New methods for the preparations of 2-arylaziridines, α-imidostyrenes, and allylamines from olefins via diphenylvinylsulfonium triflates

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Dedicated to Professor Mieczysław Mąkosza on his 70th birthday

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Abstract

Reactions of diphenylvinylsulfonium triflates with primary amines and imides afforded 2-arylaziridines and α-imidostyrenes, respectively. These products were also obtained from styrenes in one vessel without isolation of the intermediate sulfonium salts. In addition, 1,1-disubstituted and trisubstituted alkenes were converted into allylamines via isomerization of initially formed vinylsulfonium salts to allylsulfonium salts in the presence of primary or secondary amines.

Keywords: Diphenylvinylsulfonium triflate, aziridine, α-imidostyrene, allylic amine

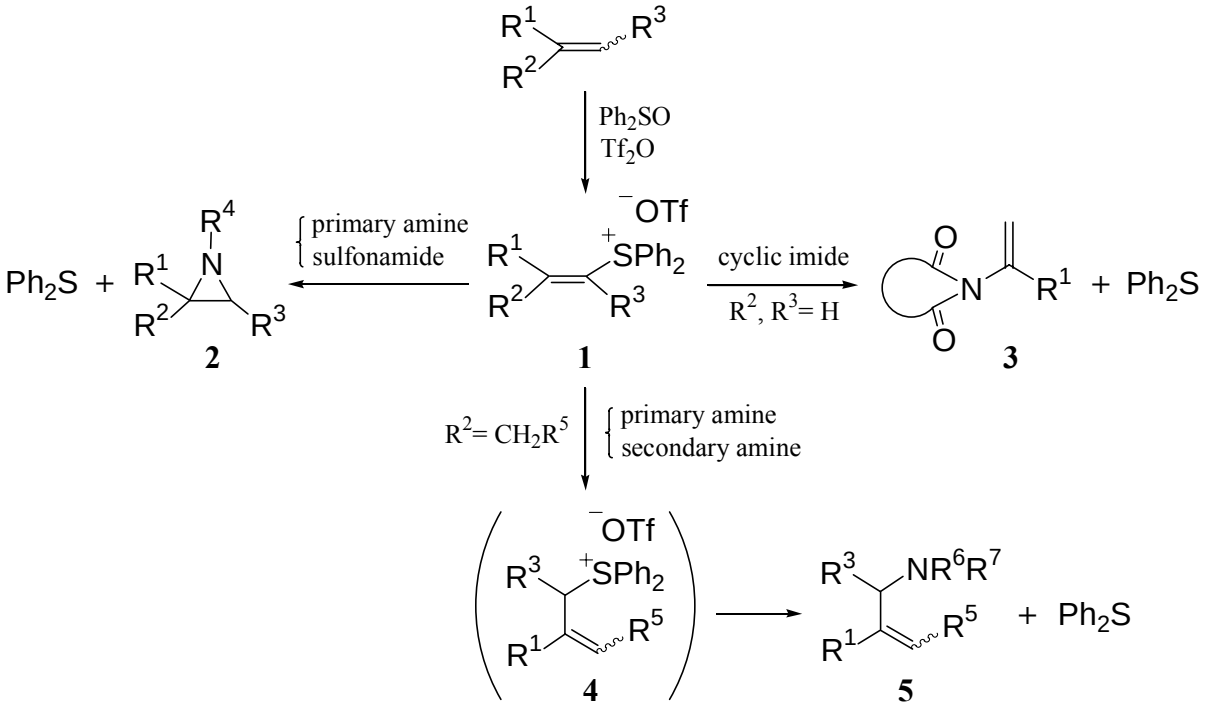
Introduction

Vinylphosphonium and vinylsulfonium salts are known as good Michael acceptors that undergo addition reactions with various nucleophiles. The former salts have been widely used as precursors of phosphonium ylides in the syntheses of heterocyclic compounds[1] and allylamines[2] via initial Michael addition and subsequent Wittig reaction (Schweizer reaction). On the other hand, synthetic applications of vinylsulfonium salts are limited to a few reactions such as cyclopropanation reactions with active methylene compounds[3] or enolates[4] in which dimethylvinylsulfonium salts are frequently used and act as ethylene transfer reagents by liberating dimethyl sulfide.

During our study on the reactions of dimethylvinylsulfonium salts with amines or imides, conversion of the salts into methyl vinyl sulfides along with *N*-methylated amines or imides was

observed. The result of this methyl transfer reaction prompted us to study on reactions of *diphenyl*vinylsulfonium salts with nitrogen nucleophiles in order to investigate chemical behaviors of the salts.

We recently reported three unique reactions of diphenylvinylsulfonium triflates **1** in a preliminary form as shown in Scheme 1: new synthetic approaches to (i) 2-arylaziridines **2**[5] and (ii) *α*-imidostyrenes **3**[6] from styrene derivatives via **1**, and (iii) allylamines **5**[7] from alkenes via unusual conversion of **1** to allylsulfonium salts **4**. In this article, we would like to describe these three reactions in detail.



Scheme 1

Results and Discussion

Preparation of diphenylvinylsulfonium triflates

Diphenylvinylsulfonium triflates were prepared according to Nenajdenko's procedure.[8] The reaction of triflic anhydride (Tf_2O) with diphenyl sulfoxide gave diphenyl(trifluoromethanesulfonyloxy)sulfonium triflate, "diphenyl sulfide ditriflate" (DPSD). Styrene derivatives reacted with DPSD to form diphenylstyrylsulfonium triflates. Of these salts, [(*E*)-2-(4-chlorophenyl)vinyl]diphenylsulfonium triflate (**1a**) was obtained as crystals and was used in the model experiments.

Synthesis of 2-arylaziridines from styrenes

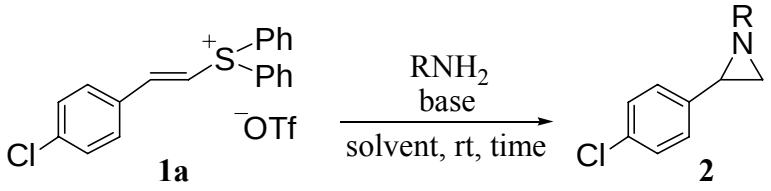
An aziridine ring is known as a unique skeleton that is found in many natural products having interesting biological activities.[9] Aziridines are also used as useful building units in organic

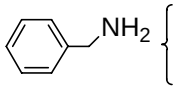
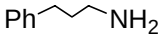
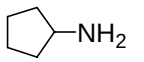
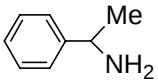
syntheses and are often employed in various synthetic reactions[10] such as highly regio- and stereoselective ring opening reactions.[11] Therefore, many methods for the synthesis of aziridines have been developed. It is already known that cyclopropanation reactions proceed on treating dimethylvinylsulfonium salts with carbon nucleophiles,[3,4] which gave us a hint that aziridines might be formed if nitrogen nucleophiles such as primary amines were used. However, the attempted aziridination using dimethylvinylsulfonium salts did not proceed at all, and *N*-methylation of the amines was what mostly took place. It was then considered that the aziridination reaction would proceed successfully if *diphenyl*vinylsulfonium salts **1** were used instead, because the above methylation reaction could be excluded.

The so-called Gabriel-Cromwell reaction of α, β-unsaturated α-halo carbonyl compounds[12] or 1-haloethenesulfonic acid derivatives[13] is commonly used for the synthesis of aziridines from alkenes and primary amines or ammonia. Johnson et al.[14] reported that (dimethylamino)phenylvinyloxosulfonium salts reacted with primary amines to give aziridines. However, several troublesome steps were required for the preparation of the above salts, and only a few examples of aziridination were reported.

In the first place, the aziridination using isolated **1a** and various primary amines was tried,[15] and 2-(4-chlorophenyl)aziridines **2** were successfully synthesized in high yields (Table 1). When 1.1 equiv. of benzylamine alone was used, complete consumption of **1a** was not observed even after prolonged reaction time or heating of the reaction mixture. On the other hand, when 2.2 equiv. of benzylamine was used, the aziridination led to completion to give **2a** in 98% yield (entry 1). Combined use of 1.2 equiv. of benzylamine and 3 equiv. of *tert*-butylamine was preferable for shortening the reaction time because of the following reasons: The excess amount of *tert*-butylamine (bp 46 ^{o}C) was removed easily in the work-up procedure, and 1-*tert*-butyl-2-(4-chlorophenyl)aziridine was not formed because *tert*-butylamine was much less reactive than benzylamine. In the case of aziridination with 1-phenylethylamine, a mixture of diastereomeric aziridines **2d** was obtained without any significant diastereoselectivity (entry 4). The aziridination with *tert*-butylamine proceeded very slowly as expected; therefore, it was carried out without the solvent to give **2e** in 96% yield (entry 5). *N*-Nonsubstituted aziridine **2f** was synthesized by using gaseous ammonia (entry 6). Moreover, sodium salts of sulfonamides reacted with **1a** to afford "activated aziridines" in high yields (entries 7 and 8).

Table 1. Aziridines from **1a** and primary amines, ammonia, or sulfonamides

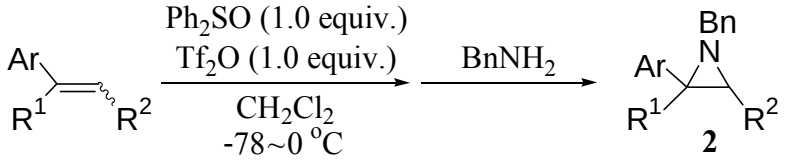


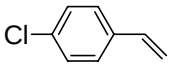
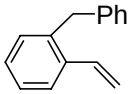
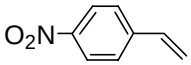
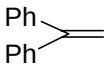
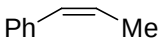
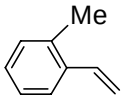
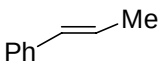
Entry	RNH_2 / Equiv.	Base / Equiv.	Solvent	Time / h	Product	Yield / %[a]
1	 / 2.2	none	DMSO	12	**2a**	98
	/ 1.2	*t*-$BuNH_2$ / 3.0	DMSO	1		96
2	 / 1.2	*t*-$BuNH_2$ / 3.0	DMSO	1	**2b**	97
3	 / 1.2	*t*-$BuNH_2$ / 3.0	DMSO	1	**2c**	94
4	 / 4.0	none	DMSO	18	**2d**	98[b]
5	*t*-$BuNH_2$ / 9.0	none	none	1	**2e**	96[c]
6[d]	NH_3 / excess	none	DMSO	1	**2f**	82[c]
7	$PhSO_2NH_2$ / 1.2	NaH / 1.2	THF	12	**2g**	97
8	$TsNH_2$ / 1.2	NaH / 1.2	THF	19	**2h**	91

[a] Isolated yield unless otherwise noted. [b] Combined yield of the chromatographically separable diastereomers (1.2:1). [c] Determined by ^1H NMR analysis using an internal standard. [d] An excess amount of NH_3 gas was used.

