	-
16	-	TFE	-

[a]Reaction condition unless otherwise mentioned: **1a** (0.25 mmol), **3a** (1.2 equiv.), catalyst (1.0-5.0 mol %), solvent, rt, 16 h. [b]Isolated yield after silica gel column chromatography. [c]Isolated yield after work-up using saturated $NaHCO_3$ aqueous solution; silica gel chromatography was not needed. TFE = 2,2,2-trifluroethanol. esp = α,α,α',α'-tetramethyl-1,3-benzenedipropionic acid.

Scheme 2. Preparation of *N*-Me Aziridines[a]



[a]Reaction condition unless otherwise mentioned: **1** (0.5 mmol), **3a** (1.2 equiv.), $Rh_2(esp)_2$ (1 mol %), TFE (2.0 mL), rt. Yields are the isolated yield after an aqueous work-up. [b]Reaction was performed at -10 °C. [c]The purity of this compound was checked by HPLC. [d]Column purification was required. [e]5 mol % of Rh-catalyst was used. [f]A mixture of TFE:$CHCl_3$ (1:1) was used as the solvent.

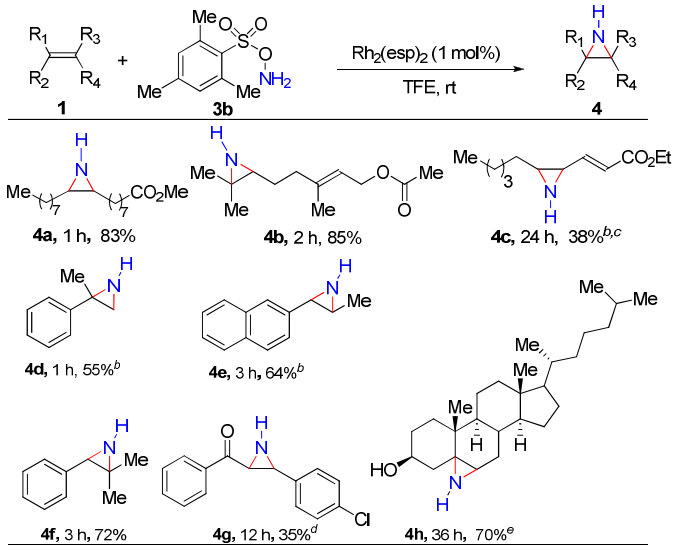
not affect the yield significantly (93%, entry 10). The screening of various other solvents under a condition similar to entry 10 had detrimental effect on the reaction outcome (entries 11-15). To our delight, a simple work-up using saturated $NaHCO_3$ aqueous solution completely removed the by-product (TsOH), giving the desired product with a good purity (by NMR).

To explore the scope of this method, a variety of alkenes were evaluated under the standard condition (as in entry 10, Table 1). Both *cis*- and *trans*-alkenes reacted well within an hour to give the corresponding aziridines in excellent yields (**2a** and **2b**, Scheme 2). Olefins bearing even unprotected hydroxy group smoothly aziridinated with 91% (**2c**) isolated yield, while its TBS-protected derivative produced **2d** in 95% yield at a lower reaction temperature. This TBS-protected alkene/aziridine partially got deprotected on stirring the reaction at room temperature. Cyclic alkene also participated in the reaction affording **2e** with 96% yield. Switching to a terminal alkene required a minor variation in the reaction condition as it was sluggish under the above optimized condition and a prolongation of the reaction time under this condition led to the decomposition of the product. This reaction proceeded well with a slightly higher Rh-catalyst loading of 5 mol% and at a

lower reaction temperature (-10 °C), giving **2f** in 63% isolated yield.

We next investigated the regioselectivity of the reaction using geraniol, which exclusively aziridinated at $\Delta^{6,7}$-olefinic position to furnish **2g** in 73% yield. Different derivatives of geraniol also

Scheme 3. Preparation of *N*-H Aziridines[a]



[a]Reaction condition unless otherwise stated: **1** (0.5 mmol), **3b** (1.2 equiv.) $Rh_2(esp)_2$ (1 mol %), TFE (2.0 mL), rt. Yields are isolated yield after silica gel column chromatography. [b]Reaction stirred at -10 °C. [c]Reaction was clean but with low conversion, and the olefin could be recovered. [d]A mixture of TFE:$CHCl_3$ (1:1) was used as the solvent. [e]2.5 equiv. of **3b** and 2.5 mol % of Rh-catalyst was used.

