Facile Generation and Synthetic Utility of Nitrogen-Centered Aziridinyl Radicals

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Abstract: Nitrogen-centered aziridinyl radicals can be generated through homolysis of *N*-haloaziridines, which can be easily produced upon treatment of NH aziridines with *N*-bromo- or *N*-iodosuccinimide. This methodology allows synthesis of a variety of β-haloaziridines in moderate to good yields. Further transformation into piperazine scaffolds can be achieved via nucleophilic substitution at the β-position and aziridine ring opening initiated by oxalyl chloride.

Key words: *N*-aziridinyl radicals, β-haloaziridines, nucleophilic substitution, aziridine ring opening, piperazine synthesis

Aziridines are valuable three-membered-ring systems in modern synthetic chemistry.[1] Based on their ring strain, various manipulations of aziridine-containing compounds, including nucleophilic ring opening[2] and cycloaddition,[3] have been extensively explored. The use of aziridines as highly versatile and readily available radical precursors has received an increased attention over the past few years.[4]

Either carbon- or nitrogen-centered radicals can be generated from aziridines. The carbon-centered aziridinyl radicals were first reported by Yamanaka et al. in the 1970s,[5] but the synthetic applications of these species were not developed until Ziegler reported an intramolecular radical cyclization of chiral aziridinyl radicals onto indole rings in 1994.[6] Later, this method was successfully utilized in the synthesis of FR-900482, a mitomycin-like antitumor agent.[7]

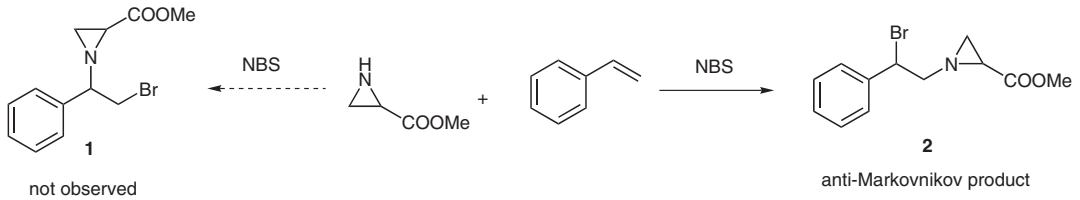
Although much effort has been devoted to carbon-centered aziridinyl radicals, nitrogen-centered aziridinyl radicals have not been extensively studied. The basic physical and chemical properties of the nitrogen-centered aziridinyl radicals were examined in the 1970s by the Danen and Ingold groups.[8] Our interest in synthetic applications of functionalized aziridines has led to an investigation of the utility of nitrogen-centered aziridinyl radicals in the synthesis of heterocyclic derivatives.

In the course of our study, we have found that methyl aziridine-2-carboxylate, when treated with styrene in the presence of *N*-bromosuccinimide (NBS), did not furnish the expected primary bromide product **1**, affording instead the unexpected anti-Markovnikov product **2** (Scheme 1).

Table 1 Optimization of Haloamination of Styrene with Aziridine Carboxylate **2**[a]

Entry	Halogen source	Solvent	Temp	Additive	Yield (%)
1	NBS	CH_2Cl_2	r.t.	–	20
2	NBS	THF	r.t.	–	15
3	NBS	hexane	r.t.	–	trace
4	NBS	toluene	r.t.	–	10
5	NBS	DME	r.t.	–	12
6	NBS	DCE	r.t.	–	8
7	NBS	DME–H_2O (4:1)	r.t.	–	–
8	NCS	CH_2Cl_2	r.t.	–	–
9	NIS	CH_2Cl_2	r.t.	–	40
10	NIS	CH_2Cl_2	0 °C to r.t.	–	50
11	NBS	CH_2Cl_2	0 °C to r.t	4 Å MS	80
12	NIS	CH_2Cl_2	0 °C to r.t	4 Å MS	90

[a] All reactions were carried out with 1 equiv of aziridine carboxylate (0.2 M), 1 equiv of styrene, and 1.2 equiv of NXS for 12 h.