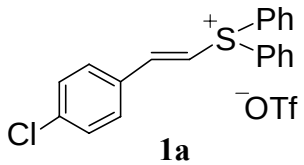
Next, a one-pot synthesis of aziridines from styrenes and benzylamine without isolating the intermediate sulfonium salts **1** was examined (Table 2). The results of entries 1 and 5 indicated that the one-pot procedure (Method A) was more effective than the stepwise one (Method B), and would be useful even when the salts **1** were not stable. In the case of 1,1-diphenylethylene, the aziridination reaction proceeded very slowly compared to the others, which was due to its steric hindrance (entry 6). Aziridination of *cis*- and *trans*-*β*-methylstyrene gave the two diastereomeric aziridines in almost the same yields and diastereomeric ratios (1:1) (entries 7 and 8), which suggested that the stereochemistry of formed aziridines was not influenced by the configuration of styrenes.

Table 2. One-pot synthesis of aziridines from styrenes and benzylamine

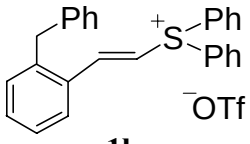


Entry	Styrene	Method[a]	Product	Yield /%[b]	Entry	Styrene	Method[a]	Product	Yield /%[b]
1		A B	**2a**	89 78	5		A B	**2l**	99 73
2		A	**2i**	95	6		C	**2m**	66
3		A	**2j**	94	7		A	**2n**	39[d]
4[c]		A	**2k**	71	8		A	**2n**	39[d]

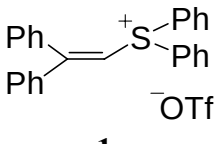
[a] Method A: one-pot procedure described in the text. Method B: Benzylamine (1.2 equiv.) and *tert*-butylamine (3 equiv.) were added to a solution of isolated sulfonium salt **1a** (entry 1) or **1b** (entry 5) in DMSO, and the mixture was stirred at rt for 1 h. Method C: A mixture of benzylamine (9 equiv.) and isolated sulfonium salt **1c** was stirred at rt for 1 day. [b] Isolated yield (2 steps). [c] The reaction time for the second step was 12 h. [d] Combined yield of the chromatographically separable diastereomers (1:1).



1a



1b



1c

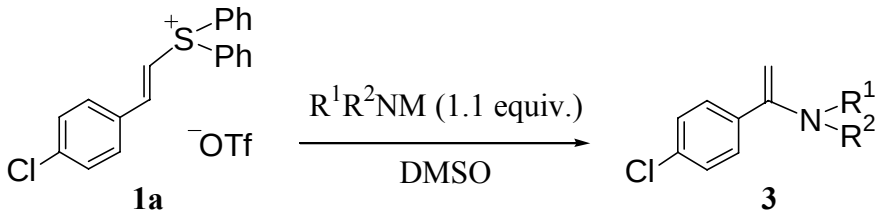
α-Imidation of styrenes

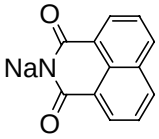
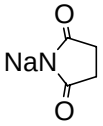
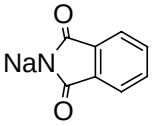
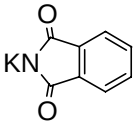
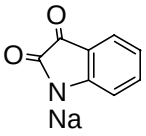
Aziridine formation was accomplished by using diphenylsulfonium salts **1** and NH_2 type of nucleophiles. Next, we examined the reactions of **1** with NH type of nucleophiles such as imide compounds, and we found that an imido group was introduced regioselectively to the *α*-position of the styrenes to give *α*-imidostyrenes **3**, useful precursors of vinylamines.

In the first place, the reaction of isolated [(*E*)-2-(4-chlorophenyl)vinyl]diphenylsulfonium triflate (**1a**) with metal salts of imides was tried (Table 3, entries 1−4). The corresponding *α*-imidostyrenes **3** were synthesized smoothly in DMSO[15] at room temperature although the reaction with sodium 1,8-naphthalimide (entry 1) proceeded rather slowly. Isatin, a cyclic amide,

gave the similar product (**3d**) in moderate yield (entry 5).[16] 4-Chloro-*α*-phthalimidostyrene (**3c**) was obtained in 90% yield by using potassium phthalimide (entry 4); however, when [(*E*)-2-(4-chlorophenyl)vinyl]*dimethyl*sulfonium triflate was used instead of **1a**, compound **3c** was not detected and *N*-methylphthalimide was obtained along with (*E*)-4-chlorostyryl methyl sulfide.

Table 3. Reactions of **1a** with cyclic imide or amide compounds



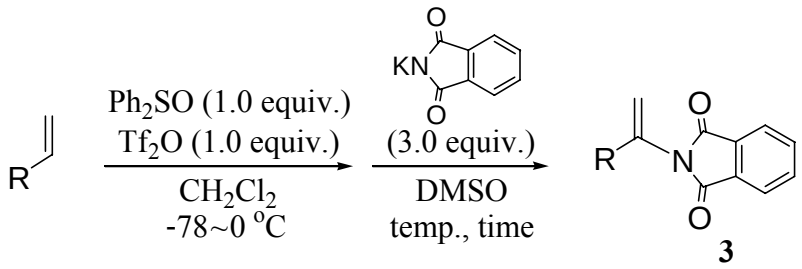
Entry	R^1R^2NM	Method[a]	Conditions	Product	Yield /%[b]
1		A	rt, 40 h	**3a**	36
2		A	rt, 3 h	**3b**	69
3		A	rt, 12 h	**3c**	84
4		B	rt, 12 h	**3c**	90
5		A	rt, 1 h	**3d**	62

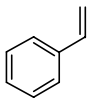
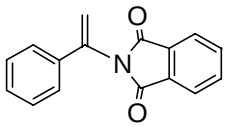
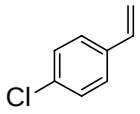
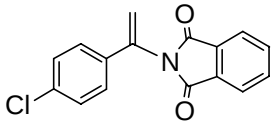
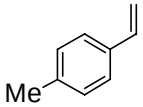
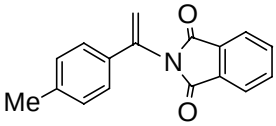
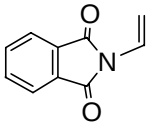
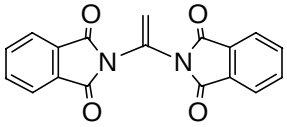
[a] Method A: A cyclic imide or amide was added to a stirred suspension of sodium hydride in DMSO. After 0.5 h, salt **1a** was added. Method B: A mixture of **1a** and potassium phthalimide in DMSO was stirred. [b] Isolated yield.

Next, *α*-phthalimidation of several styrenes via sulfonium salts **1** in one vessel was examined (Table 4). Styrene and 4-chlorostyrene were converted into the corresponding *α*-

phthalimidostyrenes in high yields without isolating the intermediates **1** (entries 1 and 2). An electron-donating group in a benzene ring lowered the yield and afforded several unknown by-products (entry 3). Furthermore, *N*-vinylphthalimide gave 1,1-diphthalimidoethylene (**3g**) in moderate yield (entry 4). In these reactions, 1 equiv. of potassium phthalimide was used for neutralizing 1 equiv. of triflic acid generated by the formation of **1**; therefore, at least 2 equiv. of potassium phthalimide was necessary to complete the present reaction.

Table 4. Phthalimidation of olefins via diphenylvinylsulfonium triflates



Entry	Olefin	Temp., Time	Product		Yield /%[a]
1		rt, 16 h		**3e**	87
2		rt, 3 h		**3c**	86
3		rt, 24 h		**3f**	50
4		60 °C, 1 h		**3g**	48

[a] Isolated yield.

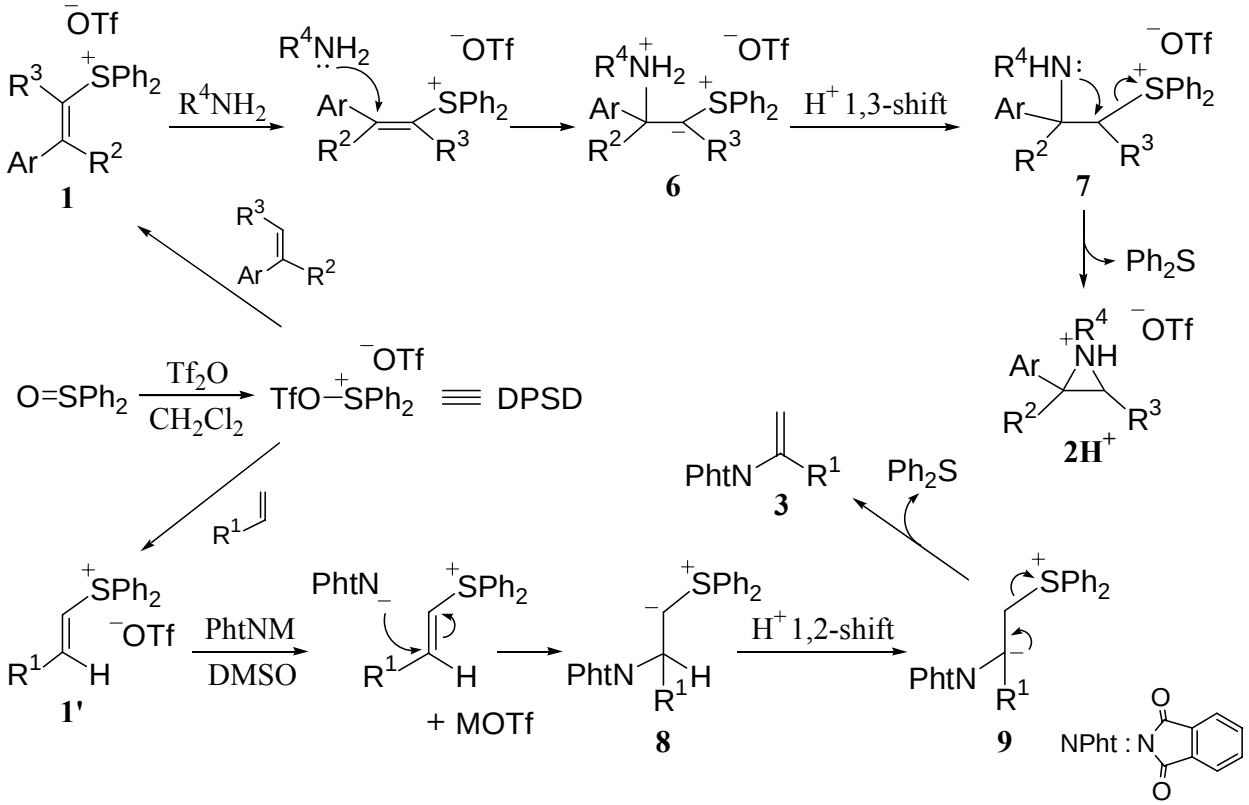
Reaction mechanisms for aziridination and *α*-imidation of styrenes

Proposed mechanisms for (i) aziridination and (ii) *α*-imidation of styrene derivatives are shown in Scheme 2. It was considered that these two reactions proceeded via the similar reaction paths. Initially, DPSD was formed from diphenyl sulfoxide and Tf_2O at low temperature and was allowed to react with styrenes.

