Aziridination of Activated Imines with Monocarbonyl Iodonium Ylides Generated from (*Z*)-(2-Acetoxyvinyl)iodonium Salts via Ester Exchange: Stereoselective Synthesis of 2-Acylaziridines

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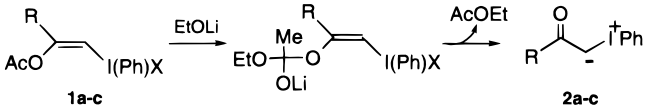
Monocarbonyl iodonium ylides, generated in situ from (*Z*)-(2-acetoxyvinyl)iodonium salts via an ester exchange reaction with EtOLi, undergo alkylidene transfer reactions to activated imines yielding 2-acylaziridines in good yields. The stereochemical outcome of this aziridination was shown to be dependent on both the activating groups of the imines and the reaction solvents: that is, the aziridination of *N*-(2,4,6-trimethylbenzenesulfonyl)imines in THF affords *cis*-aziridines as a major product while that of *N*-benzoylimines in THF−DMSO or THF gives the *trans* isomer stereoselectively.

β-Dicarbonyl and *β*-disulfonyl iodonium ylides, relatively stable species, are readily prepared in high yields from the corresponding active methylene compounds by the reaction with aryl-λ^3-iodane in aqueous or alcoholic alkali.[1,2] Reactive intermediates generated by photochemical and transition metal-catalyzed decomposition of these stable iodonium ylides undergo several types of reactions. These include cyclopropanation of olefins, inter- and intramolecular carbon−hydrogen insertion reaction, transylidation with various S, N, and P nucleophiles to give other ylides, carbonyl ylide formation, and cycloaddition reactions leading to the formation of five-membered heterocycles.[3]

Despite the increasing interest in and research on these stable iodonium ylides, the chemistry of iodonium ylides derived from unactivated monocarbonyl compounds remains unknown, and no unstabilized monocarbonyl iodonium ylides have yet been isolated and characterized.[1a] Recently, we found that the ester exchange reaction between (*Z*)-(2-acetoxyvinyl)iodonium bromides **1** (X = Br) and EtOLi generates quantitatively the monocarbonyl iodonium ylides **2** in THF at −78 °C with the liberation of ethyl acetate (Scheme 1).[4] The monocarbonyl iodonium ylide **2b** with *n*-octyl substituent is stable up to −30 °C in THF, but gradually decomposes at −20 °C to 1-bromo-2-decanone.

Scheme 1



a: R = Me, **b**: R = *n*-C_8H_{17}, **c**: R = *t*-Bu

The stable iodonium ylides having *β*-dicarbonyl groups possess a highly delocalized ylidic carbanion directly bound to an aryliodonio group. Consequently, they exhibit relatively low basicity and nucleophilicity, which, in turn, renders these ylides inactive toward aldehydes and

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Table 1. Reaction of (*Z*)-(*β*-Acetoxyvinyl)iodonium Salt 1 with Imine 3 in THF−DMSO[a]

entry	iodonium 1	iodonium X	imine **3** (R^1, R^2)	conditions temp/°C, time/h	product (yield[b]/%, ratio[c]) 4	5	6
1	**1b**	Br	**3a** (Ph, Ph)	−30, 2	**4ba** (0)[d]		
2	**1b**	Br		−30, 2	**4ba** (0)[e]		
3	**1b**	Br	**3b** (Ph, SOC_6H_4-*p*-Me)	−30, 2	**4bb** (3, −)[f]		
4	**1b**	Br	**3c** (Ph, SO_2Ph)	−30, 2	**4bc** (78, 61:39)		
5	**1b**	BF_4	**3c**	−30, 2	**4bc** (76, 69:31)		
6	**1b**	Br	**3c**	0, 2	**4bc** (74, 62:38)		
7	**1b**	Br	**3d** (Ph, $SO_2C_6H_2$-2,4,6-Me_3)	−30, 2	**4bd** (85, 67:33)		
8	**1b**	Br	**3e** (Ph, SO_2Me)	−30, 2	**4be** (51, 36:64)		
9	**1c**	Br	**3d**	−30, 2	**4cd** (81, 18:82)		
10	**1a**	Br	**3f** (Ph, CO_2Me)	−30, 2	**4af** (5, 100:0)		**6f** (75)
11	**1b**	Br	**3f**	−30, 2	**4bf** (65, 100:0)		**6f** (49)
12	**1b**	Br	**3g** (Ph, COPh)	−30, 2	**4bg** (68, 98:2)	**5bg** (9, 100:0)	**6g** (41)
13	**1b**	Br	**3h** (*p*-ClC_6H_4, COPh)	−30, 2	**4bh** (66, 92:8)	**5bh** (22, 67:33)	**6h** (24)
14	**1c**	Br	**3f**	−30, 2	**4cf** (39, 83:17)		**6f** (55)
15	**1c**	Br	**3g**	−30, 2	**4cg** (72, 93:7)	**5cg** (7, 100:0)	**6g** (50)
16	**1c**	Br	**3h**	−30, 2	**4ch** (69, 92: 8)	**5ch** (16, 100:0)	**6h** (40)

[a] Reactions were carried out using 1 equiv of EtOLi and 1.5 equiv of an imine **3** in THF−DMSO (12:1) under argon. [b] Isolated yields. [c] *Trans:cis* ratios, determined by ^{1}H NMR of the crude product. [d] Unsaturated 1,4-diketone **7** (82%, *trans:cis* = 50:50) was obtained. [e] 1,4-Diketone **7** (79%, *trans:cis* = 42:58) was obtained. [f] −: not determined. 1,4-Diketone **7** (26%, *trans:cis* = 43:57) was obtained.

ketones.[1a,5] The monocarbonyl iodonium ylides **2**, however, are moderately nucleophilic in nature and act as an alkylidene transfer agent to carbonyl compounds. Thus, the reaction with aldehydes in THF−DMSO (12:1) at −30 °C gives α,*β*-epoxy ketones in good yields with *trans* isomers as a major product.[4]

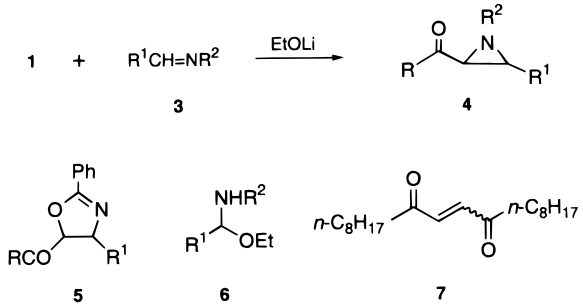
Aziridines are useful intermediates in organic synthesis because of their chemical reactivity, mostly derived from large ring strain.[6] We report herein an addition reaction of the monocarbonyl iodonium ylide **2** to imines **3**, which provides a stereoselective route for the synthesis of *trans*- and *cis*-2-acylaziridines **4**.[7,8]

Results and Discussion

Aziridination in THF−DMSO. No alkylidene transfer reaction of the ylide **2b** with *N*-benzylideneaniline (**3a**) was observed. Reaction of (*Z*)-(2-acetoxy-1-decenyl)(phenyl)iodonium bromide (**1b**) with **3a** in THF−DMSO (12:1) at −30 °C afforded a 1:1 mixture of (*E*)- and (*Z*)-10-eicosene-9,12-dione **7** in 82% yield with no evidence of the formation of aziridinyl ketone **4ba**. This result is probably due to the low electrophilicity of the *N*-arylimine **3a**.[9] Dimerization of the ylide **2b** explains the formation of the unsaturated 1,4-diketone **7**; in fact, when the imine **3a** was not added, the reaction of **1b** with EtOLi gave **7** (79%, *E:Z* = 42:58) (Table 1, entry 2).[10]

The same trend holds for the reaction with the more reactive *N*-sulfinylimine **3b** (entry 3); however, the direct aziridination of C=N bonds took place smoothly when activated *N*-sulfonylaldimines were employed. Treatment of a THF−DMSO (12:1) solution of vinyliodonium bromide **1b** and *N*-(benzenesulfonyl)benzaldimine (**3c**) (1.5 equiv) with 1 equiv of EtOLi at −30 °C for 2 h resulted in the formation of a stereoisomeric mixture of α,*β*-aziridino ketone **4bc** (R = *n*-C_8H_{17}, R^1 = Ph, R^2 = SO_2-Ph) in 78% yield (Scheme 2). The *trans:cis* ratio was determined to be 61:39 by ^{1}H NMR analysis of the crude product (entry 4). Changing the ligand on iodine(III) of **1b** from Br to BF_4 slightly increased the selectivity for *trans*-aziridine **4bc**. The reaction temperature appeared to have no effect on the product profiles (entry 6). Interestingly, the reaction of *N*-(methanesulfonyl)imine **3e** with **1b** resulted in reversal of the stereochemical outcome, giving the *cis*-aziridine **4be** as a major product, albeit with low selectivity (compare entries 4 and 8). This is the first example of the preparation of aziridines by the addition of iodonium ylide to imines. Recently, Matano and Suzuki reported the stereoselective synthesis of α,*β*-aziridinyl ketones via the reaction of monocarbonyl bismuthonium ylides with *N*-sulfonylimines.[8e]

Scheme 2



Using carbonyl groups instead of sulfonyl groups to increase the electrophilicity of the imines led to higher *trans* selectivity for the formation of α,*β*-aziridino ketones **4**: thus, the only detectable stereoisomer was found to be *trans*-aziridine **4bf** (65%) in the reaction of the monocarbonyl iodonium ylide **2b** with *N*-(methoxycarbonyl)imine **3f** in THF−DMSO at −30 °C (entry 11). As one of the byproducts, this reaction afforded the amino acetal **6f** (R^1 = Ph, R^2 = CO_2Me) in 49% yield, presumably produced by nucleophilic attack of EtOLi to **3f**. A similar stereochemical outcome was obtained in the reaction with *N*-benzoylimine **3g**, which gave a 98:2 mixture of *trans*- and *cis*-2-acylaziridines **4bg** in 68% yield. In addition to the amino acetal **6g** (41%), a small amount of *trans*-2-phenyl-2-oxazoline **5bg** (R = *n*-C_8H_{17}, R^1 = Ph; 9%) was obtained in this reaction. The reaction of (*Z*)-(2-acetoxy-1-propenyl)iodonium bromide **1a** with *N*-(methoxycarbonyl)imine **3f** in THF−DMSO resulted in poor yield of aziridine **4af** (5%) and also the formation of a large amount of the amino acetal **6f** (75%), which is probably due to poor solubility of the iodonium salt **1a** under these

(9) The reported semiempirical AM1 calculations of the atomic net charges of benzaldehyde, *N*-benzylideneaniline **3a**, and *N*-tosylimine **3j** predict the following order of reactivity toward nucleophiles, PhCH=NTs **3j** > PhCHO > PhCH=NPh **3a**. See ref 8h.