reacted smoothly to give **2h** and **2i** in 94% and 96% yields, respectively, as a single regiomer. This regioselectivity can be attributed to the inductive deactivation of the proximal double bond ($\Delta^{2,3}$) by acetoxy or benzoyloxy group towards aziridination. This observation was further supported by a much slower reactivity of the electron deficient chalcone requiring 16 h for completion of the reaction (**2k**). A mixture of TFE and $CHCl_3$ (1:1) was used as the solvent as the chalcone was not soluble in TFE alone. For conjugated diene ester also, the aziridination occurred at the distal ($\Delta^{3,4}$) double bond selectively (**2j**, 58% yield). Both electron-rich as well as electron-deficient trisubstituted styrenes smoothly reacted to give the desired products (**2l** and **2m**) in good yield, albeit the reaction was slower in the case of electron-deficient styrene. Tetra-substituted olefin, like β-ionone, failed to react under this optimized condition for *N*-Me (as well as for *N*-H) aziridination. It is worth noting that all the reactions proceeded with high stereospecificity and without formation of any allylic aminated side product.

After demonstrating the method for *N*-Me aziridination, we turned our attention to the direct *N*-H aziridination of alkenes. The literature survey and our own studies using unprotected analog of **3a** ($TsONH_2$) to achieve *N*-H aziridination was not successful as this reagent was unstable under this condition. A 2,4,6-trimethyl derivative of tosyl hydroxylamine (**3b**, Scheme 3) was found to be a good aminating agent under a condition similar to Scheme 2. Under this condition, different alkenes reacted well to give the desired products in good to excellent yield. For example, methyl oleate furnished the *N*-H aziridine **4a** in 83% yield. Geranyl acetate & (2*E*,4*Z*)-ethyl deca-2,4-dienoate (a conjugated diene ester) afforded **4b** (85% yield) and **4c** (38% yield), respectively, as a single regiomer. Simple as well as substituted styrenes were good substrates for this reaction at lower temperature to give the corresponding *N*-H aziridines in good yield (**4d** and **4f**). *β*-Naphthyl styrene was also examined to obtain **4e** in 64% yield. Chalcone reacted slowly to give the corresponding aziridine in 35% yield (**4g**). We also examined our reaction on complex substrate like cholesterol. Under the optimized condition with TFE as the solvent, only a minor conversion was observed; the yield improved dramatically when a mixture of TFE:$CHCl_3$ (1:1) was used as the solvent (**4h**, 70% yield), albeit the reaction took a longer time to complete (36 h). We expect these reactions to follow the same mechanistic pathway as previously proposed by Falck, Kurti and Ess.[6]

In conclusion, we have developed a direct, stereospecific Rh(II)-catalyzed *N*-H/*N*-Me aziridination method for alkenes using *O*-(sulfonyl)hydroxylamines as the aminating agents. These reagents do not generate explosive/interfering byproducts and do not require base (pyridine) as an additive. This method provides various unactivated aziridines in good to excellent yield and *N*-Me aziridines in many cases could be isolated with high purity just after an aqueous work-up. Even highly reactive and labile functional groups like keto, ester, alcohol and silyl were well tolerated. The reactions proceeded with a good chemoselectivity as neither the undesired amination nor the nitrene insertion on the aromatic ring was observed.

EXPERIMENTAL SECTION

General Information: Unless otherwise specified, all reactions were carried out under an open atmosphere in a round bottom flask. All aldehydes were of commercial quality and used without further purification. The olefins **1b**, **1i**, **1l**, **1m** and *β*-naphthyl styrene were prepared following a literature known procedure.[10] Solvents were dried and distilled following the standard procedures. TLC was carried out on precoated plates (Merck silica gel 60, f254), and the spots were visualized with UV light or by charring the plates dipped in PMA or $KMNO_4$ solution. The compounds were purified by flash column chromatography using silica gel (230-400 mesh) with distilled solvents. ^1H and ^{13}C NMR spectra were recorded at 400 MHz instrument, and 100 MHz instrument, respectively, in $CDCl_3$ as the solvent. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references ($CDCl_3$: δ H = 7.26 ppm, δ C = 77.0 ppm). High-resolution mass spectrometry (HRMS) was performed on agilent 6530 Q-TOF using electrospray ionization (ESI) and a time-of-flight (TOF) analyzer, in positive-ion or negative-ion detection mode.