The aziridination was considered to proceed via the upper path in Scheme 2: Michael-type addition of R^4NH_2 to (2-arylvinyl)diphenylsulfonium salt **1** gave sulfonium ylide **6**, in which 1,3-prototropic shift took place spontaneously to form **7**. A subsequent intramolecular nucleophilic substitution of **7** with the amino group afforded aziridinium triflate **2H**$^+$ and diphenyl sulfide. It was assumed that the excess amount of R^4NH_2 captured triflic acid from **2H**$^+$ to prevent the protonation of R^4NH_2 with **2H**$^+$.[17]

On the other hand, *α*-imidation of styrenes was considered to proceed via the lower path in Scheme 2: Michael-type addition of phthalimide anion, for example, to sulfonium triflate **1'** gave sulfonium ylide **8** that was converted immediately into **9** by 1,2-prototropic shift. Successive regeneration of a double bond along with elimination of diphenyl sulfide produced *α*-phthalimidostyrene **3**.

The behaviors of diphenylvinylsulfonium salts shown in the steps of **6** to **7** and **8** to **9** are unique and quite different from those of vinylphosphonium salts that undergo the so-called Schweizer reaction[1,2] via phosphonium ylides.



Scheme 2

Synthesis of allylamines from alkenes

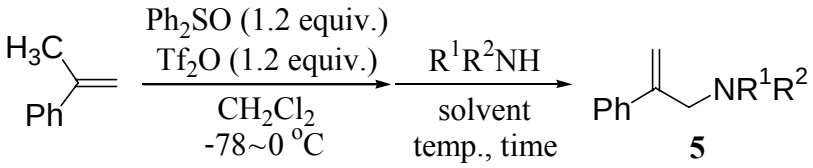
Allylic amines are valuable target products in medicinal chemistry[18] and are versatile synthetic intermediates.[19] Although many methods are available for the preparation of allylic alcohols by allylic oxidation of alkenes,[20] a direct synthesis of allylamines from alkenes involves only a few

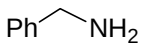
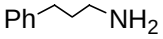
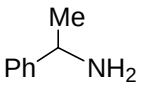
reactions such as stoichiometric allylic aminations using imido derivatives of sulfur[21] or selenium[22] and catalytic aminations using the palladium,[23] molybdenum,[24] or iron[25] catalyst.

In the attempted aziridination of *α*-methylstyrene with benzylamine according to our procedure mentioned above, expected 1-benzyl-2-methyl-2-phenylaziridine was not formed, but *N*-benzyl-2-phenyl-2-propenylamine (**5a**) was obtained instead in 80% yield. This result might be attributed to the steric hindrance that prevented the initial Michael-type addition of benzylamine. The above reaction was then considered to be useful for introducing amino functions into alkenes to produce the corresponding allylamines.

The results of Table 5 indicated that *α*-methylstyrene was converted successfully into *α*-(aminomethyl)styrenes without forming aziridines by treatment with DPSD, followed by various primary or secondary amines. The reactions with monoalkylamines proceeded smoothly at room temperature (entries 1−4), whereas higher temperature (100 ^{o}C) was required in the case with aniline (entry 5). In a similar fashion, the reactions with secondary amines provided the corresponding tertiary allylic amines in good yields (entries 6 and 7).

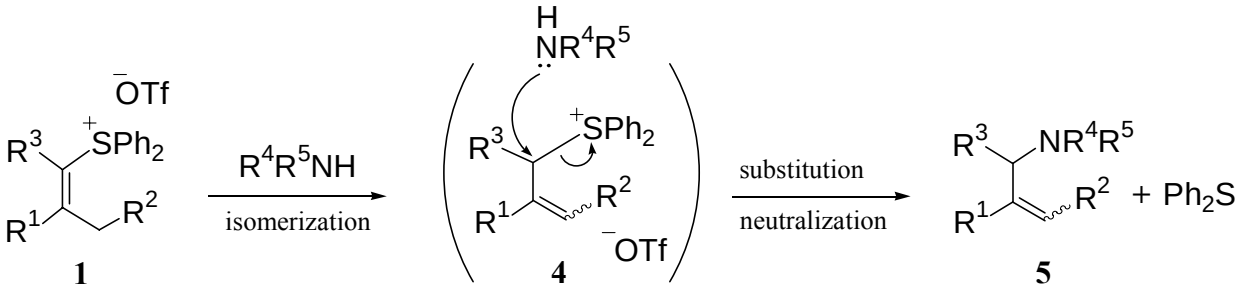
Table 5. *α*-(Aminomethyl)styrenes from *α*-methylstyrene and primary or secondary amines via diphenyl(2-phenyl-1-propenyl)sulfonium triflate



Entry	R^1R^2NH / Equiv.	Solvent	Temp., Time	Product	Yield /%[a]
1	 / 5.0	CH_2Cl_2	rt, 2 h	**5a**	80
2	 / 10	none	rt, 2 h	**5b**	78
3	 / 5.0	CH_2Cl_2	rt, 24 h	**5c**	84
4	*t*-$BuNH_2$ / 5.0	CH_2Cl_2	rt, 12 h	**5d**	91
5	$PhNH_2$ / 10	DMF	100 ^{o}C, 5 h	**5e**	82
6	*i*-Pr_2NH / 5.0	CH_2Cl_2	rt, 12 h	**5f**	89
7	Bn_2NH / 5.0	DMF	100 ^{o}C, 2 h	**5g**	81

[a] Isolated yield.

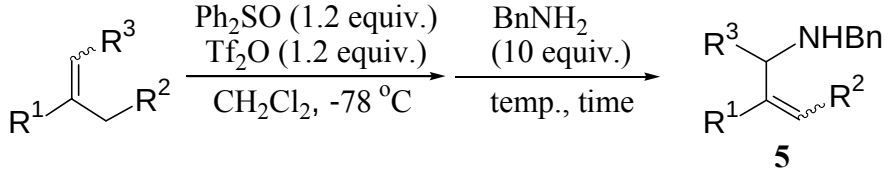
The above reaction was explained as follows (Scheme 3). Initially, an alkene was treated with DPSD to form the corresponding diphenylvinylsulfonium triflate **1**, which was supported by ^{1}H NMR analysis. Then, triflate **1** reacted with a primary or secondary amine to give the corresponding allylamine **5** and diphenyl sulfide via isomerization[26] of vinylsulfonium salt **1** to allylsulfonium salt **4** and the subsequent nucleophilic substitution of **4** with the amine.

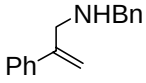
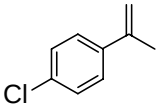
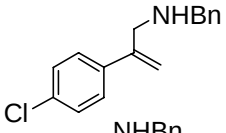
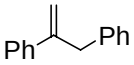
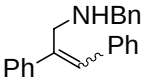
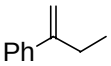
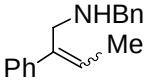
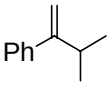
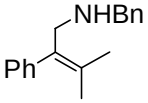
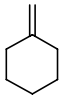
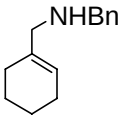
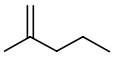
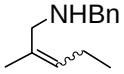
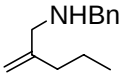
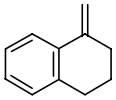
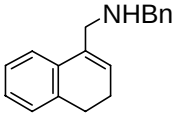
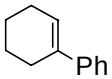
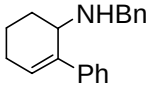
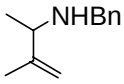


Scheme 3

Next, the scope and limitation of the present reaction were studied by using benzylamine as a model amine (Table 6). 1,1-Disubstituted alkenes gave the allylamines in moderate to good yields (entries 1−8). 2,3-Diphenyl-1-propene and 2-phenyl-1-butene afforded a mixture of *E*, *Z* stereoisomers of **5i** and **5j**, respectively (entries 3 and 4). In the case of 3-methyl-2-phenyl-1-butene, consumption of the corresponding sulfonium salt **1** was incomplete even after prolonged reaction time or heating, presumably because the steric hindrance at C-3 inhibited smooth double bond migration of **1** (entry 5). 2-Methyl-1-pentene gave the expected two regioisomers with no significant regioselectivity (entry 7). Furthermore, trisubstituted alkenes gave the corresponding allylamines (entries 9 and 10). In these cases, the yields were rather low, which was presumably due to substantial steric repulsion between the corresponding allylsulfonium salt **4** and benzylamine. In the cases of aliphatic monosubstituted and 1,2-disubstituted alkenes, the desired allylamines were not obtained. It seemed that the intermediate vinylsulfonium salts **1** were not formed from these alkenes presumably because secondary carbocations generated from alkenes and DPSD were not stable enough to form the adducts.