(10) Reaction of **1b** with EtOLi in THF−DMSO at −30 °C in the presence of styrene (10 equiv) yielded no the addition products, i.e., cyclopropanes, and gave **7** (55%, *E:Z* = 43:57).

Table 2. Reaction of (*Z*)-(*β*-Acetoxyvinyl)iodonium Salt 1 with Imine 3 in THF[a]

entry	iodonium 1	iodonium X	imine **3** (R^1, R^2)	conditions temp, °C	product (yield[b]/%, ratio[c]) 4	5	6
17	**1a**	BF_4	**3d** (Ph, $SO_2C_6H_2$-2,4,6-Me_3)	−78 → 25	**4ad** (22, 80:20)		
18	**1b**	Br	**3c** (Ph, SO_2Ph)	−78 → 25	**4bc** (73, 31:69)		
19	**1b**	BF_4	**3c**	−78 → 25	**4bc** (67, 75:25)		
20	**1b**	BF_4	**3c**	25[d]	**4bc** (47, 78:22)		
21	**1b**	Br	**3d**	−78 → 25	**4bd** (73, 15:85)		
22	**1b**	Br	**3e** (Ph, SO_2Me)	−78 → 25	**4be** (74, 25:75)		
23	**1b**	Br	**3i** (Ph, $SO_2C_6H_4$-*p*-OMe)	−78 → 25	**4bi** (83, 27:73)		
24	**1b**	Br	**3j** (Ph, $SO_2C_6H_4$-*p*-Me)	−78 → 25	**4bj** (64, 29:71)		
25	**1b**	Br	**3k** (Ph, $SO_2C_6H_4$-*p*-Cl)	−78 → 25	**4bk** (59, 37:63)		
26	**1b**	Br	**3l** (Ph, SO_2-2-naphthyl)	−78 → 25	**4bl** (68, 35:65)		
27	**1b**	Br	**3m** (*p*-MeC_6H_4, $SO_2C_6H_2$-2,4,6-Me_3)	−78 → 25	**4bm** (82, 18:82)		
28	**1b**	Br	**3n** (*p*-ClC_6H_4, $SO_2C_6H_2$-2,4,6-Me_3)	−78 → 25	**4bn** (76, 18:82)		
29	**1b**	Br	**3o** (1-naphthyl, SO_2Ph)	−78 → 25	**4bo** (65, 44:56)		
30	**1b**	Br	**3p** (2-naphthyl, SO_2Ph)	−78 → 25	**4bp** (67, 31:69)		
31	**1b**	Br	**3q** (2-naphthyl, $SO_2C_6H_2$-2,4,6-Me_3)	−78 → 25	**4bq** (80, 14:86)		
32	**1b**	Br	**3r** (*t*-Bu, $SO_2C_6H_2$-2,4,6-Me_3)	−78 → 25	**4br** (36, 19:81)		
33	**1c**	Br	**3d**	−78 → 25	**4cd** (83, 5:95)		
34	**1c**	Br	**3m**	−78 → 25	**4cm** (85, 8:92)		
35	**1c**	Br	**3n**	−78 → 25	**4cn** (89, 5:95)		
36	**1b**	Br	**3f** (Ph, CO_2Me)[e]	−78 → 25	**4bf** (50, 100:0)		**6f** (98)
37	**1b**	Br	**3g** (Ph, COPh)	−78 → 25	**4bg** (60, 90:10)	**5bg** (12)	**6g** (42)

[a] Reactions were carried out using 1 equiv of EtOLi and 1.5 equiv of an imine **3** in THF under argon. [b] Isolated yields. [c] *Trans:cis* ratios, determined by ^{1}H NMR of the crude product. [d] Reaction time, 2 h. [e] 3 equiv of imine **3f** were used.

conditions. The reaction of the monocarbonyl iodonium ylide **2c** with sterically demanding *tert*-butyl group with imines **3f**−**h** activated by carbonyl groups selectively afforded *trans*-aziridines **4cf**−**ch** in moderate to good yields (entries 14−16).

The stereochemistry of the α,*β*-aziridino ketones **4** was easily determined by ^{1}H NMR: the typical coupling constant for the vicinal ring hydrogens of *cis*-aziridines **4** is about 7 Hz whereas the value for the *trans* ring hydrogens is much smaller (about 2.4−4.3 Hz).[6b] Identification of 2-phenyl-2-oxazolines **5** was made possible by comparing their NMR data with data of similar compounds.[11] The stereochemistry of **5** was determined by the vicinal coupling constants between the ring hydrogens, C_4−H and C_5−H: 6.8 Hz for *trans*-**5bg**, 6.8 Hz for *trans*-**5bh**, 11.0 Hz for *trans*-**5bh**.

Aziridination in THF. The results of alkylidene transfer of the ylides **2** to a C=N bond of the activated imines **3** in THF are summarized in Table 2. In general, the reactions were carried out simply by adding an equivalent amount of EtOLi to a THF solution of vinyliodonium salts **1** and imines **3** (1.5 equiv) at −78 °C. After being stirred for 2 h, the mixture was allowed to warm to ambient temperature. α,*β*-Aziridino ketones **4** were obtained after workup. Whereas the reaction of vinyliodonium bromide **1b** with *N*-(benzenesulfonyl)imine **3c** in THF−DMSO gave predominantly the *trans*-aziridine **4bc** (entry 4), the aziridination in THF gave the *cis* isomer as the major product with *trans:cis* ratio of 31:69 (entry 18). Interestingly, changing the ligand on iodine(III) of **1b** from Br to BF_4 was found to reverse the stereochemistry of the major product from *cis* to *trans* (entry 19).[12]

Introduction of the electron-donating *p*-MeO and *p*-Me groups on the benzenesulfonyl group of **3c** slightly increased the *cis*-selectivity while that of the electron-withdrawing *p*-Cl substituent decreased the *cis*-selectivity. The higher *cis*-selectivity (85%) for the synthesis of 2-acylaziridines **4** was observed when *N*-(2,4,6-trimethylbenzenesulfonyl)aldimine **3d** was used (entry 21). Similar levels of *cis*-selectivity (81−86%) were obtained in the reaction of vinyliodonium bromide **1b** with other aromatic **3m**,**n**,**q** and aliphatic *N*-sulfonylaldimines **3r** having a mesitylenesulfonyl group on the nitrogen. The effect of this mesitylenesulfonyl group was confirmed again by the reaction of (*Z*)-(2-acetoxy-3,3-dimethyl-1-butenyl)(phenyl)iodonium bromide (**1c**), which led to more than 90% *cis*-selectivity (entries 33−35).

The *trans*/*cis* selectivity in the aziridination of imines activated with carbonyl groups seems to be independent of the nature of the solvents. Thus, changing the solvent from THF−DMSO to THF in the reaction of imines **3f**,**g** with vinyliodonium bromide **1b** did not lead to a significant change in the stereochemical outcome of the aziridination (compare entries 11, 12, 36, and 37).

Thus, the reaction of the monocarbonyl iodonium ylide **2** with the *N*-(2,4,6-trimethylbenzenesulfonyl)imines in THF gives *cis*-α,*β*-aziridino ketones as a major product, while the reaction with *N*-benzoylimines in THF−DMSO or THF gives *trans*-α,*β*-aziridino ketones.

Substituent Effect on Reactivity of *N*-Sulfonylimines. To gain some insight into the mechanism of the aziridination of aldimines with monocarbonyl iodonium ylides, we measured the relative rates of the alkylidene transfer reaction of the ylide **2b** for a series of ring-substituted *N*-(arenesulfonyl)benzaldimines **3c** and **3i**−**k** in THF in which a mixture of a 10-fold excess of each of two competing imines was used. Electron-donating *p*-MeO and *p*-Me groups decreased the rate of the reaction, and the electron-withdrawing *p*-Cl substituent increased it (the effect of substituents on the rate of aziridination is shown in Table 3). A Hammett plot for the alkylidene transfer reaction presented in Table 3

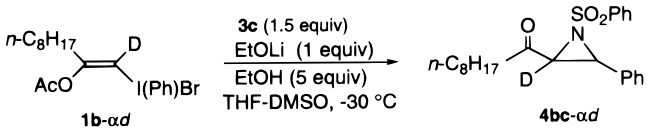
(11) (a) Pines, S. H.; Kozlowski, M. A.; Karady, S. *J. Org. Chem.* **1969**, *34*, 1621. (b) Heine, H. W.; Kaplan, M. S. *J. Org. Chem.* **1967**, *32*, 3069.

(12) The reasons for the influence of the counterion of the iodonium salt on the stereochemistry of the reaction is not clear. For similar effects of counteranion, see: (a) Bergelson, L. D.; Barsukov, L. I.; Shemayakin, M. M. *Tetrahedron Lett.* **1967**, *23*, 2709. (b) Still, W. C.; Novack, V. J. *J. Am. Chem. Soc.* **1981**, *103*, 1283. (c) Ward, W. J.; McEwen, W. E. *J. Org. Chem.* **1990**, *55*, 493. (d) Bellucci, G.; Chiappe, C.; Moro, G. L. *Tetrahedron Lett.* **1996**, *37*, 4225.