Scheme 1 NBS-promoted haloamination of styrene with aziridine

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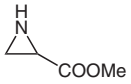
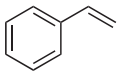
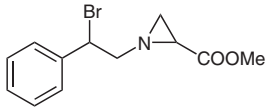
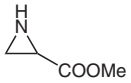
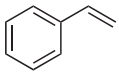
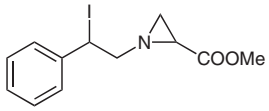
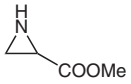
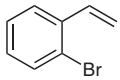
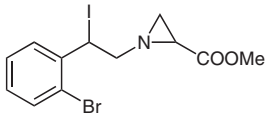
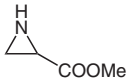
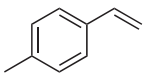
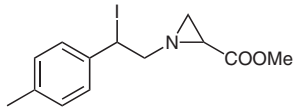
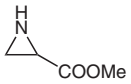
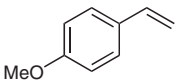
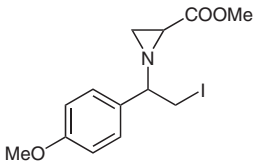
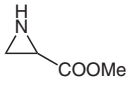
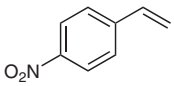
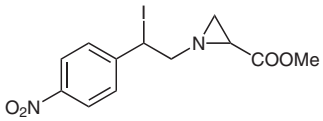
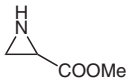
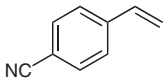
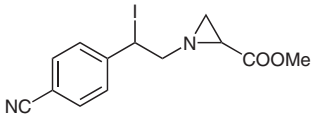
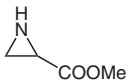
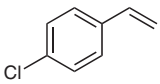
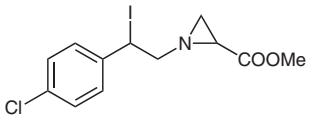
Encouraged by this result, a systematic study was undertaken to optimize the reaction conditions. Different solvents, halogen sources, reaction temperatures, and additives were investigated in order to obtain the optimal condition for the anti-Markovnikov product **2**. The results are summarized in Table 1. Dichloromethane is superior to other solvent systems, such as THF, hexane, toluene, DME, DCE, and DME–H_2O. Better yields were achieved by lowering the reaction temperature to 0 °C and using 4 Å molecular sieves. *N*-Iodosuccinimide (NIS) was the superior reagent for the reaction, although NBS also afforded good yields. We applied the optimized protocol to various styrenes, and the results are shown in Table 2.[9]

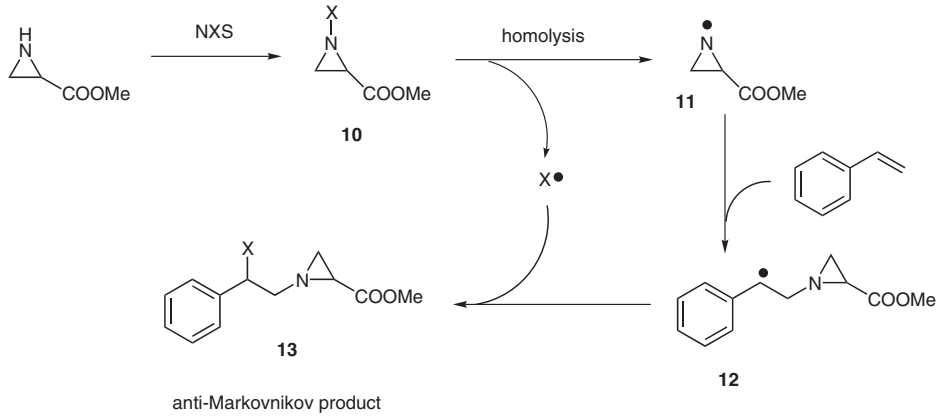
A radical, rather than cationic, mechanism appears to operate in this process. Homolysis of the N–X bond of the intermediate **10**, which can be isolated from the reaction system after stirring the NXS reagent with an aziridine in dichloromethane for five minutes, leads to the nitrogen-centered radical **11**. Compound **11** then attacks the double bond of the olefin. The resulting intermediate **12** gives rise to anti-Markovnikov product **13** (Scheme 2).