Table 6. Allylamines from alkenes and benzylamine via diphenylvinylsulfonium triflates



Entry	Alkene	Method[a]	Temp., Time	Product		Yield /%[b]
1[c]		A	rt, 2 h		**5a**	79
2[c]		A	rt, 2 h		**5h**	82
3		A	rt, 45 h		**5i**	80[d]
4[e]		A	rt, 42 h		**5j**	55[f]
5		A	rt, 45 h		**5k**	45
6[g]		B	rt, 2 h		**5l**	79
7[g]		B	rt, 2 h		**5m**	44[h]
					**5n**	34
8		A	100 °C, 6 h		**5o**	50
9		B	rt, 2 h		**5p**	45
10		B	rt, 2 h		**5q**	47

[a] Method A: After a solution of the sulfonium salt was evaporated at 0 °C, $BnNH_2$ was added to the residue and stirred. Method B: $BnNH_2$ was added to a solution of the sulfonium salt at -78 °C, and then the mixture was warmed up to rt. [b] Isolated yield. [c] $BnNH_2$ (5 equiv.) was used. [d] *E/Z* ratio was 4.4:1, confirmed by the NOE difference experiment. [e] 1-Benzyl-2-ethyl-2-

phenylaziridine was obtained as a by-product. [f] *E/Z* ratio was 1:1. [g] Ph_2SO (1.5 equiv.) and Tf_2O (1.5 equiv.) were used. [h] 2:1 mixture of the stereoisomers.

Conclusions

Novel and convenient methods for the syntheses of (i) 2-arylaziridines **2**, (ii) *α*-imidostyrenes **3**, and (iii) allylamines **5** from olefins via the intermediate diphenylvinylsulfonium salts **1** were established. The key steps of these syntheses are considered to be (i) 1,3- and (ii) 1,2-prototropic shift of **1**; and (iii) isomerization of **1** to allylsulfonium salts **4**, respectively.

Experimental Section

General Procedures. Melting points were determined with a micro melting point apparatus (Yanaco MP-J3) and were not corrected. Infrared (IR) spectra were recorded on a Shimadzu IR-440 infrared spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL JNM-EX270 (270 MHz), or a JEOL JNM-ECA500 (500 MHz) spectrometer; chemical shifts (δ_H) are reported in parts per million (ppm) relative to tetramethylsilane (TMS). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sext, sextet; hept, heptet; m, multiplet; br, broad. ^{13}C NMR spectra were recorded on a JEOL JNM-EX270 (68 MHz) spectrometer with complete proton decoupling. Chemical shifts (δ_C) are reported in ppm relative to TMS using the solvent resonance ($CDCl_3$: δ_C 77.0 ppm) as the internal standard. High resolution mass spectra (HRMS) were recorded on a JEOL LCmate, a JEOL MS700, or an Applied Biosystems Mariner Ver. 4.0 mass spectrometer. Analytical thin-layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 F_{254}, 0.25 mm). Preparative TLC was carried out on silica gel Wakogel B-5F. All solvents were distilled from appropriate drying agents, and commercially available reagents were used without purification. Unless otherwise noted, reactions were carried out in oven-dried glassware with magnetic stirring under an atmosphere of argon.

[(*E*)-2-(4-Chlorophenyl)vinyl]diphenylsulfonium trifluoromethanesulfonate (1a). Nenajdenko's procedure[8] was slightly modified. To a stirred solution of diphenyl sulfoxide (2.43 g, 12.0 mmol) in CH_2Cl_2 (40 mL) was added dropwise triflic anhydride (2.0 mL, 12.2 mmol), followed by dropwise addition of a solution of 4-chlorostyrene (1.66 g, 12.0 mmol) in CH_2Cl_2 (12 mL) at –78 °C. After 10 min, the reaction mixture was gradually warmed up to 0 °C for 50 min and concentrated in vacuo. Diethyl ether (10 mL) was added to the residue to afford **1a** as a white powder (4.61 g, 81%). mp 106–107 °C. IR (KBr, cm^{-1}) 3050, 1595, 1490, 1480, 1445, 1270, 1250, 1220, 1150, 1090, 1035, 1000, 990, 810, 750, 740, 680, 640. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 8.00–7.87 (m, 6H), 7.78 (d, J = 8.5 Hz, 2H), 7.68–7.58 (m, 6H), 7.31 (d, J = 8.5 Hz, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 151.75, 138.61, 134.16, 131.38, 130.81, 130.47, 129.85, 129.42, 127.02, 110.41. HRMS ($APCI^+$) Calcd. for $C_{20}H_{16}ClS^+$: 323.0656. Found: *m*/*z* 323.0657, ($APCI^-$) Calcd. for

$CF_3O_3S^-$: 148.9526. Found: *m*/*z* 148.9524. The *E* geometry was determined on the basis of the result in the literature.[8]

[(*E*)-2-(2-Benzylphenyl)vinyl]diphenylsulfonium trifluoromethanesulfonate (1b). Synthesized according to the above procedure described for **1a**. Yield 89%, off-white powder, mp 159–161 °C. IR (KBr, cm^{-1}) 1450, 1275, 1260, 1220, 1150, 1030, 755, 750, 680, 640. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.93 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.87 (d, *J* = 14.7 Hz, 1H), 7.74–7.52 (m, 10H), 7.45 (d, *J* = 14.7 Hz, 1H), 7.46–7.30 (m, 2H), 7.29–7.09 (m, 4H), 6.99 (d, *J* = 6.8 Hz, 2H), 4.11 (s, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 149.67, 140.22, 139.95, 134.08, 132.27, 131.29, 131.26, 131.13, 129.99, 128.65, 128.55, 128.41, 127.86, 126.22, 126.06, 111.19, 39.32. HRMS (ESI-TOF) Calcd. for $C_{27}H_{23}S^+$: 379.1515. Found: *m*/*z* 379.1521, Calcd. for $CF_3O_3S^-$: 148.9526. Found: *m*/*z* 148.9522. The *E* geometry was confirmed by the large coupling constant [^3J (H,H)= 14.7 Hz].

Diphenyl(2,2-diphenylvinyl)sulfonium trifluoromethanesulfonate (1c). Synthesized according to the above-mentioned procedure for **1a**. Yield 80%, white powder, mp 126–127 °C. IR (KBr, cm^{-1}) 1445, 1270, 1255, 1220, 1150, 1030, 750, 685, 640. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.98–7.87 (m, 4H), 7.85 (s, 1H), 7.75–7.35 (m, 14H), 7.17 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 164.61, 136.07, 135.57, 134.17, 132.00, 131.57, 130.60, 129.79, 129.41, 129.16, 128.97, 128.91, 127.70, 108.90. HRMS (ESI-TOF) Calcd. for $C_{26}H_{21}S^+$: 365.1358. Found: *m*/*z* 365.1362, Calcd. for $CF_3O_3S^-$: 148.9526. Found: *m*/*z* 148.9518.

Typical experimental procedure for the synthesis of aziridines (Table 1 and Table 2, Method B)

To a stirred solution of **1a** or **1b** (0.20 mmol) in DMSO (0.2 mL) was added a solution of a primary amine (0.24 mmol) in DMSO (0.3 mL) at room temperature. Then, a solution of *tert*-butylamine (0.60 mmol) in DMSO (0.3 mL) was added and the mixture was stirred at room temperature for 1 h. The reaction was quenched with a 0.1 M NaOH solution (10 mL), and the organic material was extracted with $CHCl_3$ (10 mL x 2). The organic layer was dried over anhydrous Na_2SO_4 and filtrated. The filtrate was concentrated in vacuo, and the residue was purified by preparative TLC to give the corresponding aziridine **2**.

1-Benzyl-2-(4-chlorophenyl)aziridine (2a). Colorless syrup. IR (Nujol, cm^{-1}) 3050, 3000–2850, 1490, 1450, 1350, 1085, 1015, 800, 730, 700. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.36–7.16 (m, 9H), 3.70 (d, *J* = 14.0 Hz, 1H), 3.55 (d, *J* = 13.8 Hz, 1H), 2.45 (dd, *J* = 6.5, 3.2 Hz, 1H), 1.93 (d, *J* = 3.2 Hz, 1H), 1.85 (d, *J* = 6.5 Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 138.74, 138.55, 132.34, 128.26, 128.24, 127.63, 127.44, 126.91, 64.56, 40.79, 38.13. HRMS (EI) Calcd. for $C_{15}H_{14}ClN^+$, $[M]^+$: 243.0809. Found: *m*/*z* 243.0808.

2-(4-Chlorophenyl)-1-(3-phenylpropyl)aziridine (2b). Slightly yellow syrup. IR (Nujol, cm^{-1}) 3050–2830, 1490, 1455, 1205, 1085, 1020, 750, 700. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.31–7.21 (m, 4H), 7.21–7.13 (m, 5H), 2.71 (t, *J* = 7.7 Hz, 2H), 2.57–2.45 (m, 1H), 2.42–2.29 (m, 1H), 2.26 (dd, *J* = 6.5, 3.2 Hz, 1H), 1.93 (quin, *J* = 7.4 Hz, 2H), 1.84 (d, *J* = 3.2 Hz, 1H), 1.66 (d, *J* = 6.5 Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 141.88, 138.89, 132.27, 128.25, 128.21, 127.35,

125.68, 60.83, 40.59, 38.03, 33.59, 31.39. HRMS (APCI$^+$) Calcd. for $C_{17}H_{19}ClN^+$, $[M+H]^+$: 272.1201. Found: *m*/*z* 272.1203.

2-(4-Chlorophenyl)-1-cyclopentylaziridine (2c). Colorless syrup. IR (Nujol, cm^{-1}) 2980, 2890, 1490, 1380, 1350, 1210, 1085, 1015, 830, 780. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.25–7.17 (m, 4H), 2.34 (dd, *J* = 6.5, 3.2 Hz, 1H), 2.06 (quin, *J* = 5.1 Hz, 1H), 1.80–1.53 (m, 10H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 139.19, 132.11, 128.15, 127.62, 72.24, 40.18, 37.21, 32.96, 32.23, 24.44, 24.34. HRMS (APCI$^+$) Calcd. for $C_{13}H_{17}ClN^+$, $[M+H]^+$: 222.1044. Found: *m*/*z* 222.1043.