General Procedure for N-H and N-Me Aziridination: To a round bottom flask equipped with a magnetic stirring bar, was added alkene **1** (0.5 mmol), aminating agent **3a** or **3b** (1.2 equiv.) and TFE (2 mL) at room temperature. To this stirred solution, $Rh_2(esp)_2$ (1 mol %) was added. The reaction mixture was stirred at the specified temperature and monitored by TLC. After completion, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and washed with a saturated aqueous $NaHCO_3$ solution (2 x 5 mL). The aqueous layer was extracted

twice with CH_2Cl_2 (5 mL) and the combined organic layer was dried over anhydrous Na_2SO_4.

Purification method for Scheme 2: Organic layer was concentrated in *vacuo* to afford the pure desired product **2**, unless reported otherwise.

Purification method for Scheme 3: The crude product obtained after concentration of the organic layer in *vacuo* was purified by silica gel column chromatography to give the pure desired product **4** using 1% Bu_3N in EtOAc/hexane or MeOH/CH_2Cl_2 as an eluent.

(E)-3,7-Dimethylocta-2,6-dienyl 4-nitrobenzoate (1j): To a solution of geraniol (200 mg, 1.29 mmol) and *p*-nitrobenzoyl chloride (289 mg, 1.54 mmol) in CH_2Cl_2 (15 mL) at 0 ^oC, was added pyridine (136 µL, 1.54 mmol) and DMAP (18 mg, 0.15 mmol) and the reaction was stirred at room temperature for 18 h. After completion of the reaction, CH_2Cl_2 (10 mL) was added and the organic layer was washed with water (2 x 5 ml) and brine solution (5 ml). The organic layer was dried over anhydrous Na_2SO_4, concentrated in *vacuo* and the crude product was purified by silica gel column chromatography (2% EtOAc in hexane) to give the title compound as a thick oil. (325 mg, 83%). TLC: R_f = 0.5 (5% EtOAc in hexane). ^1H NMR (400 MHz, $CDCl_3$) δ 8.28-8.23 (m, 2H), 8.22-8.17 (m, 2H), 5.49-5.42 (m, 1H), 5.10-5.04 (m, 1H), 4.87 (d, *J* = 7.1 Hz, 2H), 2.14-2.03 (m, 4H), 1.76 (s, 3H), 1.65 (s, , 3H), 1.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 150.4, 143.3, 135.8, 131.8, 130.6, 123.5, 123.4, 117.6, 62.7, 39.4, 26.2, 25.6, 17.6, 16.5. HRMS (ESI) $[M+H]^+$ calcd. for $C_{17}H_{22}NO_4$: 304.1543, found: 304.1525.

***Methyl 8-(1-methyl-3-octylaziridin-2-yl)octanoate (2a)*:**[6] Following the general aziridination procedure, the title aziridine was obtained as a colorless oil (151 mg, 93% yield) whose spectral data were in accord with the literature values.

2,3-Dibutyl-1-methylaziridine(2b): Following the general aziridination procedure, the title product was obtained as a colorless oil (80 mg, 94% yield). TLC: R_f = 0.3 (50% EtOAc in hexane). ^1H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 1.64-1.56 (m, 2H), 1.46-1.28 (m, 11H), 0.93-0.86 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.2, 42.9, 38.6, 32.8, 30.6, 29.6, 25.3, 22.6, 22.5, 14.0, 13.9. HRMS (ESI) *m/z* $[M+H]^+$ calcd. for $C_{11}H_{24}N$:170.1903, found: 170.1903.

2-(3-Ethyl-1-methylaziridin-2-yl)ethanol (2c): Following the general aziridination procedure, the title product was obtained as a pale-yellow oil (58 mg, 91% yield). TLC: R_f = 0.3 (5% MeOH in CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 3.84-3.71 (m, 2H), 2.34 (s, 3H), 1.76-1.68 (m, 1H), 1.56-1.29 (m, 4H), 1.25-1.19 (m, 1H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 61.9, 47.8, 46.2, 43.1, 29.5, 21.2, 11.8. HRMS (ESI) *m/z* $[M+H]^+$ calcd. for $C_7H_{16}NO$: 130.1226, found: 130.1225.