Table 3. Relative Reactivity of Sulfonylimines 3 with 2b in THF

substrate	k_{rel}	substrate	k_{rel}
3i (*p*-MeO)	0.56	**3c** (H)	1.0
3j (*p*-Me)	0.84	**3k** (*p*-Cl)	1.82

Scheme 3



showed a linear correlation of relative rate factors with the σ constants of substituents in the aromatic ring and afforded the reaction constant $\rho = 0.96$ ($r = 0.98$).[13] This small positive ρ value indicates moderate nucleophilicity of the monocarbonyl iodonium ylide **2b**, which is in a good agreement with the results obtained for the reaction of **2b** with a series of substituted benzaldehydes yielding α,β-epoxy ketones.[4]

Reaction Mechanism. One of the possible reaction mechanisms that should be considered, and which was also discussed in our previous paper,[4] involves base-induced α-vinylic proton abstraction of (*Z*)-(*β*-acetoxyvinyl)iodonium salt **1** with EtOLi, yielding the vinyliodonium ylides which, in turn, react with imines **3** to give the 2-acylaziridines **4**.[14] The following results, however, clearly indicate that this α-proton abstraction does not occur; the α-deuterated vinyliodonium salt **1b**-α*d*, on treatment with EtOLi in the presence of *N*-(benzenesulfonyl)benzaldimine (**3c**) (1.5 equiv) and *ethanol (5 equiv)* in THF−DMSO at −30 °C, afforded the α,β-aziridino ketone **4bc**-α*d* (59%, *trans*/*cis* = 55:45), in which 84% of the deuterium was retained (Scheme 3). Under these conditions, the α-proton abstraction mechanism predicts loss of most of the deuterium because of kinetic deuterium isotope effects on protonation from ethanol.

The mechanism of the reaction presumably involves nucleophilic attack of the in situ generated monocarbonyl iodonium ylides **2** via an ester exchange reaction (shown in Scheme 1) on the imine **3**, which produces the zwitterion **8** (Scheme 4). Subsequent intramolecular reductive cyclization by nucleophilic attack of the nitrogen yields the aziridines **4** with concomitant liberation of iodobenzene. The latter step may compete with an alternative intramolecular cyclization via attack of the nucleophilic oxygen, yielding the byproducts 2-oxazolines **5** when *N*-(benzoyl)imines **3g**,**h** are used. Because of the very high nucleofugality of the phenyliodonio group (about 10^6 times greater than triflate,[15] a so-called superleaving group), it seems reasonable to assume that these intramolecular reductive cyclizations of the zwitterion **8** might be very fast and, therefore, the reverse reaction of **8** regenerating the monocarbonyl iodonium ylides **2** will not be important. Furthermore, the relative rate studies for a series of ring-substituted *N*-(arenesulfonyl)benzaldimines **3c** and **3i**−**k** (Table 3) suggest that the nucleophilic attack of the ylide carbanion on the activated imines **3** will probably be a rate-limiting step in this alkylidene transfer reaction in THF.

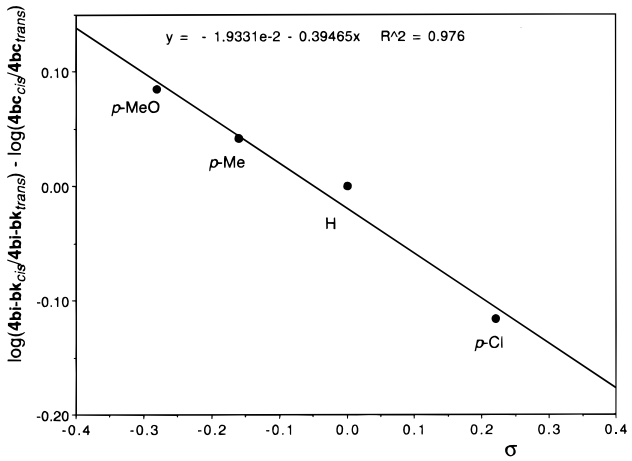
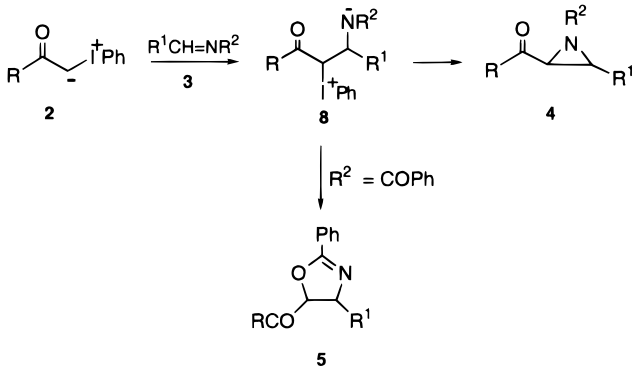


Figure 1. Linear free energy relationship for *trans*/*cis* stereoselectivity on aziridination of *N*-(arenesulfonyl)imines **3c** and **3i**−**k** with iodonium ylide **2b** in THF.

Scheme 4



As was described above, the electron-donating *para* substituents of *N*-sulfonylimines **3i**,**j** slightly increased the *cis*-aziridine selectivity when the reaction with the ylide **2b** was carried out in THF whereas lower *cis*-selectivity resulted from the presence of an electron-withdrawing substituent, i.e., **3k** (Table 2, entries 18 and 23−25). Using the method developed by Braun and Opdenbusch,[16] the difference of the logarithms of the stereoisomeric ratios of substituted and unsubstituted products [log(**4bi**−**bk**$_{cis}$/**4bi**−**bk**$_{trans}$) − log(**4bc**$_{cis}$/**4bc**$_{trans}$)] is plotted against Hammett σ constants, which shows a good linear relationship with $r = 0.99$ (Figure 1). As indicated in Figure 1, *cis*-selectivity clearly decreases with an increase in the electron-withdrawing nature of the *para* substituent.

Scheme 5 represents a mechanistic proposal that is compatible with these stereochemical outcomes. The electron-donating *para* substituent of *N*-sulfonylimine **3i**, by enhancing the electron density of the sulfonyl oxygen, will lead to a more tightened transition state **9** in THF, wherein one of the sulfonyl oxygen atoms is coordinated to the positively charged iodine(III) of the ylide. Coordination of both sulfonyl oxygen atoms to the charged iodine(III) is a possible alternative. The degree of the tightness in this transition state **9** might control stereo-

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(14) (a) Stang, P. J.; Wingert, H.; Arif, A. M. *J. Am. Chem. Soc.* **1987**, *109*, 7235. (b) Ochiai, M.; Kunishima, M.; Fuji, K.; Shiro, M.; Nagao, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 1076. (c) Ochiai, M.; Takaoka, Y.; Nagao, Y. *J. Am. Chem. Soc.* **1988**, *110*, 6565. (d) Ochiai, M.; Kunishima, M.; Tani, S.; Nagao, Y. *J. Am. Chem. Soc.* **1991**, *113*, 3135. (e) Ochiai, M.; Sueda, T.; Uemura, K.; Masaki, Y. *J. Org. Chem.* **1995**, *60*, 2624.

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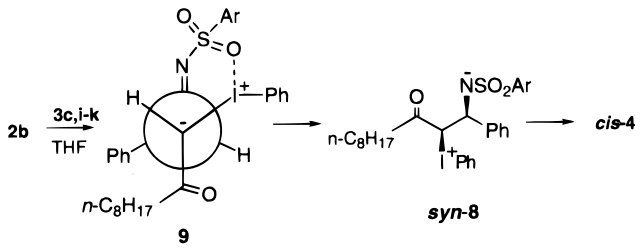
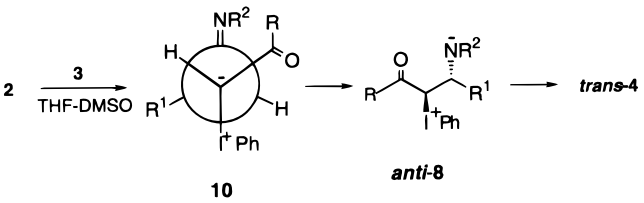
(16) Braun, M.; Opdenbusch, K. *Liebigs Ann. Recl.* **1997**, 141.

Scheme 5



Scheme 6



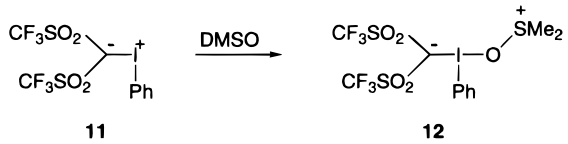
selectivity for aziridination of *N*-sulfonylimines **3** in THF, since **9** produces *syn* zwitterion **8** which, in turn, furnishes the *cis*-2-acylaziridines **4**. On the other hand, it seems reasonable to assume that such a coordination of the carbonyl oxygen atom of *N*-(methoxycarbonyl)imine **3f** and *N*-benzoylimine **3g** to the iodine(III) is not important. We have reported that observation of a negative NOE between α-methine and γ-methylene protons at − 70 °C in THF-d_8 suggests a preference for the cisoid conformation in **2b**,[4] as was observed in other monocarbonyl onium (P, S, and As) ylides in solution[17] and/or in a solid state.[18] Intramolecular interaction between the charged iodine(III) and the carbonyl oxygen in **2b** will stabilize this cisoid conformation.[19] Trapping experiments with benzoyl chloride confirmed the cisoid conformation in **2b**.[4]

An alternative explanation is that these electronic effects on *trans*/*cis* stereoselectivity result from changes imparted by the *para* substituents on the reactivity of the *N*-sulfonylimines **3**. The *p*-MeO substituent of **3i** decreases the rate of aziridination with the ylide **2b** to one-half (Table 3), and this less reactive imine **3i** would be expected to react with **2b** via a more product-like transition state compared to the unsubstituted imine **3c**, resulting in more severe nonbonded interactions that lead to higher *cis*/*trans* stereoselectivity.

For the reactions in THF−DMSO, we propose an *anti* transition state **10** (see Scheme 6), which can be expected to produce the *trans*-2-acylaziridines **4** as a major product via the intervention of *anti* zwitterion **8**. This mechanism accounts for the *trans*/*cis* stereoselectivity shown in Table 1.