2-(4-Chlorophenyl)-1-(1-phenylethyl)aziridine (2d). Major diastereomer: 54% yield, colorless syrup. R_f = 0.21 (hexane/EtOAc 10:1). IR (Nujol, cm^{-1}) 2990, 1490, 1090, 1020, 805, 705. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.40–7.03 (m, 9H), 2.68 (q, *J* = 6.8 Hz, 1H), 2.36 (dd, *J* = 6.8, 3.2 Hz, 1H), 2.00 (d, *J* = 3.2 Hz, 1H), 1.85 (d, *J* = 6.8 Hz, 1H), 1.48 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 144.42, 138.63, 132.19, 128.18, 127.56, 126.80, 126.47, 70.33, 40.21, 37.84, 23.45. HRMS (APCI$^+$) Calcd. for $C_{16}H_{17}ClN^+$, $[M+H]^+$: 258.1044. Found: *m*/*z* 258.1044. Minor diastereomer: 44% yield, colorless syrup. R_f = 0.39 (hexane/EtOAc 10:1). IR (Nujol, cm^{-1}) 2980, 1490, 1085, 1015, 840, 800, 700. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.46–7.22 (m, 9H), 2.66 (q, *J* = 6.5 Hz, 1H), 2.50 (dd, *J* = 6.5, 3.2 Hz, 1H), 1.78 (d, *J* = 3.2 Hz, 1H), 1.70 (d, *J* = 6.5 Hz, 1H), 1.45 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 144.35, 139.05, 132.36, 128.27, 128.22, 127.65, 126.97, 126.74, 70.15, 40.95, 37.50, 23.64. HRMS (APCI$^+$) Calcd. for $C_{16}H_{17}ClN^+$, $[M+H]^+$: 258.1044. Found: *m*/*z* 258.1057.

1-*tert*-Butyl-2-(4-chlorophenyl)aziridine (2e). Colorless syrup. IR (Nujol, cm^{-1}) 3000, 1495, 1385, 1365, 1235, 1220, 1090, 1020, 995, 840, 815. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.24 (s, 4H), 2.58 (dd, *J* = 6.2, 3.0 Hz, 1H), 1.90 (dd, *J* = 6.2, 1.1 Hz, 1H), 1.59 (dd, *J* = 3.0, 1.1 Hz, 1H), 1.04 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 139.81, 132.06, 128.15, 127.81, 53.27, 33.31, 30.69, 26.61. HRMS (APCI$^+$) Calcd. for $C_{12}H_{17}ClN^+$, $[M+H]^+$: 210.1044. Found: *m*/*z* 210.1054. The yield of **2e** was determined by ^{1}H NMR analysis using triphenylmethane (δ_H 5.55) as an internal standard.

2-(4-Chlorophenyl)aziridine (2f).[27] Colorless syrup. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.31–7.23 (m, 2H), 7.21–7.13 (m, 2H), 3.01 (dd, *J* = 6.2, 3.2 Hz, 1H), 2.23 (d, *J* = 6.2 Hz, 1H), 1.71 (d, *J* = 3.2 Hz, 1H), 1.00 (br s, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 138.88, 132.45, 128.37, 126.94, 31.36, 29.53. The yield of **2f** was determined by ^{1}H NMR analysis using triphenylmethane (δ_H 5.55) as an internal standard.

2-(4-Chlorophenyl)-1-phenylsulfonylaziridine (2g).[28] To a stirred suspension of NaH (55% dispersion in mineral oil, 15.7 mg, 0.36 mmol) in THF (1.0 mL) was added benzenesulfonamide (56.6 mg, 0.36 mmol) at room temperature. After 0.5 h, a solution of **1a** (141.9 mg, 0.30 mmol) in THF (1.0 mL) was added, and the reaction mixture was stirred at room temperature for 12 h. The reaction was quenched with a 0.1 M NaOH solution (10 mL), and the organic material was extracted with EtOAc (10 mL x 2). The organic layer was dried over anhydrous Na_2SO_4 and filtrated. The filtrate was concentrated in vacuo, and the residue was purified by preparative TLC to give **2g** (85.3 mg, 97%) as a slightly yellow syrup. IR (Nujol, cm^{-1}) 1490, 1450, 1320, 1160, 1090, 910, 810, 740, 690, 605, 590. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.98 (d, *J* = 7.6 Hz, 2H),

7.68–7.50 (m, 3H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 3.77 (dd, *J* = 7.0, 4.6 Hz, 1H), 3.01 (d, *J* = 7.0 Hz, 1H), 2.37 (d, *J* = 4.6 Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 137.62, 134.10, 133.66, 133.33, 129.06, 128.65, 127.76, 127.74, 40.36, 36.21. HRMS (APCI$^+$) Calcd. for $C_{14}H_{13}ClNO_2S^+$ $[M+H]^+$: 294.0350. Found: *m*/*z* 294.0355.

2-(4-Chlorophenyl)-1-tosylaziridine (2h).[29] Synthesized according to the above procedure described for **2g**. White amorphous solid. IR (KBr, cm^{-1}) 1490, 1320, 1305, 1160, 1090, 910, 820, 735, 700, 575, 555. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H.7.85 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 3.73 (dd, *J* = 7.0, 4.3 Hz, 1H), 2.98 (d, *J* = 7.0 Hz, 1H), 2.44 (s, 3H), 2.34 (d, *J* = 4.3 Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 144.67, 134.68, 134.08, 133.52, 129.69, 128.66, 127.82, 127.79, 40.31, 36.10, 21.74. HRMS (APCI$^+$) Calcd. for $C_{15}H_{15}ClNO_2S^+$, $[M+H]^+$: 308.0507. Found: *m*/*z* 308.0512.

Typical experimental procedure for the one-pot synthesis of aziridines (Table 2, Method A) To a stirred solution of diphenyl sulfoxide (0.50 mmol) in CH_2Cl_2 (2.0 mL) was added Tf_2O (0.50 mmol) at –78 °C. A solution of a styrene (0.50 mmol) in CH_2Cl_2 (1.5 mL) was then added dropwise at –78 °C. After 10 min, the mixture was warmed up to 0 °C, and a solution of benzylamine (2.50 mmol) in CH_2Cl_2 (1.5 mL) was added. The reaction mixture was warmed and stirred at room temperature for 2 h. The reaction was quenched with a 0.1 M NaOH solution (10 mL), and the organic material was extracted with CH_2Cl_2 (20 mL x 2). The organic layer was dried over anhydrous Na_2SO_4 and filtrated. The filtrate was concentrated in vacuo, and the residue was purified by preparative TLC to give the corresponding *N*-benzylaziridine.

1-Benzyl-2-(4-nitrophenyl)aziridine (2i). Slightly yellow syrup. IR (Nujol, cm^{-1}) 3030, 2980, 2840, 1595, 1505, 1450, 1380–1290, 1210, 1190, 1135, 1100, 1070, 1020, 850, 810, 760–730, 690. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 8.14 (d, *J* = 8.9 Hz, 2H), 7.41 (d, *J* = 8.9 Hz, 2H), 7.38–7.22 (m, 5H), 3.75 (d, *J* = 13.8 Hz, 1H), 3.60 (d, *J* = 13.8 Hz, 1H), 2.59 (dd, *J* = 6.6, 3.1 Hz, 1H), 2.00–1.98 (m, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 148.04, 146.71, 138.39, 128.32, 127.62, 127.09, 126.76, 123.47, 64.39, 40.63, 39.23. HRMS (APCI$^+$) Calcd. for $C_{15}H_{15}N_2O_2^+$, $[M+H]^+$: 255.1128. Found: *m*/*z* 255.1134.

1-Benzyl-2-phenylaziridine (2j).[30] Slightly yellow syrup. IR (Nujol, cm^{-1}) 3100, 1620, 1510, 1460, 1370, 1220, 1095, 1040, 760, 750, 710. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.38–7.20 (m, 10H), 3.68 (d, *J* = 13.5 Hz, 1H), 3.59 (d, *J* = 13.8 Hz, 1H), 2.49 (dd, *J* = 6.8, 3.2 Hz, 1H), 1.97 (d, *J* = 3.2 Hz, 1H), 1.83 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 139.95, 138.93, 128.20, 128.14, 127.67, 126.81, 126.72, 126.09, 64.70, 41.50, 37.99. HRMS (APCI$^+$) Calcd. for $C_{15}H_{16}N^+$, $[M+H]^+$: 210.1277. Found: *m*/*z* 210.1288.

1-Benzyl-2-(2-methylphenyl)aziridine (2k). Slightly yellow syrup. IR (Nujol, cm^{-1}) 3020, 1490, 1450, 1375, 1350, 1025, 760, 730, 700. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.41 (d, *J* = 7.0 Hz, 2H), 7.35–7.21 (m, 4H), 7.14–7.10 (m, 3H), 3.65 (s, 2H), 2.58 (dd, *J* = 6.8, 3.2 Hz, 1H), 2.36 (s, 3H), 1.90 (d, *J* = 3.2 Hz, 1H), 1.84 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 138.98, 137.76, 136.15, 129.39, 128.23, 127.90, 126.91, 126.51, 125.85, 64.97, 39.57, 36.71, 19.23. HRMS (APCI$^+$) Calcd. for $C_{16}H_{18}N^+$, $[M+H]^+$: 224.1434. Found: *m*/*z* 224.1442.

1-Benzyl-2-(2-benzylphenyl)aziridine (2l). Colorless crystals, mp 50–52 °C. IR (KBr, cm^{-1}) 1490, 1450, 1360, 740, 700. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.37–7.03 (m, 14H), 4.11 (s, 2H), 3.53 (s, 2H), 2.54 (dd, J = 6.5, 3.5 Hz, 1H), 1.81 (d, J = 3.5 Hz, 1H), 1.71 (d, J = 6.5 Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 140.39, 138.91, 138.53, 138.04, 129.71, 128.60, 128.29, 128.22, 127.96, 126.90, 126.73, 126.60, 126.28, 125.87, 64.82, 39.33, 38.83, 37.10. HRMS ($APCI^+$) Calcd. for $C_{22}H_{22}N^+$, $[M+H]^+$: 300.1747. Found: *m*/*z* 300.1735.

1-Benzyl-2,2-diphenylaziridine (2m). A mixture of **1c** (103 mg, 0.20 mmol) and benzylamine (0.20 mL, 1.8 mmol) was stirred at room temperature for 1 day (Table 2, Method C). The reaction was quenched with a 0.1 M NaOH solution (10 mL), and the organic material was extracted with EtOAc (10 mL x 2). The organic layer was dried over anhydrous Na_2SO_4 and filtrated. The filtrate was concentrated in vacuo, and the residue was purified by preparative TLC to give **2m** (47.0 mg, 82%) as colorless crystals. mp 82–83 °C. IR (KBr, cm^{-1}) 1490, 1440, 760, 730, 710. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.38–7.12 (m, 15H), 3.52 (d, J = 14.0 Hz, 1H), 3.13 (d, J = 14.0 Hz, 1H), 2.38 (s, 1H), 2.19 (s, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 144.55, 139.83, 137.17, 131.34, 128.02, 127.98, 127.81, 127.67, 127.07, 126.56, 126.33, 58.35, 50.43, 42.21. HRMS ($APCI^+$) Calcd. for $C_{21}H_{20}N^+$, $[M+H]^+$: 286.1590. Found: *m*/*z* 286.1593.