2-(2-(tert-Butyldimethylsilyloxy)ethyl)-3-ethyl-1-methyl aziridine (2d): The product was prepared following the general aziridination procedure and the crude product was purified by silica gel column chromatography using Bu_3N:EtOAc:hexane (1:29:70) as an eluent to give the title product as a colorless oil (115 mg, 95% yield). TLC: R_f = 0.2 (50% EtOAc in hexane). ^1H NMR (400 MHz, $CDCl_3$; a mixture of invertomers) δ 3.77-3.65 (m, 2H), 2.39 (s, 1.5H), 2.38 (s, 1.5H), 1.90-1.78 (m, 0.5H), 1.71-1.53 (m, 3H), 1.52-1.43 (m, 0.5H), 1.42.1.33 (m, 1H), 1.29-1.11 (m, 2H), 1.07-1.01 (m, 2H), 0.95 (t, *J* = 7.4Hz, 1H), 0.91-0.85 (m, 8H), 0.07-0.03 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 62.2, 61.3, 48.3, 44.4, 44.0, 39.8, 39.1, 38.5, 36.4, 29.6, 29.1, 26.1, 25.9, 19.0, 18.3, 12.7, 11.4, 1.0, -5.3. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{13}H_{30}NOSi$, 244.2091; found, 244.2090.

7-Methyl-7-azabicyclo[4.1.0]heptanes (2e):[11] Following the general aziridination procedure, the title aziridine was obtained as a light yellow oil (53 mg, 96% yield). TLC: R_f = 0.4 (50% EtOAc in hexane), whose spectral data were in accord with the literature values.

9-(1-Methylaziridin-2-yl)nonan-1-ol (2f): The product was prepared following the general aziridination procedure and the crude product was purified by silica gel column chromatography using Bu_3N:MeOH:CH_2Cl_2 (1:2:97) as an eluent to give the title compound as an oil (63 mg, 63% yield). TLC: R_f = 0.25 (5% MeOH in CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 3.63 (t, *J* = 6.6 Hz, 2H), 2.30 (s, 3H), 1.70 (brs, 1H), 1.58-1.53 (m, 2H), 1.48 (d, *J* = 3.5 Hz, 1H), 1.40-1.17 (m, 17H), 1.11 (d, *J* = 3.1, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 62.8, 53.4, 47.8, 40.8, 34.8, 32.9, 32.7, 29.6, 29.4, 29.3, 29.3, 27.5, 25.7. HRMS (ESI) *m/z* $[M+H]^+$ calcd. for $C_{12}H_{26}NO$: 200.2009, found: 200.2017.

(E)-3-Methyl-5-(1,3,3-trimethylaziridin-2-yl)pent-2-en-1-ol (2g): The product was prepared following the general aziridination procedure and the crude product was purified by silica gel column chromatography using Bu_3N:MeOH:CH_2Cl_2 (1:4:95) as an eluent to give the title product as an oil (66 mg, 73% yield). TLC: R_f = 0.3 (10% MeOH in CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 5.47-5.40 (m, 1H), 4.15 (d, *J* = 6.9 Hz, 2H), 2.36 (s, 3H), 2.20-2.04 (m, 2H), 1.68 (s, 3H), 1.58-1.42 (m, 2H), 1.24 (s, 1H), 1.17 (s, 3H), 1.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 123.7, 59.3, 52.0, 39.5, 39.3, 37.7, 27.5, 21.6, 17.9, 16.2. HRMS (ESI) *m/z* $[M+H]^+$ calcd. for $C_{11}H_{22}NO$: 184.1623, found: 184.1642.

(E)-3-Methyl-5-(1,3,3-trimethylaziridin-2-yl)pent-2-en-1-yl acetate (2h):[6] Following the general aziridination procedure, the title aziridine was obtained as an oil (106 mg, 94% yield). ^1H NMR and ^{13}C NMR data were in accord with the literature value.