In the presence of DMSO in excess, coordination of the sulfonyl oxygen atom of the *N*-sulfonylimines **3** to the charged iodine(III) of the ylide **2** will, as in **9**, no longer participate. Rather, because of the excellent solvent donicity of DMSO (DN = 29.8),[20] the oxygen atom of DMSO will coordinate to the positively charged iodine(III) of the ylide **2**, making coordination of the sulfonyl oxygen atoms of **3** difficult. These hypotheses were

Scheme 7



supported by the recent observations that irradiation or heating of the stable iodonium ylide **11** in DMSO gave a 1:1 complex **12** (Scheme 7, the structure of which was confirmed by X-ray diffraction analysis.[21] Tight hypervalent interaction between the iodine atom and the oxygen atom of DMSO makes the adduct **12** stable at room temperature.

In conclusion, our results demonstrate that the monocarbonyl iodonium ylide **3** is moderately nucleophilic in nature and undergoes stereoselective alkylidene transfer reaction to the C═N bond of the activated aldimines.

Experimental Section

General. For general experimental details, see ref 4. Preparative thin-layer chromatography (TLC) was carried out on precoated plates of silica gel (Merck, silica gel F-254). Kieselgel 60 (Merck, 230−400 mesh) was used for flash chromatography.

(*Z*)-(2-Acetoxy-1-alkenyl)(phenyl)iodonium bromides (**1a**−**c**: X = Br) were prepared from 1-alkynyl(phenyl)iodonium tetrafluoroborates[22] via Michael addition of acetic acid in the presence of sodium acetate according to literature procedure.[4] *N*-Sulfonylimines **3c**−**d** and **3i**−**r** were prepared according to literature methods.[15,23] *N*-(Methoxycarbonyl)imine **3f**[24] and *N*-benzoylimines **3g**,**h**[25] were obtained by a literature procedure.

Synthesis of (*Z*)-(2-Acetoxy-1-propenyl)(phenyl)iodonium Tetrafluoroborate (1a: X = BF_4). (*Z*)-(2-Acetoxy-1-propenyl)(phenyl)iodonium bromide (**1a**: X = Br) (80 mg, 0.21 mmol) was dissolved in dichloromethane (15 mL), and the solution was vigorously shaken with a saturated aqueous sodium tetrafluoroborate solution (5 mL) five times. The organic layer was filtered and concentrated under aspirator vacuum to give an oil, which was washed several times with hexane by decantation at −78 °C to give (*Z*)-(β-acetoxyvinyl)-iodonium tetrafluoroborate (**1a**: X = BF_4, 71 mg, 87%) as colorless needles: mp 88−89 °C (recrystallized from dichloromethane−THF); IR (KBr) 1770, 1639, 1473, 1188, 1128, 742 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.97 (br d, *J* = 8.5 Hz, 2H), 7.66 (br t, *J* = 7.3 Hz, 1H), 7.51 (br dd, *J* = 8.5, 7.3 Hz, 2H), 6.51 (q, *J* = 1.0 Hz, 1H), 2.40 (d, *J* = 1.0 Hz, 3H), 2.29 (s, 3H); FAB MS *m*/*z* 303 [$(M - BF_4)^+$]. Anal. Calcd for $C_{11}H_{12}BF_4IO_2$: C, 33.88; H, 3.10. Found: C, 33.79; H, 3.07.

Synthesis of (*Z*)-(2-Acetoxy-1-decenyl)(phenyl)iodonium Tetrafluoroborate (1b: X = BF_4). In a similar manner, (*Z*)-(β-acetoxyvinyl)iodonium tetrafluoroborate (**1b**: X = BF_4) was prepared in 98% yield from (*Z*)-(2-acetoxy-1-decenyl)(phenyl)iodonium bromide (**1b**: X = Br) (420 mg, 0.87 mmol): white powder; mp 58−60 °C (recrystallized from

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(21) Bond length of I−O of the adduct **12** is 2.59(2) Å. See: Zhu, S.-Z. *Heteroatom Chem.* **1994**, *5*, 9.

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dichloromethane−hexane); IR (KBr) 1763, 1639, 1474, 1372, 1189 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.99 (br d, J = 8.1 Hz, 2H), 7.64 (br t, J = 7.1 Hz, 1H), 7.48 (br dd, J = 8.1, 7.1 Hz, 2H), 6.61 (s, 1H), 2.64 (t, J = 7.6 Hz, 2H), 2.28 (s, 3H), 1.61−1.42 (m, 2H), 1.40−1.18 (m, 10H), 0.87 (t, J = 6.3 Hz, 3H); FAB MS m/z 575 [$(M + BF_4)^+$]. Anal. Calcd for $C_{18}H_{26}BF_4IO_2$: C, 44.29; H, 5.37. Found: C, 44.18; H, 5.29.

General Procedure for Synthesis of 2-Acylaziridines 4 in THF−DMSO. A Typical Example (Table 1, Entry 4): *N*-(Benzenesulfonyl)-2-(1-oxononyl)-3-phenylaziridine (4bc). To a stirred solution of (*Z*)-(2-acetoxy-1-decenyl)iodonium bromide (**1b**: X = Br, 30 mg, 0.062 mmol) and *N*-(benzenesulfonyl)benzaldimine (**3c**) (23 mg, 0.094 mmol) in THF−DMSO (12:1, 6.5 mL) was added a 0.43 M THF solution of EtOLi (0.14 mL, 0.062 mmol) at −30 °C under argon. The solution immediately turned pale yellow. After being stirred for 2 h, the mixture was quenched with water and extracted with diethyl ether. The organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The *trans*:*cis* ratio of 2-acylaziridines **4bc** was determined to be 69:31 by ^1H NMR of the crude reaction mixture. Preparative TLC (25% ethyl acetate in hexane) of the crude material using silica gel gave a mixture of *trans*- and *cis*-**4bc** (19.4 mg, 78%), in which isomerization of *trans*-**4bc** to the more stable *cis* isomer makes it difficult to isolate pure *trans*-**4bc** to some extent.[26] **4bc** (*trans*:*cis* = 50:50); IR ($CHCl_3$) 1720, 1335, 1165 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.06 (br d, J = 8.2 Hz, *cis* isomer), 7.84 (br d, J = 8.1 Hz, *trans* isomer), 7.71−7.42 (3H), 7.35−7.17 (m, 5H), 4.30 (d, J = 4.3 Hz, *trans* isomer), 4.18 (d, J = 7.8 Hz, *cis* isomer), 3.74 (d, J = 4.3 Hz, *trans* isomer), 3.67 (d, J = 7.8 Hz, *cis* isomer), 2.62 (t, J = 7.1 Hz, *trans* isomer), 2.12 (dt, J = 18.1, 7.8 Hz, *cis* isomer), 1.94 (dt, J = 18.1, 7.8 Hz, *cis* isomer), 1.70−0.80 (m, 15H). Anal. Calcd for $C_{23}H_{29}NO_3S$: C, 69.14; H, 7.32; N, 3.51. Found: C, 69.43; H, 7.58; N, 3.44. Pure *cis*-**4bc** was obtained by repeated preparative TLC (15% ethyl acetate in hexane). *cis*-**4bc**: colorless crystals; mp 39−40 °C (recrystallized from dichloromethane−hexane); IR (KBr) 1723, 1342, 1312, 1164 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.06 (br d, J = 8.3 Hz, 2H), 7.71 (br t, J = 7.2 Hz, 1H), 7.60 (br dd, J = 8.3, 7.2 Hz, 2H), 7.35−7.17 (m, 5H), 4.18 (d, J = 7.8 Hz, 1H), 3.67 (d, J = 7.8 Hz, 1H), 2.12 (dt, J = 18.1, 7.8 Hz, 1H), 1.94 (dt, J = 18.1, 7.1 Hz, 1H), 1.63−0.90 (m, 12H), 0.86 (t, J = 6.7 Hz, 3H); MS m/z (relative intensity) 399 (1, M^+), 258 (20), 115 (100); HRMS calcd for $C_{23}H_{29}NO_3S$ (M^+) 399.1868, found 399.1845.

***N*-(2,4,6-Trimethylbenzenesulfonyl)-2-(1-oxononyl)-3-phenylaziridine (4bd):** colorless oil (*trans*:*cis* = 12:88); IR ($CHCl_3$) 1710, 1605, 1330, 1165 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35−7.15 (m, 5H), 7.01 (s, *cis* isomer), 6.91 (s, *trans* isomer), 4.30 (d, J = 4.2 Hz, *trans* isomer), 4.19 (d, J = 7.8 Hz, *cis* isomer), 3.72 (d, J = 4.2 Hz, *trans* isomer), 3.64 (d, J = 7.8 Hz, *cis* isomer), 2.79 (s, *cis* isomer), 2.62 (t, J = 7.1 Hz, *trans* isomer), 2.58 (s, *trans* isomer), 2.33 (s, *cis* isomer), 2.29 (s, *trans* isomer), 2.11 (dt, J = 17.1, 7.1 Hz, *cis* isomer), 1.92 (dt, J = 17.1, 7.1 Hz, *cis* isomer), 1.66−0.78 (m, 15H); MS m/z (relative intensity) 441 (1, M^+), 258 (100); HRMS calcd for $C_{26}H_{35}NO_3S$ (M^+) 441.2338, found 441.2333. Anal. Calcd for $C_{26}H_{35}NO_3S$: C, 70.71; H, 7.99; N, 3.17. Found: C, 70.62; H, 8.07; N, 2.91.