1-Benzyl-2-methyl-3-phenylaziridine (2n)[31]

***cis*-2n.** Yield 19.5%, light yellow syrup. R_f = 0.32 (hexane/EtOAc 10:1). IR (Nujol, cm^{-1}) 1605, 1495, 1450, 1410, 1350, 1150, 1120, 1070, 1030, 730, 700. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.41–7.18 (m, 10H), 3.79 (d, J = 13.8 Hz, 1H), 3.56 (d, J = 14.0 Hz, 1H), 2.67 (d, J = 6.8 Hz, 1H), 1.93 (quin, J = 5.9 Hz, 1H), 0.97 (d, J = 5.7 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 139.29, 137.37, 128.18, 127.74, 127.64, 126.71, 126.36, 64.54, 46.34, 41.92, 13.00. HRMS ($APCI^+$) Calcd. for $C_{16}H_{18}N^+$, $[M+H]^+$: 224.1434. Found: *m*/*z* 224.1441.

***trans*-2n.** Yield 19.5%, light yellow syrup. R_f = 0.13 (hexane/EtOAc 10:1). IR (Nujol, cm^{-1}) 1600, 1495, 1450, 1380, 1355, 1150, 1090, 1070, 1030, 735, 700. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.39–7.20 (m, 10H), 3.95 (d, J = 14.6 Hz, 1H), 3.77 (d, J = 14.3 Hz, 1H), 2.32–2.20 (m, 2H), 1.44 (d, J = 5.9 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 140.53, 139.92, 130.11, 128.11, 127.43, 126.51, 126.46, 125.91, 55.36, 48.51, 42.98, 11.63. HRMS ($APCI^+$) Calcd. for $C_{16}H_{18}N^+$, $[M+H]^+$: 224.1434. Found: *m*/*z* 224.1440.

Reaction of [(*E*)-2-(4-chlorophenyl)vinyl]dimethylsulfonium triflate with potassium phthalimide

To a stirred solution of [(*E*)-2-(4-chlorophenyl)vinyl]dimethylsulfonium triflate (34.9 mg, 0.10 mmol) in DMSO (1.0 mL) was added potassium phthalimide (37.0 mg, 0.20 mmol), and the mixture was stirred at room temperature for 4 h. The reaction was quenched with cold water (10 mL), and the organic material was extracted with Et_2O (10 mL x 2). The organic layer was dried over anhydrous Na_2SO_4 and filtrated. The filtrate was concentrated in vacuo, and the residue was purified by preparative TLC (hexane) to give (*E*)-4-chlorostyryl methyl sulfide (16.2 mg, 88%) and higher polarity material [R_f = ~0 (hexane)] that was again purified by preparative TLC ($CHCl_3$) to give *N*-methylphthalimide (9.3 mg, 58%).

[(*E*)-2-(4-Chlorophenyl)vinyl]dimethylsulfonium trifluoromethanesulfonate. Nenajdenko's procedure[8] was employed. Yield 87%, white powder, mp 92–94 °C. IR (KBr, cm^{-1}) 1280, 1260, 1170, 1160, 1030, 1010, 640. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.60–7.48 (m, 3H), 7.38 (d, J = 8.6 Hz, 2H), 7.15 (d, J = 15.4 Hz, 1H), 3.15 (s, 6H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 148.83, 138.24, 130.27, 129.98, 129.49, 112.42, 28.64. HRMS ($APCI^+$) Calcd. for $C_{10}H_{12}ClS^+$: 199.0343. Found: m/z 199.0350, ($APCI^-$) Calcd. for $CF_3O_3S^-$: 148.9526. Found: m/z 148.9524.

(*E*)-4-Chlorostyryl methyl sulfide. Colorless crystals, mp 53–54 °C. R_f = 0.36 (hexane). IR (KBr, cm^{-1}) 1595, 1485, 1090, 930, 785. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.26 (d, J = 8.6 Hz, 2H), 7.20 (d, J = 8.6 Hz, 2H), 6.78 (d, J = 15.5 Hz, 1H), 6.24 (d, J = 15.5 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 135.51, 132.00, 128.65, 126.60, 126.39, 123.17, 14.87. HRMS ($APCI^+$) Calcd. for $C_9H_{10}ClS^+$, $[M+H]^+$: 185.0186. Found: m/z 185.0199.

Typical experimental procedure for the synthesis of *α*-imidostyrenes (Table 3, Method A) To a stirred suspension of NaH (55% dispersion in mineral oil, 0.22 mmol) in DMSO (0.4 mL) was added an imide compound (0.22 mmol) at 10 ^{o}C. After stirring the mixture for 0.5 h at room temperature, the salt **1a** (0.20 mmol) was added, and the mixture was stirred at room temperature for the time indicated in Table 3. The reaction was quenched with cold water (10 mL), and the organic material was extracted with Et_2O (10 mL x 2). The organic layer was dried over anhydrous Na_2SO_4 and filtrated. The filtrate was concentrated in vacuo, and the residue was purified by preparative TLC to give the corresponding *α*-imidostyrene **3**. An analytical sample was prepared by crystallizing **3** from MeOH.

***N*-[1-(4-Chlorophenyl)vinyl]naphthalimide (3a).** Slightly yellow crystals. mp 160–161 °C. IR (KBr, cm^{-1}) 1705, 1660, 1580, 1370, 1350, 1230, 890, 840, 780. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 8.64 (d, J = 7.3 Hz, 2H), 8.28 (d, J = 8.1 Hz, 2H), 7.79 (t, J = 7.8 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H), 7.28 (d, J = 8.6 Hz, 2H), 6.17 (s, 1H), 5.49 (s, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 163.60, 139.76, 134.40, 134.36, 134.14, 131.69, 131.63, 128.74, 128.42, 126.97, 126.55, 122.35, 116.52. HRMS ($APCI^+$) Calcd. for $C_{20}H_{13}ClNO_2^+$, $[M+H]^+$: 334.0629. Found: m/z 334.0629.

1-[1-(4-Chlorophenyl)vinyl]pyrrolidine-2,5-dione (3b). Colorless crystals, mp 137–138 °C. IR (KBr, cm^{-1}) 1770, 1705, 1490, 1380, 1180, 840, 815. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.31 (d, J = 8.8 Hz, 2H), 7.24 (d, J = 8.8 Hz, 2H), 5.93 (s, 1H), 5.34 (s, 1H), 2.88 (s, 4H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 175.58, 136.70, 134.82, 133.09, 128.79, 126.49, 116.62, 28.57. HRMS ($APCI^+$) Calcd. for $C_{12}H_{11}ClNO_2^+$, $[M+H]^+$: 236.0473. Found: m/z 236.0479.

2-[1-(4-Chlorophenyl)vinyl]isoindoline-1,3-dione (3c). Method B: A mixture of **1a** (23.6 mg, 0.05 mmol) and potassium phthalimide (10.2 mg, 0.055 mmol) in DMSO (0.25 mL) was stirred at room temperature for 12 h. The reaction was quenched with cold water (10 mL), and the organic material was extracted with Et_2O (10 mL x 2). The organic layer was dried over anhydrous Na_2SO_4 and filtrated. The filtrate was concentrated in vacuo, and the residue was purified by preparative TLC to give **3c** (12.8 mg, 90%) as slightly yellow crystals. An analytical sample was prepared by crystallizing **3c** from MeOH. Colorless crystals, mp 132–133 °C. IR (KBr, cm^{-1}) 1780, 1720, 1630, 1370, 1360, 1120, 1110, 1070, 890, 840, 730, 720. ^{1}H NMR (270

MHz, $CDCl_3$) δ_H 8.00–7.86 (m, 2H), 7.86–7.72 (m, 2H), 7.31 (s, 4H), 5.98 (s, 1H), 5.46 (s, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 166.80, 136.07, 134.70, 134.40, 133.90, 131.60, 128.75, 126.66, 123.80, 116.44. HRMS ($APCI^+$) Calcd. for $C_{16}H_{11}ClNO_2^+$, $[M+H]^+$: 284.0473. Found: *m*/*z* 284.0470.

1-[1-(4-Chlorophenyl)vinyl]indoline-2,3-dione (3d). Orange crystals, mp 147–148 °C. IR (KBr, cm^{-1}) 1725, 1600, 1455, 1350, 1295, 840, 750. ^1H NMR (270 MHz, $CDCl_3$) δ_H 7.68 (d, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.42–7.30 (m, 4H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.56 (d, *J* = 8.1 Hz, 1H), 6.00 (s, 1H), 5.60 (s, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 182.12, 157.20, 150.89, 138.32, 137.17, 135.33, 132.27, 129.13, 127.01, 125.44, 124.15, 117.28, 115.63, 112.33. HRMS (EI) Calcd. for $C_{16}H_{10}ClNO_2^+$, $[M]^+$: 283.0395. Found: *m*/*z* 283.0401.

Typical experimental procedure for *α*-phthalimidation of styrenes in one vessel (Table 4)

2-(1-Phenylvinyl)isoindoline-1,3-dione (3e).[32] To a stirred solution of diphenyl sulfoxide (30.3 mg, 0.15 mmol) in CH_2Cl_2 (0.3 mL) was added Tf_2O (0.025 mL, 0.15 mmol) at –78 °C. A solution of styrene (15.6 mg, 0.15 mmol) in CH_2Cl_2 (0.3 mL) was then added dropwise at –78 °C. After 10 min, the mixture was warmed up to 0 °C, and the solvent was removed in vacuo. After dilution of the residue with DMSO (0.3 mL), potassium phthalimide (83.3 mg, 0.45 mmol) was added and stirred at room temperature for 16 h. The reaction was quenched with cold water (10 mL), and the organic material was extracted with Et_2O (10 mL x 2). The organic layer was dried over anhydrous Na_2SO_4 and filtrated. The filtrate was concentrated in vacuo, and the residue was purified by preparative TLC to give **3e** (32.5 mg, 87%) as colorless crystals. mp 100–101 °C (Lit.[32] mp 97–98 °C). IR (KBr, cm^{-1}) 1720, 1375, 1120, 890, 775, 735, 720, 705. ^1H NMR (270 MHz, $CDCl_3$) δ_H 7.98–7.86 (m, 2H), 7.86–7.73 (m, 2H), 7.46–7.27 (m, 5H), 6.01 (s, 1H), 5.44 (s, 1H) ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 166.94, 137.05, 135.24, 134.27, 131.71, 128.81, 128.52, 125.26, 123.72, 116.02. HRMS ($APCI^+$) Calcd. for $C_{16}H_{12}NO_2^+$, $[M+H]^+$: 250.0863. Found: *m*/*z* 250.0854.