Interestingly, a reversal in regioselectivity was observed in entry 5. This is attributed to a competition between the cationic and radical pathways. The olefins with functional groups that destabilize the carbocationic intermediates more than the corresponding radicals are likely to afford

Table 2 NXS-Facilitated Haloamination of Olefins with Aziridines[a]

Entry	Aziridine	Olefin	NXS	Product	Yield (%, dr)
1			NBS	 **2**	80 (1:1)
2			NIS	 **3**	90 (1:1)
3			NIS	 **4**	96 (1:1)
4			NIS	 **5**	80 (1:1)
5			NIS	 **6**	53 (1:1)
6			NIS	 **7**	60 (1:1)
7			NIS	 **8**	65 (1:1)
8			NIS	 **9**	70 (1:1)

[a] All reactions were carried out using 1 equiv of aziridine (0.2 M), 1 equiv of olefin, 1.2 equiv of NXS, and 4 Å MS in anhyd CH_2Cl_2 for 12 h.



Scheme 2 Proposed mechanism of NXS-facilitated haloamination of olefin with aziridine

free-radical adducts, while olefins with the functional groups, which stabilize the carbocationic intermediates, give the product with reversed selectivity. When it comes to aliphatic alkenes, neither the cationic pathway nor radical pathway appears to be strongly favored, leading to a mixture of both free-radical and cationic products.

To verify the predominant radical pathway, we carried out the reaction in the presence of galvinoxyl, a well-known radical scavenger used in exploring reactions with *N*-chlorosuccinimide.[10] No product was detected after 12 hours.[11] The effect of light was also investigated. It was found that the reaction proceeded smoothly in the dark, giving rise to anti-Markovnikov product.

Furthermore, in order to compare the reactivity of aziridines with other secondary amines, piperidine was subjected to the reaction. After 12 hours, no olefin addition product was obtained. The difference in reactivity between aziridine and piperidine lies in the different stability of the corresponding N-halo species. When treated with NXS, piperidine can readily eliminate HX to form an unstable imine, while aziridine is reluctant to go through this process due to the kinetic barrier for the formation of a highly strained azirine species. The long lifetime of the *N*-haloaziridine intermediate facilitates homolysis and subsequent attack on the olefin (Scheme 3).

To further evaluate reactivity of the radical adducts, we subjected them to treatment with different nucleophiles including alcohols, amines, thiols, and salts. The results are shown in Table 3.[12]

Table 3 Nucleophilic Substitution of β-Haloaziridines[a]