***N*-(Methanesulfonyl)-2-(1-oxononyl)-3-phenylaziridine (4be):** colorless plates (*trans*:*cis* = 39:61); recrystallized from dichloromethane−hexane; IR ($CHCl_3$) 1720, 1330, 1155 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.36−7.27 (m, 5H), 4.28 (d, J = 4.2 Hz, *trans* isomer), 4.13 (d, J = 8.1 Hz, *cis* isomer), 3.74 (d, J = 8.1 Hz, *cis* isomer), 3.60 (d, J = 4.2 Hz, *trans* isomer), 3.22 (s, *cis* isomer), 3.13 (s, *trans* isomer), 2.71 (t, J = 7.3 Hz, *trans* isomer), 2.24 (dt, J = 17.2, 7.4 Hz, *cis* isomer), 2.17 (dt, J = 17.2, 7.4 Hz, *cis* isomer), 1.78−0.80 (m, 15H). Anal. Calcd for $C_{18}H_{27}NO_3S$: C, 64.06; H, 8.06; N, 4.15. Found: C, 64.19; H, 8.21; N, 4.07. ***cis*-4be:** colorless plates; mp 71−73 °C (recrystallized from dichloromethane−hexane); IR (KBr) 1721, 1320, 1151 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38−7.28 (m, 5H), 4.13 (d, J = 8.1 Hz, 1H), 3.74 (d, J = 8.1 Hz, 1H), 3.22 (s, 3H), 2.24 (dt, J = 17.2, 7.4 Hz, 1H), 2.17 (dt, J = 17.2, 7.4 Hz, 1H), 1.60−0.90 (m, 12H), 0.86 (t, J = 6.7 Hz, 3H); MS m/z (relative intensity) 337 (2, M^+), 258 (100), 158 (44); HRMS calcd for $C_{18}H_{27}NO_3S$ (M^+) 337.1712, found 337.1703.

***N*-(2,4,6-Trimethylbenzenesulfonyl)-2-(2,2-dimethy1−1-oxopropyl)-3-phenylaziridine (4cd):** colorless oil (*trans*:*cis* = 16:84); IR ($CHCl_3$) 1715, 1600, 1330, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.33−7.23 (m, 5H), 6.97 (s, *cis* isomer), 6.90 (s, *trans* isomer), 4.38 (d, J = 4.2 Hz, *trans* isomer), 4.22 (d, J = 7.6 Hz, *cis* isomer), 4.06 (d, J = 7.6 Hz, *cis* isomer), 3.95 (d, J = 4.2 Hz, *trans* isomer), 2.79 (s, *cis* isomer), 2.58 (s, *trans* isomer), 2.29 (s, 3H), 1.28 (s, *trans* isomer), 0.95 (s, *cis* isomer); MS m/z (relative intensity) 385 (1, M^+), 202 (100), 160 (43); HRMS calcd for $C_{22}H_{27}NO_3S$ (M^+) 385.1712, found 385.1718.

***trans*-*N*-Carbomethoxy-2-acetyl-3-phenylaziridine (*trans*-4af):** colorless oil; IR ($CHCl_3$) 1725, 1440, 1320 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.43−7.25 (m, 5H), 3.78 (s, 3H), 3.69 (d, J = 2.4 Hz, 1H), 3.35 (d, J = 2.4 Hz, 1H), 2.39 (s, 3H); MS m/z (relative intensity) 219 (58, M^+), 176 (91), 118 (100); HRMS calcd for $C_{12}H_{13}NO_3$ (M^+) 219.0895, found 219.0898.

***trans*-*N*-Carbomethoxy-2-(1-oxononyl)-3-phenylaziridine (*trans*-4bf):** colorless oil; IR ($CHCl_3$) 1730, 1320 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.41−7.26 (m, 5H), 3.77 (s, 3H), 3.68 (d, J = 2.4 Hz, 1H), 3.32 (d, J = 2.4 Hz, 1H), 2.65 (t, J = 7.2 Hz, 2H), 1.77−1.55 (m, 2H), 1.42−1.19 (m, 10H), 0.88 (t, J = 6.8 Hz, 3H); MS m/z (relative intensity) 317 (100, M^+), 258 (34), 176 (83); HRMS calcd for $C_{19}H_{27}NO_3$ (M^+) 317.1991, found 317.1971. Anal. Calcd for $C_{19}H_{27}NO_3 \cdot 1/4H_2O$: C, 70.89; H, 8.61; N, 4.35. Found: C, 70.94; H, 8.78; N, 4.15.

***trans*-*N*-Benzoyl-2-(1-oxononyl)-3-phenylaziridine (*trans*-4bg):** colorless needles; mp 51−52 °C (recrystallized from dichloromethane−hexane); IR ($CHCl_3$) 1705, 1675, 1320 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.89 (br d, J = 8.5 Hz, 2H), 7.55−7.26 (m, 8H), 3.87 (d, J = 2.3 Hz, 1H), 3.58 (d, J = 2.3 Hz, 1H), 2.60 (t, J = 7.3 Hz, 2H), 1.75−1.45 (m, 2H), 1.40−1.10 (m, 10H), 0.87 (t, J = 6.3 Hz, 3H); MS m/z (relative intensity) 363 (23, M^+), 258 (31), 105 (100); HRMS calcd for $C_{24}H_{29}NO_2$ (M^+) 363.2198, found 363.2210. Anal. Calcd for $C_{24}H_{29}NO_2$: C, 79.30; H, 8.04; N, 3.85. Found: C, 79.50; H, 8.22; N, 3.80.

***cis*-*N*-Benzoyl-2-(1-oxononyl)-3-phenylaziridine (*cis*-4bg):** colorless needles; mp 76−77 °C (recrystallized from dichloromethane−hexane); IR ($CHCl_3$) 1715, 1675, 1280 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.08 (br d, J = 8.5 Hz, 2H), 7.60−7.26 (m, 8H), 4.02 (d, J = 7.0 Hz, 1H), 3.73 (d, J = 7.0 Hz, 1H), 2.33−2.23 (m, 2H), 1.45−0.90 (m, 12H), 0.86 (t, J = 6.7 Hz, 3H); MS m/z (relative intensity) 363 (9, M^+), 105 (100); HRMS calcd for $C_{24}H_{29}NO_2$ (M^+) 363.2198, found 363.2198.

***trans*-*N*-Benzoyl-3-(4-chlorophenyl)-2-(1-oxononyl)aziridine (*trans*-4bh):** colorless needles; mp 61−62 °C (recrystallized from dichloromethane−hexane); IR (KBr) 1709, 1673, 1328 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.87 (br d, J = 8.6 Hz, 2H), 7.56−7.20 (m, 7H), 3.85 (d, J = 2.4 Hz, 1H), 3.54 (d, J = 2.4 Hz, 1H), 2.60 (t, J = 7.3 Hz, 2H), 1.70−1.45 (m, 2H), 1.40−1.15 (m, 10H), 0.87 (t, J = 7.1 Hz, 3H); MS m/z (relative intensity) 397 (14, M^+), 105 (100); HRMS calcd for $C_{24}H_{28}ClNO_2$ (M^+) 397.1809, found 397.1810. Anal. Calcd for $C_{24}H_{28}ClNO_2$: C, 72.44; H, 7.09; N, 3.52. Found: C, 72.22; H, 7.21; N, 3.49.

***cis*-*N*-Benzoyl-3-(4-chlorophenyl)-2-(1-oxononyl)aziridine (*cis*-4bh):** white powder; mp 104−105 °C; IR (KBr) 1719, 1689, 1318, 707 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.04 (br d, J = 8.6 Hz, 2H), 7.62−7.26 (m, 7H), 3.99 (d, J = 6.8 Hz, 1H), 3.73 (d, J = 6.8 Hz, 1H), 2.36 (dt, J = 16.8, 6.8 Hz, 1H), 2.24 (dt, J = 16.8, 6.8 Hz, 1H), 1.50−0.90 (m, 12H), 0.87 (t, J = 7.1 Hz, 3H); MS m/z (relative intensity) 397 (8, M^+), 292 (10), 105 (100); HRMS calcd for $C_{24}H_{28}ClNO_2$ (M^+) 397.1809, found 397.1832.

***trans*-*N*-Carbomethoxy-2-(2,2-dimethyl-1-oxopropyl)-3-phenylaziridine (*trans*-4cf):** colorless plates; mp 110−112 °C (recrystallized from dichloromethane−hexane); IR (KBr) 1723, 1308, 1202, 1179, 1082 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.34 (br s, 5H), 3.78 (s, 3H), 3.63 (d, J = 2.4 Hz, 1H), 3.52 (d,

(26) Palladium-catalyzed reactions of *N*-(arenesulfonyl)-3-alkyl-2-vinylaziridines reveal that 2,3-*cis*-ariridines are more stable than the *trans* isomers. See: Ibuka, T.; Mimura, N.; Aoyama, H.; Akaji, M.; Ohno, H.; Miwa, Y.; Taga, T.; Nakai, K.; Tamamura, H.; Fujii, N.; Yamamoto, Y. *J. Org. Chem.* **1997**, *62*, 999.

J = 2.4 Hz, 1H), 1.23 (s, 9H); MS m/z (relative intensity) 261 (100, M^+), 246 (30), 202 (16); HRMS calcd for $C_{15}H_{19}NO_3$ (M^+) 261.1365, found 261.1358. Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 68.72; H, 7.32; N, 5.39.

***cis*-*N*-Carbomethoxy-2-(2,2-dimethyl-1-oxopropyl)-3-phenylaziridine (*cis*-4cf):** colorless oil; IR ($CHCl_3$) 1725, 1600, 1270 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40−7.26 (m, 5H), 3.95 (d, J = 7.0 Hz, 1H), 3.90 (d, J = 7.0 Hz, 1H), 3.79 (s, 3H), 0.99 (s, 9H); MS m/z (relative intensity) 261 (100, M^+), 246 (55), 202 (26); HRMS calcd for $C_{15}H_{19}NO_3$ (M^+) 261.1365, found 261.1355.

***trans*-*N*-Benzoyl-2-(2,2-dimethyl-1-oxopropyl)-3-phenylaziridine (*trans*-4cg):** colorless needles; mp 123−124 °C (recrystallized from dichloromethane−hexane); IR (KBr) 1701, 1681, 1325, 719 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.90 (br d, J = 8.5 Hz, 2H), 7.57−7.30 (m, 8H), 3.80 (d, J = 2.2 Hz, 1H), 3.78 (d, J = 2.2 Hz, 1H), 1.17 (s, 9H); MS m/z (relative intensity) 307 (39, M^+), 202 (41), 105 (100); HRMS calcd for $C_{20}H_{21}NO_2$ (M^+) 307.1572, found 307.1580. Anal. Calcd for $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56. Found: C, 78.20; H, 6.93; N, 4.48.