(E)-3-Methyl-5-(1,3,3-trimethylaziridin-2-yl)pent-2-enyl 4-nitrobenzoate (2i): Following the general aziridination procedure, the title product was obtained as a thick yellow liquid. (158 mg, 96% yield). TLC: R_f = 0.3 (40% EtOAc in hexane). ^1H NMR (400 MHz, $CDCl_3$) δ 8.28-8.23 (m, 2H), 8.21-8.16 (m, 2H), 5.52-5.44 (m, 1H), 4.87 (d, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 2.25-2.09 (m, 2H), 1.77 (s, 3H), 1.62-1.43 (m, 2H), 1.15 (s, 3H), 1.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 150.4, 143.1, 135.8, 130.6, 123.4, 117.9, 62.6, 51.8, 39.5, 39.3, 37.7, 27.5, 21.7, 17.9, 16.4. HRMS (ESI) *m/z* $[M+H]^+$ calcd. for $C_{18}H_{25}N_2O_4$: 333.1809, found: 333.1815.

***(E)-Ethyl-3-(1-methyl-3-pentylaziridin-2-yl)acrylate (2j)*:** The product was prepared following the general aziridination procedure and the crude product was purified by silica gel column chromatography using Bu_3N:EtOAc:hexane (1:29:70) as an eluent to give the title product as a colorless oil (64 mg, 58% yield). TLC: R_f = 0.6 (20% EtOAc in hexane). ^1H NMR (400 MHz, $CDCl_3$) δ 6.71 (dd, *J* = 15.6, 7.8 Hz, 1H), 6.00 (dd, *J* = 15.6, 0.7 Hz, 1H), 4.22-4.09 (m, 2H), 2.38 (s, 3H), 1.91 (t, *J* =

7.1 Hz, 1H), 1.59 (q, *J* = 5.8 Hz, 1H), 1.31-1.19 (m, 10H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 145.9, 123.0, 60.1, 49.3, 47.4, 45.0, 31.4, 28.4, 27.2, 22.5, 14.2, 13.9. HRMS (ESI) *m/z* $[M+H]^+$ calcd. for $C_{13}H_{24}NO_2$: 226.1802, found: 226.1800.

(3-(4-Chlorophenyl)-1-methylaziridin-2-yl) (phenyl) methanone (2k): The product was prepared following the general aziridination procedure and the crude product was purified by silica gel column chromatography using Bu_3N:EtOAc:hexane (1:5:94) as an eluent to give the title compound as a light yellow sticky semi-solid (81 mg, 60% yield). TLC: R_f = 0.5 (10% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.4 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7, 2H), 7.32 - 7.23 (m, 4H), 3.53 (d, *J* = 2.4 Hz, 1H), 3.33 (d, *J* = 2.2 Hz, 1H), 2.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 137.9, 137.2, 133.5, 133.2, 128.7, 128.5, 128.4, 127.5, 48.7, 48.5, 38.6. HRMS (ESI) *m/z* $[M+H]^+$ calcd. for $C_{16}H_{15}ClNO$: 272.0837, found: 272.0843.

3-(4-Methoxyphenyl)-1,2,2-trimethylaziridine (2l): The product was prepared following the general aziridination procedure and the crude product was purified by silica gel column chromatography using Bu_3N:EtOAc:hexane (1:5:94) as an eluent to give the title compound as a light yellow sticky semi-solid (74 mg, 78% yield). TLC: R_f = 0.5 (10% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.17 (m, 2H), 6.87-6.81 (m, 2H), 3.79 (s, 3H), 2.54 (s, 3H), 2.28 (s, 1H), 1.33 (s, 3H), 0.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 130.8, 128.4, 113.4, 55.2, 53.9, 42.3, 39.5, 21.4, 17.6. HRMS (ESI) *m/z* $[M+H]^+$ calcd. for $C_{12}H_{17}NO$: 192.1344, found: 192.1389.

1,2,2-Trimethyl-3-(4-nitrophenyl)aziridine (2m): The product was prepared following the general aziridination procedure and the crude product was purified by silica gel column chromatography using Bu_3N:EtOAc:hexane (1:5:94) as an eluent to give the title compound as a light yellow sticky semi-solid (62 mg, 60% yield). TLC: R_f = 0.5 (10% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.12 (m, 2H), 7.47-7.42 (d, 2H), 2.57 (s, 3H), 2.39(s, 1H), 1.38 (s, 3H), 0.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 146.7, 128.18, 123.2, 53.6, 44.2, 39.3, 21.3, 17.6. HRMS (ESI) *m/z* $[M+H]^+$ calcd. for $C_{11}H_{14}N_2O_2$: 207.1139, found: 207.1089.