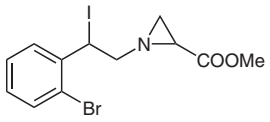
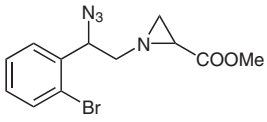
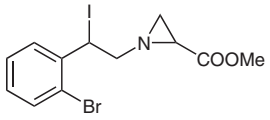
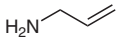
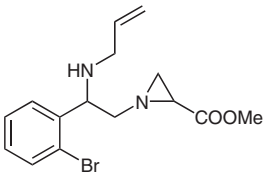
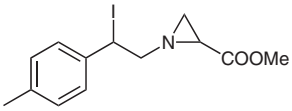
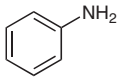
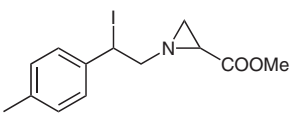
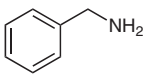
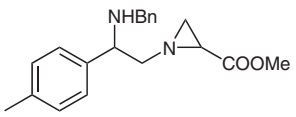
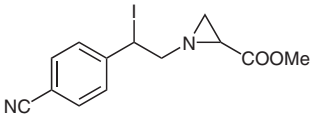
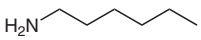
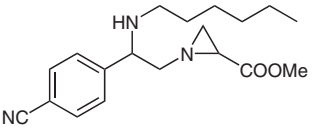
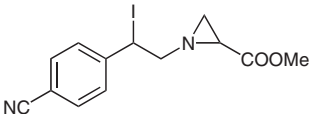
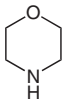
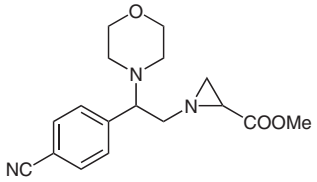
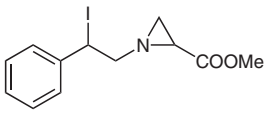
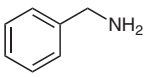
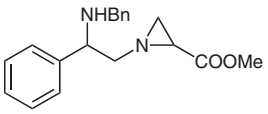
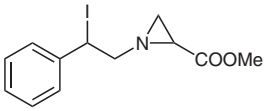
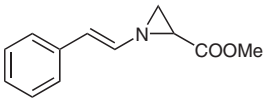
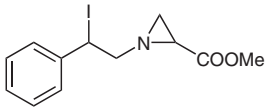
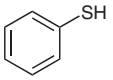
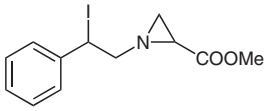
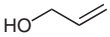
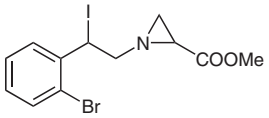
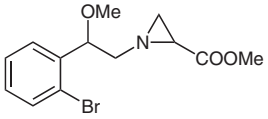
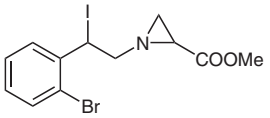
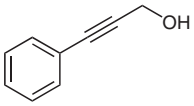
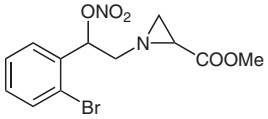
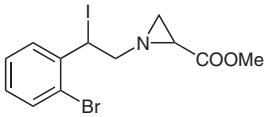
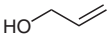
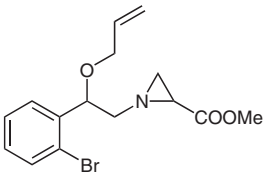
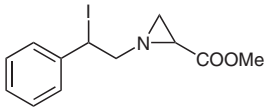
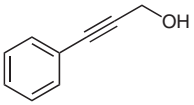
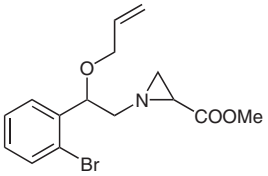
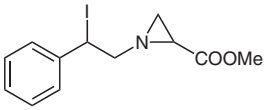
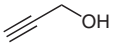
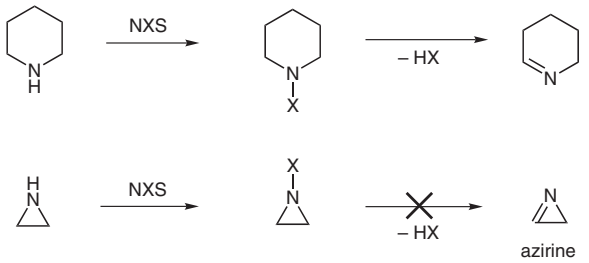
Entry	β-Haloaziridine	Nucleophile	Additive	Product		Yield (%, dr)
1		NaN_3	–	**14**		80 (1:1)
2			–	**15**		75 (1:3)
3			–		unisolable products	–
4			–	**16**		78 (1:1)
5			–	**17**		55 (1:1)

Table 3 Nucleophilic Substitution of β-Haloaziridines[a] (continued)

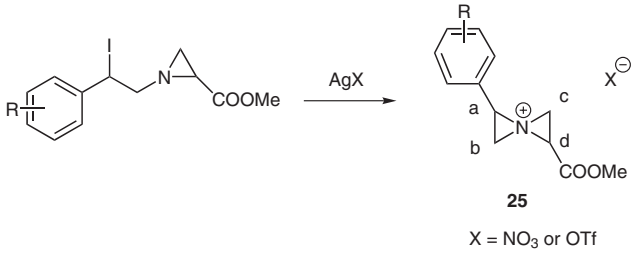
Entry	β-Haloaziridine	Nucleophile	Additive	Product	Yield (%, dr)
6			–	**18**		50 (1:1)
7			–	**19**		70 (1:1)
8		NaOAc	–	**20**		80
9			–		unisolable products	–
10			–		no reaction	–
11[b]		MeOH	$AgNO_3$	**21**		30 (5:1)
12[b]			$AgNO_3$	**22**		40 (4:1)
13[b]			AgOTf	**23**		36 (1:1)
14[b]			AgOTf	**24**		20 (1:1)
15[b]			AgOTf		no product isolated	–

[a] Unless noted, reactions were carried out with 1 equiv of β-haloaziridine (0.05 M) and 10 equiv of nucleophile in DMF at r.t. for 12 h.
[b] Reactions were carried out with 1 equiv of β-haloaziridine, 1.0 equiv of alcohol, 1.2 equiv of K_2CO_3, and 1.0 equiv of Ag salt in anhyd CH_2Cl_2 at r.t. for 30 min.