***cis*-*N*-Benzoyl-2-(2,2-dimethyl-1-oxopropyl)-3-phenylaziridine (*cis*-4cg):** colorless needles; mp 129−131 °C (recrystallized from dichloromethane−hexane); IR (KBr) 1708, 1684, 1323, 1088, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.06 (br d, J = 8.5 Hz, 2H), 7.60−7.20 (m, 8H), 4.06 (d, J = 6.8 Hz, 1H), 4.00 (d, J = 6.8 Hz, 1H), 0.99 (s, 9H); MS m/z (relative intensity) 307 (34, M^+), 202 (41), 105 (100); HRMS calcd for $C_{20}H_{21}NO_2$ (M^+) 307.1572, found 307.1564.

***trans*-*N*-Benzoyl-3-(4-chlorophenyl)-2-(2,2-dimethyl-1-oxopropyl)aziridine (*trans*-4ch):** colorless needles; mp 141−143 °C (recrystallized from dichloromethane−hexane); IR (KBr) 1699, 1683, 1324, 1086 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.88 (br d, J = 8.5 Hz, 2H), 7.55−7.32 (m, 7H), 3.76 (d, J = 2.4 Hz, 1H), 3.74 (d, J = 2.4 Hz, 1H), 1.16 (s, 9H); MS m/z (relative intensity) 341 (16, M^+), 236 (14), 105 (100); HRMS calcd for $C_{20}H_{20}ClNO_2$ (M^+) 341.1183, found 341.1208. Anal. Calcd for $C_{20}H_{20}ClNO_2$: C, 70.27; H, 5.90; N, 4.10. Found: C, 70.03; H, 5.97; N, 3.99.

***cis*-*N*-Benzoyl-3-(4-chlorophenyl)-2-(2,2-dimethyl-1-oxopropyl)aziridine (*cis*-4ch):** white powder; mp 110−111 °C; IR ($CHCl_3$) 1705, 1675, 1290, 1090 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.02 (br d, J = 8.6 Hz, 2H), 7.61−7.28 (m, 7H), 4.04 (d, J = 6.8 Hz, 1H), 3.98 (d, J = 6.8 Hz, 1H), 1.01 (s, 9H); MS m/z (relative intensity) 341 (16, M^+), 236 (13), 105 (100); HRMS calcd for $C_{20}H_{20}ClNO_2$ (M^+) 341.1183, found 341.1196.

***trans*-2,4-Diphenyl-5-(1-oxononyl)-2-oxazoline (*trans*-5bg):** colorless oil; IR ($CHCl_3$) 1715, 1650, 1065 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.10 (br d, J = 7.4 Hz, 2H), 7.60−7.26 (m, 8H), 5.35 (d, J = 6.8 Hz, 1H), 4.81 (d, J = 6.8 Hz, 1H), 2.70 (dt, J = 17.8, 7.6 Hz, 1H), 2.60 (dt, J = 17.8, 7.6 Hz, 1H), 1.75−1.50 (m, 2H), 1.40−1.12 (m, 10H), 0.87 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 208.9 (s), 163.8 (s), 141.5 (s), 132.0 (d), 128.9 (d), 128.6 (d), 127.9 (d), 126.9 (s), 126.6 (d), 89.6 (d), 73.8 (d), 38.7 (t), 31.8 (t), 29.4 (t) 29.2 (t), 29.1 (t), 23.0 (t), 22.6 (t), 14.1 (q); MS m/z (relative intensity) 363 (2, M^+), 250 (15), 222 (100); HRMS calcd for $C_{24}H_{29}NO_2$ (M^+) 363.2198, found 363.2220.

***trans*-4-(4-Chlorophenyl)-5-(1-oxononyl)-2-phenyl-2-oxazoline (*trans*-5bh):** colorless oil; IR ($CHCl_3$) 1715, 1645, 1060 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.09 (br d, J = 7.4 Hz, 2H), 7.63−7.44 (m, 3H), 7.34 (br d, J = 8.1 Hz, 2H), 7.28 (br d, J = 8.1 Hz, 2H), 5.34 (d, J = 6.8 Hz, 1H), 4.74 (d, J = 6.8 Hz, 1H), 2.72 (dt, J = 17.8, 7.3 Hz, 1H), 2.59 (dt, J = 17.8, 7.3 Hz, 1H), 1.75−1.52 (m, 2H), 1.43−1.15 (m, 10H), 0.87 (t, J = 7.3 Hz, 3H); MS m/z (relative intensity) 397 (9, M^+), 284 (20), 256 (100); HRMS calcd for $C_{24}H_{28}ClNO_2$ (M^+) 397.1809, found 397.1823.

***cis*-4-(4-Chlorophenyl)-5-(1-oxononyl)-2-phenyl-2-oxazoline (*cis*-5bh):** colorless oil; IR ($CHCl_3$) 1710, 1645, 1080 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.10 (br d, J = 7.4 Hz, 2H), 7.63−7.45 (m, 3H), 7.28 (br d, J = 8.3 Hz, 2H), 7.12 (br d, J = 8.3 Hz, 2H), 5.71 (d, J = 11.0 Hz, 1H), 5.25 (d, J = 11.0 Hz, 1H), 2.25 (ddd, J = 17.8, 7.8, 6.4 Hz, 1H), 1.94 (ddd, J = 17.8, 7.3, 6.5 Hz, 1H), 1.66−0.80 (m, 15H); MS m/z (relative intensity) 397 (12, M^+), 256 (100), 227 (58), 153 (59); HRMS calcd for $C_{24}H_{28}ClNO_2$ (M^+) 397.1809, found 397.1801.

***trans*-5-(2,2-Dimethyl-1-oxopropyl)-2,4-diphenyl-2-oxazoline (*trans*-5cg):** colorless plates; mp 122−123 °C (recrystallized from dichloromethane−hexane); IR (KBr) 1708, 1655, 1061, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.06 (br d, J = 7.4 Hz, 2H), 7.60−7.25 (m, 8H), 5.41 (d, J = 6.8 Hz, 1H), 5.16 (d, J = 6.8 Hz, 1H), 1.24 (s, 9H); MS (CI, isobutene) m/z (relative intensity) 308 (100, $M^+ + 1$), 250 (60).

***trans*-4-(4-Chlorophenyl)-5-(2,2-dimethyl-1-oxopropyl)-2-phenyl-2-oxazoline (*trans*-5ch):** colorless oil; IR ($CHCl_3$) 1710, 1645, 1060 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.05 (br d, J = 7.4 Hz, 2H), 7.60−7.22 (m, 7H), 5.41 (d, J = 7.1 Hz, 1H), 5.07 (d, J = 7.1 Hz, 1H), 1.24 (s, 9H); MS (CI, isobutene) m/z (relative intensity) 342 (100, $M^+ + 1$), 284 (45).

Methyl *N*-(1-Ethoxy-1-phenylmethyl)carbamate (6f): colorless needles; mp 60−61 °C (recrystallized from dichloromethane−hexane); IR (KBr) 1703, 1543, 1263 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.50−7.27 (m, 5H), 5.97 (br d, J = 10.0 Hz, 1H), 5.36 (br d, J = 10.0 Hz, 1H), 3.87−3.46 (m, 2H), 3.73 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H).

***N*-(1-Ethoxy-1-phenylmethyl)benzamide (6g):** colorless needles; mp 97−98 °C (recrystallized from dichloromethane−hexane, lit.[27] mp 87−88 °C); ^1H NMR ($CDCl_3$) δ 7.81 (br d, J = 7.4 Hz, 2H), 7.60−7.25 (m, 8H), 6.65 (br d, J = 9.4 Hz, 1H), 6.47 (d, J = 9.4 Hz, 1H), 3.86 (dq, J = 9.5, 7.1 Hz, 1H), 3.73 (dq, J = 9.5, 7.1 Hz, 1H), 1.31 (t, J = 7.1 Hz, 3H).

***N*-[1-(4-Chlorophenyl)-1-ethoxymethyl]benzamide (6h):** white powder; IR (KBr) 1641, 1520, 1090 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.81 (br d, J = 7.5 Hz, 2H), 7.60−7.26 (m, 7H), 6.60 (br d, J = 9.4 Hz, 1H), 6.47 (d, J = 9.4 Hz, 1H), 3.86 (dq, J = 9.6, 7.1 Hz, 1H), 3.71 (dq, J = 9.6, 7.1 Hz, 1H), 1.30 (t, J = 7.1 Hz, 3H).

(*E*)-10-Eicosene-9,12-dione ((*E*)-7): colorless crystals; mp 68−70 °C (recrystallized from methanol−dichloromethane); IR ($CHCl_3$) 1680, 1250, 1175, 980 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.87 (s, 2H), 2.64 (t, J = 7.3 Hz, 4H), 1.72−1.50 (m, 4H), 1.41−1.18 (m, 20H), 0.88 (t, J = 6.8 Hz, 6H); MS m/z (relative intensity) 308 (13, M^+), 237 (28), 167 (100); HRMS calcd for $C_{20}H_{36}O_2$ (M^+) 308.2715, found 308.2692.

(*Z*)-10-Eicosene-9,12-dione ((*Z*)-7): colorless crystals; IR ($CHCl_3$) 1690, 1600, 1390 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.30 (s, 2H), 2.53 (t, J = 7.3 Hz, 4H), 1.71−1.49 (m, 4H), 1.40−1.12 (m, 20H), 0.88 (t, J = 6.8 Hz, 6H); MS m/z (relative intensity) 308 (1, M^+), 237 (27), 167 (50), 97 (100); HRMS calcd for $C_{20}H_{36}O_2$ (M^+) 308.2715, found 308.2731.

General Procedure for Synthesis of 2-Acylaziridines 4 in THF. A Typical Example (Table 2, Entry 18): *N*-(Benzensulfonyl)-2-(1-oxononyl)-3-phenylaziridine (4bc). To a stirred solution of (*Z*)-(2-acetoxy-1-decenyl)iodonium bromide (**1b**: X = Br, 30 mg, 0.062 mmol) and *N*-(benzenesulfonyl)benzaldimine (**3c**) (23 mg, 0.094 mmol) in THF (6 mL) was added a 0.43 M THF solution of EtOLi (0.14 mL, 0.062 mmol) at −78 °C under argon. After being stirred for 2 h at −78 °C, the reaction mixture was allowed to warm to room temperature during 8 h, quenched with water, and extracted with diethyl ether. The organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The *trans*:*cis* ratio of 2-acylaziridines **4bc** was determined to be 31:69 by ^1H NMR of the crude reaction mixture. Preparative TLC (15% ethyl acetate in hexane) of the crude material using silica gel gave a mixture of *trans*- and *cis*-**4bc** (18.1 mg, 73%).