2-[1-(4-Methylphenyl)vinyl]isoindoline-1,3-dione (3f). Slightly yellow crystals, mp 146–147 °C. IR (KBr, cm^{-1}) 1720, 1370, 885, 820, 715. ^1H NMR (270 MHz, $CDCl_3$) δ_H 8.00–7.85 (m, 2H), 7.85–7.72 (m, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 5.96 (s, 1H), 5.38 (s, 1H), 2.33 (s, 3H) ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 166.98, 138.79, 137.00, 134.23, 132.43, 131.74, 129.24, 125.16, 123.70, 115.04, 21.29. HRMS ($APCI^+$) Calcd. for $C_{17}H_{14}NO_2^+$, $[M+H]^+$: 264.1019. Found: *m*/*z* 264.1027.

1,1-Diphthalimidoethylene (3g).[33] Colorless crystals, mp 253–254 °C (Lit.[33] mp 247–248 °C). IR (KBr, cm^{-1}) 1785, 1720, 1350, 1110, 1060, 885, 720, 710. ^1H NMR (270 MHz, $CDCl_3$) δ_H 7.95–7.83 (m, 4H), 7.83–7.72 (m, 4H), 5.74 (s, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 165.68, 134.54, 131.18, 123.94, 123.73, 113.85. HRMS ($APCI^+$) Calcd. for $C_{18}H_{11}N_2O_4^+$, $[M+H]^+$: 319.0713. Found: *m*/*z* 319.0728.

Typical experimental procedure for the synthesis of *α*-(aminomethyl)styrenes (Table 5)
To a solution of diphenyl sulfoxide (121.4 mg, 0.60 mmol) in CH_2Cl_2 (1 mL) was added triflic anhydride (0.098 mL, 0.60 mmol) at –78 °C, followed by dropwise addition of *α*-methylstyrene (59.1 mg, 0.50 mmol) in CH_2Cl_2 (1 mL) at –78 °C. After 10 min, the reaction mixture was warmed up to 0 °C, and the solvent was removed in vacuo. A solution of an amine (2.50 mmol) in CH_2Cl_2 (1 mL) was added to the residue and stirred at room temperature. The reaction was quenched with a 0.1 M NaOH solution (20 ml), and the organic material was extracted with CH_2Cl_2 (20 mL x 2). The organic layer was dried over anhydrous Na_2SO_4 and filtrated. The filtrate was concentrated in vacuo, and the residue was purified by preparative TLC to give the corresponding allylamine **5**.

***N*-Benzyl-2-phenyl-2-propenylamine (5a).**[34] Light yellow syrup. IR (Nujol, cm^{-1}) 3020, 3000, 2770, 1660, 1615, 1480, 1440, 1110–1080, 1060, 1020, 890, 770, 730, 690. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.47–7.39 (m, 2H), 7.38–7.18 (m, 8H), 5.42 (br s, 1H), 5.26 (d, J = 1.1 Hz, 1H), 3.79 (s, 2H), 3.67 (s, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 146.11, 140.07, 139.66, 128.30, 128.23, 128.09, 127.54, 126.79, 126.08, 113.42, 52.97, 52.70. HRMS (APCI$^+$) Calcd. for $C_{16}H_{18}N^+$, $[M+H]^+$: 224.1434. Found: *m*/*z* 224.1443.

***N*-(3-Phenylpropyl)-2-phenyl-2-propenylamine (5b).** Light yellow syrup. IR (Nujol, cm^{-1}) 3100–2800, 1490, 1450, 905, 780, 750, 700. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.44–7.13 (m, 10H), 5.38 (s, 1H), 5.21 (s, 1H), 3.65 (s, 2H), 2.72–2.55 (m, 4H), 1.80 (quin, J = 7.5 Hz, 2H), 1.30 (br s, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 146.23, 141.98, 139.69, 128.31, 128.23, 128.16, 127.52, 126.02, 125.58, 113.14, 53.43, 48.66, 33.62, 31.65. HRMS (APCI$^+$) Calcd. for $C_{18}H_{22}N^+$, $[M+H]^+$: 252.1747. Found: *m*/*z* 252.1739.

***N*-(1-Phenylethyl)-2-phenyl-2-propenylamine (5c).** Light yellow syrup. IR (Nujol, cm^{-1}) 3100–2800, 1490, 1450, 905, 780, 765, 705. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.39–7.18 (m, 10H), 5.38 (s, 1H), 5.19 (d, J = 1.4 Hz, 1H), 3.80 (q, J = 6.5 Hz, 1H), 3.54 (d, J = 14.0 Hz, 1H), 3.44 (d, J = 13.8 Hz, 1H), 1.47 (br s, 1H), 1.31 (d, J = 6.5 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 146.28, 145.26, 139.62, 128.23, 128.21, 127.45, 126.77, 126.58, 126.00, 113.19, 57.39, 51.23, 24.33. HRMS (APCI$^+$) Calcd. for $C_{17}H_{20}N^+$, $[M+H]^+$: 238.1590. Found: *m*/*z* 238.1592.

***N*-*tert*-Butyl-2-phenyl-2-propenylamine (5d).** Slightly yellow syrup. IR (Nujol, cm^{-1}) 2980, 1625, 1380, 1360, 1220, 900, 780, 700. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.47–7.43 (m, 2H), 7.37–7.25 (m, 3H), 5.38 (d, J = 0.8 Hz, 1H), 5.28 (d, J = 1.4 Hz, 1H), 3.61 (br s, 2H), 1.15 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 146.97, 139.99, 128.27, 127.47, 126.04, 112.92, 50.51, 46.62, 29.08. HRMS (APCI$^+$) Calcd. for $C_{13}H_{20}N^+$, $[M+H]^+$: 190.1590. Found: *m*/*z* 190.1600.

***N*-Phenyl-2-phenyl-2-propenylamine (5e).**[25a] Yellow syrup. IR (Nujol, cm^{-1}) 3400, 3050, 1600, 1500, 1310, 1250, 905, 780, 750, 710, 690. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.47–7.13 (m, 7H), 6.74–6.59 (m, 3H), 5.47 (d, J = 1.1 Hz, 1H), 5.32 (d, J = 1.1 Hz, 1H), 4.14 (br s, 2H), 3.89 (br s, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 147.73, 144.40, 139.03, 129.07, 128.37, 127.76, 125.96, 117.39, 113.58, 112.75, 47.99. HRMS (APCI$^+$) Calcd. for $C_{15}H_{16}N^+$, $[M+H]^+$: 210.1277. Found: *m*/*z* 210.1286.

***N,N*-Diisopropyl-2-phenyl-2-propenylamine (5f).** Yellow syrup. IR (Nujol, cm^{-1}) 2970, 1590, 1440, 1390, 1220, 700. ^1H NMR (270 MHz, $CDCl_3$) δ_H 7.47–7.43 (m, 2H), 7.35–7.21 (m, 3H), 5.42 (d, J = 1.9 Hz, 1H), 5.36 (br s, 1H), 3.43 (s, 2H), 3.07 (hept, J = 6.5 Hz, 2H), 0.99 (d, J = 6.8 Hz, 12H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 147.92, 141.11, 127.82, 127.02, 126.29, 113.51, 49.30, 47.75, 20.66. HRMS ($APCI^+$) Calcd. for $C_{15}H_{24}N^+$, $[M+H]^+$: 218.1903. Found: *m*/*z* 218.1903.

***N,N*-Dibenzyl-2-phenyl-2-propenylamine (5g).** Slightly yellow syrup. IR (Nujol, cm^{-1}) 3080, 3040, 2800, 1490, 1445, 1365, 740, 695. ^1H NMR (270 MHz, $CDCl_3$) δ_H 7.29–7.16 (m, 15H), 5.42 (d, J = 1.6 Hz, 1H), 5.36 (d, J = 1.6 Hz, 1H), 3.51 (s, 4H), 3.41 (s, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 146.08, 139.99, 139.38, 128.84, 127.95, 127.74, 127.25, 126.70, 126.68, 115.00, 58.27, 57.90. HRMS ($APCI^+$) Calcd. for $C_{23}H_{24}N^+$, $[M+H]^+$: 314.1903. Found: *m*/*z* 314.1917.

Typical experimental procedure for the synthesis of allylamines from alkenes and benzylamine (Table 6)

Method A. To a solution of diphenyl sulfoxide (121.4 mg, 0.60 mmol) in CH_2Cl_2 (1 mL) was added triflic anhydride (0.098 mL, 0.60 mmol) at –78 °C, followed by dropwise addition of an alkene (0.50 mmol) in CH_2Cl_2 (1 mL) at the same temperature. After 10 min, the reaction mixture was warmed up to 0 °C, and the solvent was removed in vacuo. Then, benzylamine (535.8 mg, 5.00 mmol) was added to the residue and stirred at room temperature. **Method B.** To a solution of diphenyl sulfoxide (121.4 mg, 0.60 mmol) in CH_2Cl_2 (1 mL) was added triflic anhydride (0.098 mL, 0.60 mmol) at –78 °C, followed by dropwise addition of an alkene (0.50 mmol) in CH_2Cl_2 (1 mL) at the same temperature. After 10 min, benzylamine (535.8 mg, 5.00 mmol) was added at –78 °C, and then the reaction mixture was warmed and stirred at room temperature. The work-up procedure described above for α-methylstyrene gave the corresponding allylamine **5**.

***N*-Benzyl-2-(4-chlorophenyl)-2-propenylamine (5h).** Light yellow syrup. IR (Nujol, cm^{-1}) 1490, 1090, 1010, 835, 740, 700. ^1H NMR (270 MHz, $CDCl_3$) δ_H 7.38–7.22 (m, 9H), 5.40 (s, 1H), 5.26 (d, J = 1.1 Hz, 1H), 3.78 (s, 2H), 3.62 (s, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 145.00, 139.93, 138.07, 133.25, 128.37, 128.24, 128.05, 127.39, 126.85, 113.97, 53.00, 52.62. HRMS ($APCI^+$) Calcd. for $C_{16}H_{17}ClN^+$, $[M+H]^+$: 258.1044. Found: *m*/*z* 258.1053.