The substitution product was detected for entry 3. However, when the reaction mixture was subjected to column chromatography, the product decomposed. For entry 8, the elimination pathway dominated the reaction, since that the acetate anion is still a good leaving group. For entry 9, the starting β-haloaziridine was completely consumed after three hours, however, intractable product was formed. The crude NMR of the reaction mixture showed that the aziridine ring was opened, which indicates that the starting material also underwent ring-opening process under



Scheme 3 Different reactivity between piperidine and aziridine



Scheme 4 The formation of aziridineaziridinium ion

the reaction condition. For entry 10, the nucleophilicity of allyl alcohol was too low to react with the β-iodoaziridine. After stirring at room temperature for 12 hours, no reaction was detected and the starting material was recovered.

Silver salts were explored as additives. The substitution product was afforded when β-iodoaziridine was treated with 1.0 equivalent of silver nitrate in methanol. However, when we changed the nucleophile to 3-phenylprop-2-yn-1-ol and decreased its amount to 10 equivalents, the benzylic position was attacked by the nitrate anion, rather than the alcohol (entry 12, Table 3). To avoid the competition between the alcohol and the counterion of the silver salt, silver triflate was employed. Although substitution products were obtained, none of the isolated yields were satisfactory, ranging from 20% to 40%. For propargyl alcohol, no product was isolated, although the starting aziridine was completely consumed (Table 3, entry 15).

In the absence of nucleophiles, once silver triflate was added to the reaction system, silver iodide precipitate formed almost immediately. We suspect that the aziridineaziridinium intermediate **25** (azoniaspiro[2.2]pentane cation), has been formed (Scheme 4). The latter can conceivably lead to a number of products in subsequent reactions.

The existence of aziridineaziridinium ions have been postulated to account for some experimental observations in analytical studies.[13] According to the computational results,[14] aziridineaziridinium ions possess ring strain similar to that of a protonated aziridine, and are prone to ring-opening process from either side.

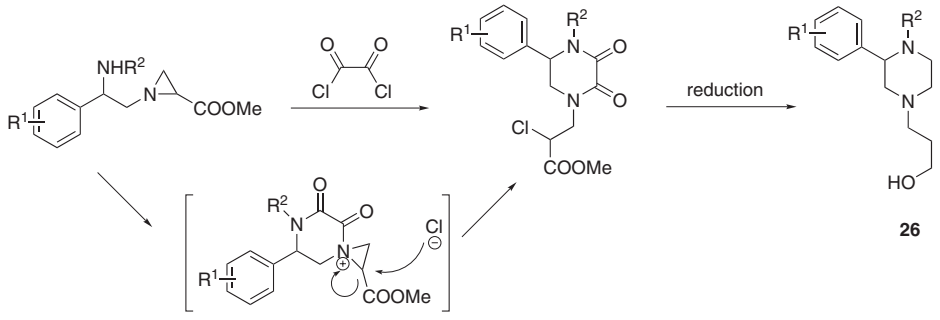
Based on our NXS-promoted coupling reaction and the protocol for substitution of primary amines, a variety of functionalized aziridines have been synthesized. We then proceeded to investigate the synthesis of piperazine derivatives of biological importance starting from these functionalized building blocks.

It has been reported that the aziridine ring opening can be initiated by the acylation of aziridine nitrogen to produce an activated aziridinium species. Acetyl chloride,[15] phosgene,[16] and methyl chloroformate[17] have been investigated in this chemistry. We envisioned a route to compound **26**, which contains a piperazine core similar to selective brain serotonin ($5HT_{2A}$) antagonists (Scheme 5).[18]