***trans*-*N*-(2,4,6-Trimethylbenzenesulfonyl)-2-(1-oxopropyl)-3-phenylaziridine (*trans*-4ad):** colorless needles; mp 74−75 °C (recrystallized from dichloromethane−hexane); IR ($CHCl_3$) 1720, 1605, 1330, 1165 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35−7.19 (m, 5H), 6.92 (s, 2H), 4.31 (d, J = 4.2 Hz, 1H), 3.72 (d, J = 4.2 Hz, 1H), 2.58 (s, 6H), 2.36 (s, 3H), 2.30 (s, 3H); MS m/z (relative intensity) 343 (1, M^+), 160 (100), 118 (92); HRMS calcd for $C_{19}H_{21}NO_3S$ (M^+) 343.1242, found 343.1243.

***cis*-*N*-(2,4,6-Trimethylbenzenesulfonyl)-2-(1-oxopropyl)-3-phenylaziridine (*cis*-4ad):** colorless oil; IR ($CHCl_3$) 1705, 1600, 1330, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.34−7.15 (m, 5H),

(27) Breuer, S. W.; Bernath, T.; Ben-Ishai, D. *Tetrahedron* **1967**, *23*, 2869.

7.02 (s, 2H), 4.20 (d, J = 7.8 Hz, 1H), 3.63 (d, J = 7.8 Hz, 1H), 2.79 (s, 6H), 2.34 (s, 3H), 1.74 (s, 3H); MS *m/z* (relative intensity) 343 (<1, M^+), 160 (100), 118 (87); HRMS calcd for $C_{19}H_{21}NO_3S$ (M^+) 343.1242, found 343.1248.

***N*-(4-Methoxybenzenesulfonyl)-2-(1-oxononyl)-3-phenylaziridine (4bi):** colorless crystals (*trans:cis* = 27:73); recrystallized from dichloromethane−hexane; IR (KBr) 1726, 1595, 1340, 1265, 1150 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.97 (br d, J = 8.8 Hz, *cis* isomer), 7.75 (br d, J = 8.8 Hz, *trans* isomer), 7.37−7.16 (m, 5H), 7.04 (br d, J = 8.8 Hz, *cis* isomer), 6.92 (br d, J = 8.8 Hz, *trans* isomer), 4.24 (d, J = 4.2 Hz, *trans* isomer), 4.12 (d, J = 7.8 Hz, *cis* isomer), 3.89 (s, *cis* isomer), 3.86 (s, *trans* isomer), 3.71 (d, J = 4.2 Hz, *trans* isomer), 3.61 (d, J = 7.8 Hz, *cis* isomer), 2.62 (t, J = 7.1 Hz, *trans* isomer), 2.13 (ddd, J = 17.6, 7.8, 6.6 Hz, *cis* isomer), 1.92 (dt, J = 17.6, 7.3 Hz, *cis* isomer), 1.68−0.78 (m, 15H); MS *m/z* (relative intensity) 429 (1, M^+), 258 (100); HRMS calcd for $C_{24}H_{31}NO_4S$ (M^+) 429.1974, found 429.1980. Anal. Calcd for $C_{24}H_{31}NO_4S$: C, 67.10; H, 7.27; N, 3.26. Found: C, 66.88; H, 7.20; N, 3.37.

***N*-(4-Methylbenzenesulfonyl)-2-(1-oxononyl)-3-phenylaziridine (4bj):** colorless leaflets (*trans:cis* = 32:68); recrystallized from dichloromethane−hexane; IR (KBr) 1724, 1341, 1156 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.93 (br d, J = 8.3 Hz, *cis* isomer), 7.72 (br d, J = 8.3 Hz, *trans* isomer), 7.42−7.22 (m, 7H), 4.27 (d, J = 4.2 Hz, *trans* isomer), 4.14 (d, J = 7.8 Hz, *cis* isomer), 3.72 (d, J = 4.2 Hz, *trans* isomer), 3.67 (d, J = 7.8 Hz, *cis* isomer), 2.61 (t, J = 7.1 Hz, *trans* isomer), 2.46 (s, *cis* isomer), 2.41 (s, *trans* isomer), 2.12 (dt, J = 17.6, 7.6 Hz, *cis* isomer), 1.92 (dt, J = 17.6, 7.6 Hz, *cis* isomer), 1.70−0.73 (m, 15H); MS *m/z* (relative intensity) 413 (1, M^+), 258 (100); HRMS calcd for $C_{24}H_{31}NO_3S$ (M^+) 413.2025, found 413.2035. Anal. Calcd for $C_{24}H_{31}NO_3S$: C, 69.70; H, 7.55; N, 3.39. Found: C, 69.44; H, 7.50; N, 3.23.

***N*-(4-Chlorobenzenesulfonyl)-2-(1-oxononyl)-3-phenylaziridine (4bk):** colorless crystals (*trans:cis* = 35:65); recrystallized from dichloromethane−hexane; IR ($CHCl_3$) 1710, 1580, 1335, 1165 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.00 (br d, J = 8.6 Hz, *cis* isomer), 7.77 (br d, J = 8.6 Hz, *trans* isomer), 7.57 (br d, J = 8.6 Hz, *cis* isomer), 7.44 (br d, J = 8.6 Hz, *trans* isomer), 7.38−7.15 (m, 7H), 4.29 (d, J = 4.1 Hz, *trans* isomer), 4.19 (d, J = 8.0 Hz, *cis* isomer), 3.73 (d, J = 4.1 Hz, *trans* isomer), 3.70 (d, J = 8.0 Hz, *cis* isomer), 2.62 (t, J = 7.1 Hz, *trans* isomer), 2.12 (dt, J = 17.3, 7.3 Hz, *cis* isomer), 1.97 (dt, J = 17.3, 7.3 Hz, *cis* isomer), 1.70−0.75 (m, 15H); MS *m/z* (relative intensity) 433 (4, M^+), 258 (100), 158 (31); HRMS calcd for $C_{23}H_{28}ClNO_3S$ (M^+) 433.1478, found 433.1476. Anal. Calcd for $C_{23}H_{28}ClNO_3S$: C, 63.65; H, 6.50; N, 3.23. Found: C, 63.30; H, 6.54; N, 3.13.

***N*-(2-Naphthalenesulfonyl)-2-(1-oxononyl)-3-phenylaziridine (4bl):** colorless oil (*trans:cis* = 35:65); IR ($CHCl_3$) 1710, 1330, 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.59 (s, *cis* isomer), 8.31 (s, *trans* isomer), 8.07−7.54 (m, 6H), 7.35−7.18 (m, 5H), 4.33 (d, J = 4.2 Hz, *trans* isomer), 4.24 (d, J = 8.1 Hz, *cis* isomer), 3.80 (d, J = 4.2 Hz, *trans* isomer), 3.73 (d, J = 8.1 Hz, *cis* isomer), 2.64 (t, J = 6.8 Hz, *trans* isomer), 2.12 (dt, J = 17.5, 6.6 Hz, *cis* isomer), 1.94 (dt, J = 17.5, 6.8 Hz, *cis* isomer), 1.70−0.76 (m, 15H); MS *m/z* (relative intensity) 449 (1, M^+), 258 (64), 158 (100); HRMS calcd for $C_{27}H_{31}NO_3S$ (M^+) 449.2025, found 449.2044. Anal. Calcd for $C_{27}H_{31}NO_3S$: C, 72.13; H, 6.95; N, 3.12. Found: C, 71.79; H, 7.10; N, 2.90.

***N*-(2,4,6-Trimethylbenzenesulfonyl)-3-(4-methylphenyl)-2-(1-oxononyl)aziridine (4bm):** colorless oil (*trans:cis* = 18:82); IR ($CHCl_3$) 1705, 1600, 1330, 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.20−7.04 (4H), 7.00 (s, *cis* isomer), 6.91 (s, *trans* isomer), 4.24 (d, J = 4.2 Hz, *trans* isomer), 4.14 (d, J = 7.8 Hz, *cis* isomer), 3.74 (d, J = 4.2 Hz, *trans* isomer), 3.62 (d, J = 7.8 Hz, *cis* isomer), 2.78 (s, *cis* isomer), 2.64−2.60 (*trans* isomer), 2.58 (s, *trans* isomer), 2.32 (s, *cis* isomer), 2.28 (s, *cis* isomer), 2.12 (dt, J = 17.3, 7.6 Hz, *cis* isomer), 1.94 (dt, J = 17.3, 7.6 Hz, *cis* isomer), 1.63−0.78 (m, 15H); MS *m/z* (relative intensity) 455 (14, M^+), 357 (10), 272 (100); HRMS calcd for $C_{27}H_{37}NO_3S$ (M^+) 455.2494, found 455.2476. Anal. Calcd for $C_{27}H_{37}NO_3S$: C, 71.17; H, 8.18; N, 3.07. Found: C, 70.94; H, 8.12; N, 2.87.

***N*-(2,4,6-Trimethylbenzenesulfonyl)-3-(4-chlorophenyl)-2-(1-oxononyl)aziridine (4bn):** colorless oil (*trans:cis* = 18:82); IR ($CHCl_3$) 1700, 1590, 1320, 1150 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.30−7.12 (4H), 7.01 (s, *cis* isomer), 6.92 (s, *trans* isomer), 4.25 (d, J = 3.9 Hz, *trans* isomer), 4.13 (d, J = 7.8 Hz, *cis* isomer), 3.67 (d, J = 3.9 Hz, *trans* isomer), 3.64 (d, J = 7.8 Hz, *cis* isomer), 2.78 (s, *cis* isomer), 2.60 (t, J = 7.3 Hz, *trans* isomer), 2.58 (s, *trans* isomer), 2.33 (s, *cis* isomer), 2.29 (s, *trans* isomer), 2.13 (dt, J = 17.6, 7.1 Hz, *cis* isomer), 1.98 (dt, J = 17.6, 7.1 Hz, *cis* isomer), 1.64−0.80 (m, 15H); MS *m/z* (relative intensity) 475 (<1, M^+), 292 (100); HRMS calcd for $C_{26}H_{34}ClNO_3S$ (M^+) 475.1948, found 475.1923. Anal. Calcd for $C_{26}H_{34}ClNO_3S$: C, 65.60; H, 7.20; N, 2.94. Found: C, 65.44; H, 7.18; N, 2.83.