Methyl 8-(3-octylaziridin-2-yl)octanoate 4a:[6] The product was prepared following the general aziridination procedure and the crude product was purified by silica gel column chromatography using Bu_3N:MeOH:CH_2Cl_2 (1:2:97) as an eluent to give the title compound as an oil (129 mg, 83% yield), whose spectral data were in accord with the literature values.

(E)-5-(3,3-Dimethylaziridin-2-yl)-3-methylpent-2-enyl acetate (4b):[6] The product was prepared following the general aziridination procedure and the crude product was purified by silica gel column chromatography using Bu_3N:MeOH:CH_2Cl_2 (1:2:97) as an eluent to give the title compound as oil (89 mg, 85% yield), whose spectral data were in accord with the literature values.

(E)-Ethyl 3-(3-pentylaziridin-2-yl)acrylate (4c): The product was prepared following the general aziridination procedure and the crude product was purified by silica gel column chromatography using Bu_3N:EtOAc:hexane (1:49:50) as an eluent to give the title compound as a light yellow oil (40 mg, 38% yield). TLC: R_f = 0.4 (40% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (dd, *J* = 15.6, 8.3 Hz, 1H), 6.07 (d, *J* = 15.6 Hz, 1H), 4.23-4.14 (m, 2H), 2.89 (brs, 1H), 2.70 (brs, 1H), 2.33 (d, *J* = 5.3 Hz, 1H), 1.54-1.36 (m, 2H), 1.34 -1.19 (m, 7H), 0.87 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 145.6, 123.7, 60.3, 38.9, 35.4, 31.4, 29.1, 27.3, 22.5, 14.2, 13.9. HRMS (ESI) $[M+H]^+$ calcd. for $C_{12}H_{22}NO_2$: 212.1645, found: 212.1633.

2-Methyl-2-phenylaziridine (4d):[6] The product was prepared following the general aziridination procedure and the crude product was purified by silica gel column chromatography using Bu_3N:EtOAc:hexane (1:19:80) as an eluent to give the title compound as a colorless oil (37 mg, 55% yield). TLC: R_f = 0.3 (50% EtOAc in hexane), whose spectral data were in accord with the literature values.

(E)-2-Methyl-3-(naphthalene-2-yl)aziridine (4e): The product was prepared following the general aziridination procedure and the crude product was purified by silica gel column chromatography using Bu_3N:EtOAc:hexane (1:19:80) as an eluent to give the title compound as a colorless oil (59 mg, 64% yield) TLC: R_f = 0.4 (20% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.75 (m, 3H), 7.68 (s, 1H), 7.49-7.39 (m, 2H), 7.31-7.24 (m, 1H), 2.83 (d, *J* = 2.9 Hz, 1H), 2.27-2.19 (m, 1H), 1.42 (d, *J* = 5.4Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 133.3, 132.6, 128.1, 127.6, 127.5, 126.1, 125.5, 124.3, 123.5, 40.6, 37.2, 19.6. HRMS (ESI) *m/z* $[M+H]^+$ calcd. for $C_{13}H_{14}N$, 184.1048; found, 184.1118.

2,2-Dimethyl-3-phenylaziridine (4f):[6] The product was prepared following the general aziridination procedure and the crude product was purified by silica gel column chromatography using Bu_3N:EtOAc:hexane (1:19:80) as an eluent to give the title compound as a colorless oil (53 mg, 72% yield). TLC: R_f = 0.5 (50% EtOAc in hexane), whose spectral data were in accord with the literature values.

(3-(4-Chlorophenyl)aziridin-2-yl)(phenyl)methanone (4g):[12] The product was prepared following the general aziridination procedure and the crude product was purified by silica gel column chromatography using Bu_3N:EtOAc:hexane (1:9:90) as an eluent to give the title compound as a light yellow sticky solid (45 mg, 35% yield), whose spectral data were in accord with the literature values.

Aziridinylcholestan-3-β-ol (4h):[6] The product was prepared following the general aziridination procedure and the crude product was purified by silica gel column chromatography using EtOAc:hexane (60:40) as an eluent to give the title compound as an off white solid (73 mg, 70% yield). ^{1}H and ^{13}C NMR data were in accord with the literature values.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

^{1}H, ^{13}C and HPLC spectra (PDF)

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