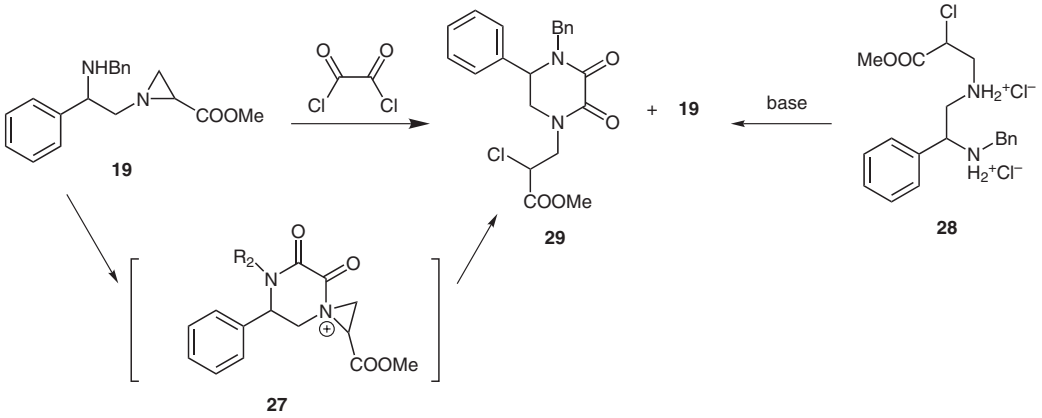
The reaction of oxalyl chloride with aziridine **19** provided a mixture of the piperazine product **29** through the aziridinium intermediate **27** and recovered starting material **19**. The recovered starting material might have been formed upon basic workup of the quaternary ammonium salt **28** which originated from the ring opening of aziridine by in situ generated HCl (Scheme 6). We varied bases, reaction solvents, and reaction temperature to obtain the optimal conditions for the piperazine product. It was found that treatment of aziridine **19** with 2.0 equivalents of K_2CO_3 and 2.2 equivalents of oxalyl chloride in acetonitrile at 60 °C provided the best result (Table 4).

Table 4 Optimization of Aziridine Ring Opening Initiated by Oxalyl Chloride

Entry	Base	Solvent	Temp	Yield (%)
1	K_2CO_3	MeCN	r.t.	60
2	K_2CO_3	MeCN	60 °C	95
3	K_2CO_3	MeCN	80 °C	80
4	Et_3N	CH_2Cl_2	r.t.	65
5	NaH	THF	r.t.	90
6	–	MeCN	60 °C	10

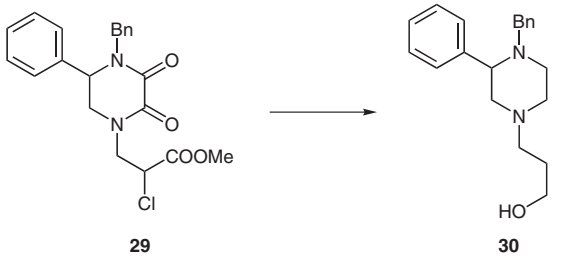


Scheme 5 Synthesis of piperazine derivatives



Scheme 6 Aziridine ring opening initiated by oxalyl chloride

The diketopiperazine product **29** was subsequently reduced by $LiAlH_4$ or $BH_3{\cdot}SMe_2$ in 40% and 20% yields, respectively.[19] Further transformation was easily achieved by hydrogenation followed by alkylation or acylation at nitrogen (Scheme 7).



Scheme 7 Reduction of diketopiperazine. *Reagents and conditions*: a) $LiAlH_4$ (12 equiv), THF, 60 °C, 40%; b) $BH_3{\cdot}SMe_2$ (9 equiv), THF, 70 °C, 20%.

In conclusion, a synthetic potential of nitrogen-centered aziridinyl radicals has been evaluated. Nitrogen-centered aziridinyl radicals can be generated upon treatment of aziridines with readily available reagents such as *N*-bromosuccinimide and *N*-iodosuccinimide. This approach was successfully applied to the synthesis of a series of β-haloaziridines in moderate to high yields. The functionalization of the β-haloaziridines was achieved by nucleophilic attack of a variety of nucleophiles at the β-position. Further transformation of the substitution products to piperazine derivatives has been reported.