***N*-Benzyl-2,3-diphenyl-2-propenylamine (5i).** The two stereoisomers were separated.

(*E*)-5i. 65% yield, yellow syrup. R_f = 0.13 (hexane/EtOAc 4:1). IR (Nujol, cm^{-1}) 3020, 2980, 1625, 1585, 1480, 1430, 750–720, 685. ^1H NMR (270 MHz, $CDCl_3$) δ_H 7.34–7.16 (m, 10H), 7.13–7.03 (m, 3H), 7.00–6.92 (m, 2H), 6.59 (s, 1H), 3.80 (s, 2H), 3.63 (s, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 140.34, 139.97, 139.45, 136.61, 129.01, 128.55, 128.47, 128.20, 128.06, 127.72, 127.29, 127.14, 126.76, 126.37, 56.93, 52.57. HRMS (EI) Calcd. for $C_{22}H_{21}N^+$, $[M]^+$: 299.1669. Found: *m*/*z* 299.1672. The *E* geometry of this compound was confirmed by the NOE difference at H-1 observed upon irradiation of H-3 (vinylic proton), whereas it was not observed in the case of the other isomer.

(*Z*)-5i. 15% yield, yellow syrup. R_f = 0.24 (hexane/EtOAc 4:1). IR (Nujol, cm^{-1}) 3080, 3050, 2950–2850, 1600, 1490, 1445, 760–740, 700. ^1H NMR (270 MHz, $CDCl_3$) δ_H 7.56–7.45 (m, 2H), 7.45–7.05 (m, 13H), 6.88 (s, 1H), 3.83 (s, 2H), 3.73 (s, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 141.36, 139.95, 139.74, 137.23, 130.50, 128.74, 128.50, 128.26, 128.18, 127.44, 126.84, 126.46, 53.43, 47.48. HRMS ($APCI^+$) Calcd. for $C_{22}H_{22}N^+$, $[M+H]^+$: 300.1747. Found: *m*/*z* 300.1748.

***N*-Benzyl-2-phenyl-2-butenylamine (5j).** The two stereoisomers (*E*/*Z* 1:1) were obtained in 55% combined yield and could not be separated. Yellow syrup. R_f = 0.21 (hexane/EtOAc 3:1). IR (Nujol, cm^{-1}) 3100–2800, 1495, 1440, 740, 705. ^1H NMR (270 MHz, $CDCl_3$) δ_H 7.40–7.20 (m, 10H x 2), 5.90 (q, *J* = 7.0 Hz, 1H), 5.73 (q, *J* = 6.8 Hz, 1H), 3.73 (s, 2H x 2), 3.68 (s, 2H), 3.51 (br s, 2H), 1.79 (d, *J* = 7.0 Hz, 3H), 1.63 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 140.11, 140.08, 139.30, 138.54, 130.92, 129.20, 128.47, 128.28, 128.18, 128.14, 128.10, 128.09, 126.76, 126.71, 126.16, 125.71, 124.65, 123.36, 56.08, 53.03, 52.63, 46.43, 14.64, 14.23. HRMS ($APCI^+$) Calcd. for $C_{17}H_{20}N^+$, $[M+H]^+$: 238.1590. Found: *m*/*z* 238.1589. 1-Benzyl-2-ethyl-2-phenylaziridine was isolated as a by-product in 25% yield.

1-Benzyl-2-ethyl-2-phenylaziridine. Light yellow syrup. R_f = 0.46 (hexane/EtOAc 3:1). IR (Nujol, cm^{-1}) 3100–2880, 1495, 1450, 1360, 1030, 760, 735, 700. ^1H NMR (270 MHz, $CDCl_3$) δ_H 7.39–7.14 (m, 10H), 3.49 (d, *J* = 14.0 Hz, 1H), 2.80 (d, *J* = 14.0 Hz, 1H), 2.30–2.10 (m, 1H), 2.05 (s, 1H), 1.84 (s, 1H), 1.56–1.38 (m, 1H), 0.80 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 139.95, 137.39, 130.27, 128.02, 127.91, 127.62, 127.38, 126.45, 58.72, 50.48, 38.20, 33.74, 10.31. HRMS ($APCI^+$) Calcd. for $C_{17}H_{20}N^+$, $[M+H]^+$: 238.1590. Found: *m*/*z* 238.1591.

***N*-Benzyl-3-methyl-2-phenyl-2-butenylamine (5k).** Light yellow syrup. IR (Nujol, cm^{-1}) 3100–2800, 1490, 1450–1435, 735, 700. ^1H NMR (270 MHz, $CDCl_3$) δ_H 7.35–7.15 (m, 10H), 3.71 (s, 2H), 3.54 (s, 2H), 1.82 (s, 3H), 1.60 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 142.06, 140.16, 133.07, 130.95, 128.87, 128.12, 128.01, 128.00, 126.65, 126.15, 52.79, 50.94, 22.44, 20.33. HRMS ($APCI^+$) Calcd. for $C_{18}H_{22}N^+$, $[M+H]^+$: 252.1747. Found: *m*/*z* 252.1737.

***N*-Benzyl(cyclohexenylmethyl)amine (5l).** Light yellow oil. IR (Nujol, cm^{-1}) 2950–2850, 1490, 1450–1435, 735, 700. ^1H NMR (270 MHz, $CDCl_3$) δ_H 7.34–7.20 (m, 5H), 5.59 (br s, 1H), 3.74 (s, 2H), 3.13 (s, 2H), 2.01–1.99 (m, 4H), 1.68–1.53 (m, 4H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 140.45, 135.89, 128.17, 128.02, 126.65, 122.63, 55.61, 53.12, 26.96, 25.13, 22.82, 22.62. HRMS ($APCI^+$) Calcd. for $C_{14}H_{20}N^+$, $[M+H]^+$: 202.1590. Found: *m*/*z* 202.1589.

***N*-Benzyl-2-methyl-2-pentenylamine (5m).** The two stereoisomers (2:1) could not be separated. Light yellow oil. R_f = 0.20 (hexane/EtOAc 3:1). IR (Nujol, cm^{-1}) 3000, 1455, 720, 705. ^1H NMR (270 MHz, $CDCl_3$) δ_H 7.38–7.05 (m, 5H x 2), 5.33–5.15 (m, 1H x 2), 3.73 (s, 2H), 3.72 (s, 2H), 3.23 (s, 2H), 3.15 (s, 2H), 2.12–1.92 (m, 2H x 2), 1.65 (s, 3H), 1.24 (s, 3H), 0.96 (t, *J* = 7.6 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H). HRMS ($APCI^+$) Calcd. for $C_{13}H_{20}N^+$, $[M+H]^+$: 190.1590. Found: *m*/*z* 190.1590.

***N*-Benzyl-2-propyl-2-propenylamine (5n).** Light yellow oil. R_f = 0.22 (hexane/EtOAc 3:1). IR (Nujol, cm^{-1}) 3080–2830, 1450, 895, 735, 700. ^1H NMR (270 MHz, $CDCl_3$) δ_H 7.33–7.23 (m, 5H), 4.94 (s, 1H), 4.85 (d, *J* = 1.1 Hz, 1H), 3.77 (s, 2H), 3.20 (s, 2H), 2.04 (t, *J* = 7.7 Hz, 2H), 1.47 (sext, *J* = 7.5 Hz, 2H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 147.54,

140.30, 128.23, 128.02, 126.76, 109.73, 53.68, 53.16, 36.57, 20.97, 13.99. HRMS ($APCI^+$) Calcd. for $C_{13}H_{20}N^+$, $[M+H]^+$: 190.1590. Found: *m*/*z* 190.1592.

***N*-Benzyl-(1,2-dihydronaphthalen-4-yl)methylamine (5o).** Yellow syrup. IR (Nujol, cm^{-1}) 3080–2820, 1625, 1485, 1445, 735, 700. ^1H NMR (270 MHz, $CDCl_3$) δ_H 7.34–7.12 (m, 9H), 6.03 (t, *J* = 4.5 Hz, 1H), 3.84 (s, 2H), 3.62 (d, *J* = 1.1 Hz, 2H), 2.75 (t, *J* = 8.0 Hz, 2H), 2.32–2.24 (m, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 140.19, 136.53, 134.35, 133.80, 128.21, 128.10, 127.54, 126.77, 126.68, 126.51, 126.28, 122.43, 53.44, 50.94, 28.20, 23.04. HRMS ($APCI^+$) Calcd. for $C_{18}H_{20}N^+$, $[M+H]^+$: 250.1590. Found: *m*/*z* 250.1588.

3-Benzylamino-2-phenylcyclohexene (5p).[35] Yellow syrup. IR (Nujol, cm^{-1}) 2950, 1490, 1450, 760, 700. ^1H NMR (270 MHz, $CDCl_3$) δ_H 7.33–7.15 (m, 10H), 6.06 (t, *J* = 3.8 Hz, 1H), 3.83–3.65 (m, 3H), 2.35–1.53 (m, 6H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 140.81, 140.26, 139.31, 128.45, 128.21, 128.18, 128.09, 126.71, 126.66, 125.99, 51.77, 51.27, 27.39, 26.24, 17.93. HRMS ($APCI^+$) Calcd. for $C_{19}H_{22}N^+$, $[M+H]^+$: 264.1747. Found: *m*/*z* 264.1754.

***N*-Benzyl-1,2-dimethyl-2-propenylamine (5q).** Light yellow oil. IR (Nujol, cm^{-1}) 3080, 3040, 2980, 2920–2820, 1490, 1450, 1365, 1110, 890, 735, 695. ^1H NMR (270 MHz, $CDCl_3$) δ_H 7.32–7.21 (m, 5H), 4.89 (s, 1H), 4.84 (s, 1H), 3.69 (d, *J* = 13.2 Hz, 1H), 3.57 (d, *J* = 13.2 Hz, 1H), 3.25 (q, *J* = 6.6 Hz, 1H), 1.71 (s, 3H), 1.35, (br s, 1H), 1.16 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 147.50, 140.60, 128.20, 128.04, 126.65, 111.25, 58.81, 51.34, 20.90, 17.05. HRMS ($APCI^+$) Calcd. for $C_{12}H_{18}N^+$, $[M+H]^+$: 176.1434. Found: *m*/*z* 176.1450.

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