***N*-(Benzenesulfonyl)-3-(1-naphthyl)-2-(1-oxononyl)aziridine (4bo):** colorless oil (*trans:cis* = 45:55); IR ($CHCl_3$) 1705, 1330, 1165 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.15−7.21 (m, 12H), 4.81 (d, J = 4.4 Hz, *trans* isomer), 4.60 (d, J = 7.8 Hz, *cis* isomer), 3.90 (d, J = 7.8 Hz, *cis* isomer), 3.82 (d, J = 4.4 Hz, *trans* isomer), 2.85−2.67 (m, *trans* isomer), 2.17−1.97 (m, *cis* isomer), 1.84−1.53 (m), 1.42−0.48 (m); MS *m/z* (relative intensity) 449 (4, M^+), 308 (32), 168 (100); HRMS calcd for $C_{27}H_{31}NO_3S$ (M^+) 449.2025, found 449.2028. Anal. Calcd for $C_{27}H_{31}NO_3S$: C, 72.13; H, 6.95; N, 3.12. Found: C, 71.76; H, 6.93; N, 3.05.

***N*-(Benzenesulfonyl)-3-(2-naphthyl)-2-(1-oxononyl)aziridine (4bp):** pale yellow oil (*trans:cis* = 31:69); IR ($CHCl_3$) 1710, 1330, 1165 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.09 (br d, J = 8.5 Hz, *cis* isomer), 7.86−7.26 (m), 4.45 (d, J = 4.2 Hz, *trans* isomer), 4.33 (d, J = 7.8 Hz, *cis* isomer), 3.85 (d, J = 4.2 Hz, *trans* isomer), 3.74 (d, J = 7.8 Hz, *cis* isomer), 2.67 (t, J = 7.2 Hz, *trans* isomer), 2.12 (dt, J = 17.5, 7.1 Hz, *cis* isomer), 1.96 (dt, J = 17.5, 7.1 Hz, *cis* isomer), 1.72- -0.69 (m, 15H); MS *m/z* (relative intensity) 449 (14, M^+), 308 (100), 168 (95); HRMS calcd for $C_{27}H_{31}NO_3S$ (M^+) 449.2025, found 449.2017. Anal. Calcd for $C_{27}H_{31}NO_3S$: C, 72.13; H, 6.95; N, 3.12. Found: C, 71.78; H, 7.08; N, 2.96.

***N*-(2,4,6-Trimethylbenzenesulfonyl)-3-(2-naphthyl)-2-(1-oxononyl)aziridine (4bq):** colorless oil (*trans:cis* = 14:86); IR ($CHCl_3$) 1705, 1600, 1330, 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.87−7.64 (m, 4H), 7.53−7.40 (m, 2H), 7.35−7.26 (m, 1H), 7.03 (s, *cis* isomer), 6.89 (s, *trans* isomer), 4.45 (d, J = 3.9 Hz, *trans* isomer), 4.33 (d, J = 7.8 Hz, *cis* isomer), 3.83 (d, J = 3.9 Hz, *trans* isomer), 3.72 (d, J = 7.8 Hz, *cis* isomer), 2.82 (s, *cis* isomer), 2.72−2.64 (m, *trans* isomer), 2.56 (s, *trans* isomer), 2.33 (s, *cis* isomer), 2.28 (s, *trans* isomer), 2.12 (dt, J = 17.3, 7.3 Hz, *cis* isomer), 1.94 (dt, J = 17.3, 7.3 Hz, *cis* isomer), 1.70−0.70 (m, 15H); MS *m/z* (relative intensity) 491 (3, M^+), 308 (100), 168 (79); HRMS calcd for $C_{30}H_{37}NO_3S$ (M^+) 491.2494, found 491.2475. Anal. Calcd for $C_{30}H_{37}NO_3S$: C, 73.28; H, 7.58; N, 2.85. Found: C, 73.01; H, 7.59; N, 2.74.

***trans*-*N*-(2,4,6-Trimethylbenzenesulfonyl)-3-(1,1-dimethylethyl)-2-(1-oxononyl)aziridine (*trans*-4br):** colorless oil; IR (film) 1723, 1605, 1328, 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.94 (s, 2H), 3.27 (d, J = 4.3 Hz, 1H), 3.16 (d, J = 4.3 Hz, 1H), 2.82−2.67 (m, 2H), 2.69 (s, 6H), 2.30 (s, 3H), 1.77−1.51 (m, 2H), 1.40−1.18 (m, 10H), 0.88 (t, J = 6.4 Hz, 3H), 0.75 (s, 9H); MS *m/z* (relative intensity) 421 (12, M^+), 238 (35), 182 (100); HRMS calcd for $C_{24}H_{39}NO_3S$ (M^+) 421.2651, found 421.2619.

***cis*-*N*-(2,4,6-Trimethylbenzenesulfonyl)-3-(1,1-dimethylethyl)-2-(1-oxononyl)aziridine (*cis*-4br):** colorless oil; IR (film) 1716, 1604, 1329, 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.00 (s, 2H), 3.22 (d, J = 8.0 Hz, 1H), 2.83−2.27 (m, 2H), 2.75 (s, 6H), 2.73 (d, J = 8.0 Hz, 1H), 2.32 (s, 3H), 1.53−1.06 (m, 12H), 0.88 (t, J = 6.4 Hz, 3H), 0.79 (s, 9H); MS *m/z* (relative intensity) 421 (37, M^+), 238 (78), 182 (85), 57 (100); HRMS calcd for $C_{24}H_{39}NO_3S$ (M^+) 421.2651, found 421.2615.

***N*-(2,4,6-Trimethylbenzenesulfonyl)-2-(2,2-dimethyl-1-oxopropyl)-3-(4-methylphenyl)aziridine (4cm):** colorless oil (*trans:cis* = 6:94); IR ($CHCl_3$) 1710, 1600, 1325, 1155 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.21−7.0 (4H), 6.96 (s, *cis* isomer), 6.89 (s, *trans* isomer), 4.33 (d, J = 4.4 Hz, *trans* isomer), 4.18 (d, J = 7.6 Hz, *cis* isomer), 4.05 (d, J = 7.6 Hz, *cis* isomer), 3.97 (d, J = 4.4 Hz, *trans* isomer), 2.78 (s, *cis* isomer), 2.57 (s, *trans* isomer), 2.29 (s, *cis* isomer), 2.28 (s, *cis* isomer), 1.27 (s, *trans* isomer), 0.96 (s, *cis* isomer); MS *m/z* (relative intensity) 399

(<1, M^+), 216 (100); HRMS calcd for $C_{23}H_{29}NO_3S$ (M^+) 399.1868, found 399.1839.

***N*-(2,4,6-Trimethylbenzenesulfonyl)-3-(4-chlorophenyl)-2-(2,2-dimethyl-1-oxopropyl)aziridine (4cn):** colorless oil (*trans:cis* = 3:97); IR ($CHCl_3$) 1710, 1600, 1325, 1155 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.30−7.15 (4H), 6.97 (s, *cis* isomer), 6.91 (s, *trans* isomer), 4.36 (d, J = 3.9 Hz, *trans* isomer), 4.17 (d, J = 7.6 Hz, *cis* isomer), 4.05 (d, J = 7.6 Hz, *cis* isomer), 3.91 (d, J = 3.9 Hz, *trans* isomer), 2.77 (s, *cis* isomer), 2.57 (s, *trans* isomer), 2.30 (s, 3H), 1.27 (s, *trans* isomer), 0.97 (s, *cis* isomer); MS *m/z* (relative intensity) 419 (<1, M^+), 236 (100), 194 (41); HRMS calcd for $C_{22}H_{26}ClNO_3S$ (M^+) 419.1322, found 419.1310.

General Procedure for the Competition Experiments. To a stirred solution of the iodonium bromide **1b** (X = Br, 30 mg, 0.062 mmol) in THF (4 mL) was added a 0.43 M THF solution of EtOLi (0.14 mL, 0.062 mmol) at −78 °C under argon, and the mixture was stirred for 5 min. After addition of a solution of *N*-(benzenesulfonyl)benzaldimine (**3c**) (153 mg, 0.623 mmol) and a substituted *N*-sulfonylbenzaldimine (0.623 mmol) in THF (2 mL), the mixture was stirred for 1 h at −78 °C. The reaction mixture was allowed to warm to room temperature during 8 h, quenched with water, and extracted with diethyl ether. The organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Preparative TLC (15% ethyl acetate in hexane) gave a mixture of *trans*- and *cis*-2-acylaziridines **4**, which was analyzed by ^1H NMR. The results are reported in Table 3.

Reaction of 1b-α*d* with *N*-(Benzenesulfonyl)benzaldimine (3c). The α-deuterated vinyliodonium bromide **1b**-α*d* (X = Br, >99% D) was prepared from 1-decynyl(phenyl)-iodonium tetrafluoroborate[22] by Michael addition of AcOD according to literature procedure.[4] To a stirred solution of **1b**-α*d* (X = Br, 30 mg, 0.062 mmol) and *N*-sulfonylimine **3c** (23 mg, 0.094 mmol) in THF−DMSO (12:1, 6.5 mL) were added EtOH (14 mg, 0.31 mmol) and a 0.43 M THF solution of EtOLi (0.14 mL, 0.062 mmol) at −30 °C under argon. The reaction was allowed to proceed at −30 °C for 2 h. Preparative TLC (15% ethyl acetate in hexane) of the crude mixture gave a 55:45 mixture of *trans*- and *cis*-2-acylaziridines **4bc**-α*d* (84% D) in 59% yield.

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