Acknowledgment

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(9) **Typical Procedure for the NXS-Facilitated *N*-Aziridinyl Radical Reaction with Olefins**
In a flame-dried Schlenk flask, equipped with septum, magnetic stir bar, and nitrogen inlet, were placed NIS (235 mg, 1.33 mmol), powdered 4 Å MS (200 mg), anhyd CH_2Cl_2 (10 mL) under nitrogen atmosphere at 0 °C. After 10 min, aziridine-2-carboxylate methyl ester (100 μL, 1.11 mmol) was added via syringe. After 30 min, when TLC showed no aziridine remaining, 2-bromostyrene (138 μL, 1.11 mmol) was added via syringe. The reaction mixture was allowed to warm up to r.t. and stirred for 8 h. When TLC showed no methyl 1-iodoaziridine-2-carboxylate remaining, the reaction mixture was filtered and concentrated in vacuo, the residue oil was subjected to chromatography on silica gel, eluted with hexane–EtOAc (60:40), to give the product as light yellow oil.
Methyl 1-[2-(2-Bromophenyl)-2-iodoethyl]aziridine-2-carboxylate (4)
Yield 96%. First diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.56 (m, 1 H), 7.51–7.49 (m, 1 H), 7.33–7.29 (m, 1 H), 7.13–7.09 (m, 1 H), 5.77–5.74 (t, *J* = 6.8 Hz, 1 H), 3.68 (s, 3 H), 3.18–3.13 (m, 1 H), 2.91–2.86 (m, 1 H), 2.31–2.30 (d, *J* = 3.2 Hz, 1 H), 2.03–2.00 (m, 1 H), 1.86–1.84 (d, *J* = 6.8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7, 140.7, 133.5, 130.1, 129.7, 128.4, 122.9, 77.6, 77.2, 76.9, 67.7, 52.4, 37.3, 34.5, 27.5. Second diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59–7.57 (m, 1 H), 7.51–7.49 (m, 1 H), 7.32–7.28 (m, 1 H), 7.12–7.08 (m, 1 H), 5.76–5.72 (t, *J* = 7.2 Hz, 1 H), 3.72 (s, 3 H), 3.19–3.14 (m, 1 H), 2.91–2.86 (m, 1 H), 2.34–2.32 (m, 1 H), 2.34–2.31 (m, 1 H), 2.20–2.19 (d, *J* = 2.8 Hz, 1 H), 1.67–1.66 (d, *J* = 6.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.8, 140.7, 133.4, 130.1, 130.0, 128.4, 122.9, 67.7, 52.5, 38.3, 33.8, 27.5.
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(11) In a flame-dried Schlenk flask, equipped with septum, magnetic stir bar, and nitrogen inlet, were placed NIS (1.2 equiv), powdered 4 Å MS (180 mg/mol aziridine), anhyd CH_2Cl_2 (0.11 mmol/mL) under nitrogen atmosphere at 0 °C. Aziridine-2-carboxylate methyl ester (1.0 equiv) was added via syringe. After 30 min, when TLC showed no aziridine remaining, galvinoxyl (1.0 equiv) was added, followed by the addition of styrene. The reaction mixture was allowed to warm up to r.t. and stirred for 8 h. A control experiment was set up at the same time to compare the effect of the radical trap. After 8 h, the control experiment in the absence of galvinoxyl proceeded smoothly and the anti-Markovnikov product was afforded, while no desired product was formed in the presence of galvinoxyl.

(12) **Typical Procedure for the Nucleophilic Substitution of β-Haloaziridines with Amines**

To a mixture of **4** (50 mg, 0.122 mmol) and DMF (2.5 mL) was added allylamine (91.5 μL, 12.2 mmol) at r.t. and the mixture stirred for 12 h. When TLC showed no **4** remaining, H_2O (4 mL) and Et_2O (2 mL) were added, the layers were then separated. The ether layer was washed with H_2O followed by drying over Na_2SO_4. The solvent was removed in vacuo and the oily residue was subjected to chromatography on alumina, eluted with hexane–EtOAc (80:20), to give the product **15** as light yellow oil.

Methyl 1-[2-Allylamino-2-(2-bromophen-yl)ethyl]aziridine-2-carboxylate (15)

Yield 75%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63–7.62 (m, 1 H), 7.52–7.49 (m, 1 H), 7.32–7.28 (m, 1 H), 7.13–7.09 (m, 1 H), 5.92–5.84 (m, 1 H), 5.19–5.06 (m, 2 H), 4.34–4.31 (m, 1 H), 3.71 (s, 3 H), 3.12–3.07 (m, 2 H), 2.76–2.71 (m, 2 H), 2.22–2.16 (m, 1 H), 2.03–2.00 (m, 1 H), 1.73–1.71 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.36, 140.20, 136.91, 133.02, 129.02, 127.91, 127.89, 124.12, 116.00, 65.72, 60.72, 52.37, 50.11, 38.13, 34.16.

Typical Procedure for the Nucleophilic Substitution of β-Haloamines with Alcohols Facilitated by Silver Salts

To a mixture of **4** (100 mg, 0.302 mmol), allyl alcohol (205 μL, 0.302 mmol), K_2CO_3 (50.0 mg, 0.362 mmol), and anhyd CH_2Cl_2 (10 mL), was added AgOTf (77.6 mg, 0.302 mmol) at r.t. and the mixture was stirred for 30 min. When TLC showed no **4** remaining, the mixture was filtered and concentrated in vacuo. The oily residue was subjected to chromatography on silica gel, eluted with hexane–EtOAc (70:30), to give the product **23** as light yellow oil.

Methyl 1-[2-(Allyloxy)-2-(2-bromophenyl)ethyl]aziridine-2-carboxylate (23)

Yield 36%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.47 (m, 4 H), 7.45–7.32 (m, 2 H), 7.16–7.12 (m, 2 H), 5.92–5.86 (m, 2 H), 5.30–5.24 (m, 2 H), 5.18–5.15 (d, *J* = 10.4 Hz, 2 H), 3.99–3.83 (m, 4 H), 3.72 (s, 6 H), 3.00–2.98 (m, 1 H), 2.69–2.67 (m, 1 H), 2.50–2.45 (m, 1 H), 2.27–2.26 (m, 2 H), 2.15–2.13 (m, 1 H), 2.13–2.08 (m, 1 H), 2.08–2.04 (m, 1 H), 1.80–1.78 (d, *J* = 6.8 Hz, 1 H), 1.59–1.57 (d, *J* = 6.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.5, 139.4, 134.8, 134.7, 133.0, 129.5, 129.4, 128.3, 128.3, 127.9, 123.1, 123.1, 117.1, 117.0, (79.9, 79.62), (70.5, 70.3), (65.3, 65.2), (52.3, 52.2), (39.1, 36.7), (35.4, 32.8).

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(19) **Procedure for the Synthesis of 30**

In a 5 mL Schlenk tube, equipped with septum and magnetic stir bar, were placed **19** (0.1 mmol), K_2CO_3 (0.22 mmol), and anhyd MeCN (1 mL). Oxalyl chloride was added via syringe and the solution was stirred at 60 °C for 2 h. When TLC showed no starting material remaining, the solution was filtered and the filtrated was washed with H_2O. The organic layer was dried over anhyd Na_2SO_4 and filtered. The filtrated was concentrated in vacuo and the light brown residue was directly used in the next step without purification.

Reduction with $LiAlH_4$

To a suspension of 300 mg $LiAlH_4$ (7.91 mmol) in 40 mL THF, 264 mg crude product of diketopiperazine **29** (0.66 mmol) dissolved in 5 mL THF was added. The mixture was stirred at 60 °C for 12 h. After cooling to 0 °C, H_2O (0.4 mL), 15% NaOH (0.4 mL), and H_2O (0.4 mL) were added dropwise while stirring. The mixture was filtered and the filtrate was concentrated in vacuo. The residue was subjected to silica gel chromatography, eluted with CH_2Cl_2–MeOH (90:10). Yield 40%.

Reduction with BH_3·SMe_2

To a solution of crude product of diketopiperazine **29** in anhyd THF (10 mL/mmol) under reflux was added dropwise 9 equiv of a 2 M solution of BH_3·SMe_2 in THF. The mixture was refluxed for 7 h, the solvent was evaporated under reduced pressure, and 4 equiv of a 0.2–0.4 M HCl solution were added. The mixture was stirred for 30 min at 100 °C, and then it was cooled to 0 °C, and 6 equiv of a 0.2–0.4 M solution of NaOH were added. Then, the mixture was stirred for a further 90 min. The aqueous mixture was saturated with solid K_2CO_3 and extracted with CH_2Cl_2 (3–4 times, 5 mL/mmol), and the combined organic extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to silica gel chromatography, eluted with CH_2Cl_2–MeOH (90:10). Yield 20%.

3-(4-Benzyl-3-phenylpiperazin-1-yl)propan-1-ol (30)

Yield 40%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50–7.19 (m, 10 H), 3.82–3.77 (m, 3 H), 3.03–2.78 (m, 4 H), 2.64–2.57 (m, 2 H), 2.42–2.11 (m, 2 H), 0.89–0.87 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.9, 139.1, 129.0, 128.9, 128.8, 128.4, 128.2, 127.9, 127.0, 67.6, 64.9, 62.3, 59.1, 53.6, 51.9, 27.2, 9.7.