JOC The Journal of Organic Chemistry
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pubs.acs.org/joc

$P(NMe_2)_3$-Mediated Aziridination of Imines with α-Ketoesters for Synthesis of Aziridine-2-carboxylates

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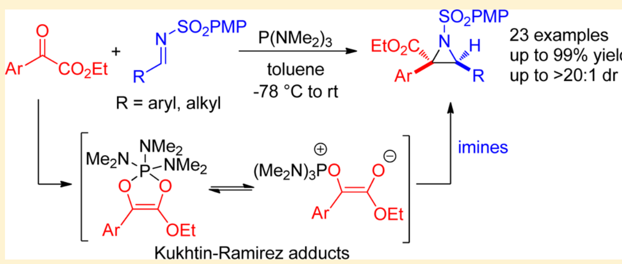
Supporting Information

ABSTRACT: Aziridination of *N*-sulfonyl imines with α-ketoesters in the presence of $P(NMe_2)_3$ is reported. Adducts derived from trivalent phosphorus reagents and α-ketoesters are effectively intercepted by imines, affording a range of aziridine-2-carboxylates. The diastereoselectivity of the reaction depends on steric hindrance from substituents on the substrates.

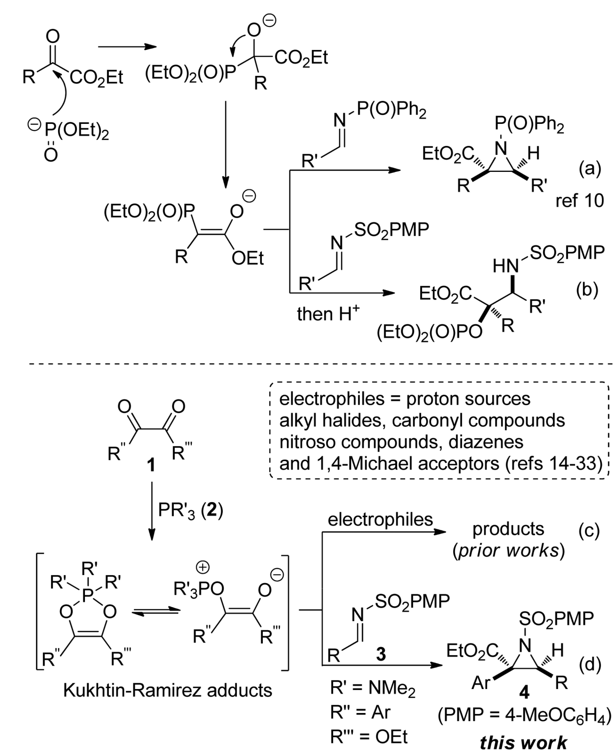


Aziridines are important structural units presented in bioactive agents and also serve as precursors for the construction of other useful nitrogen-containing compounds via ring cleavage reactions.[1−4] Synthesis of aziridines typically involves intramolecular cyclization of amine derivatives, transfer of nitrogen to olefins, and transfer of carbon to imines. Among these synthetic strategies, imine aziridination reactions are mainly realized via direct cyclization of imines with carbenes or by 1,2-addition of nucleophiles bearing α-leaving groups to imines followed by ring closure. For the addition/cyclization transformations, suitable nucleophiles include ylides, α-diazocarbonyl compounds, and Darzens or Darzens-like reagents.[5−8]

Recently, we reported that in situ formed Darzens-like reactive intermediates from α-ketoesters and deprotonated phosphites react with aldehydes and imines via addition/cyclization cascade, giving the corresponding epoxides and aziridines.[9,10] During our studies on phosphite-initiated aziridination of imines with α-ketoesters, we found that imines with *N*-sulfonyl substitutions (Ts or $PMPSO_2$) do not show identical reactivity with *N*-diphenylphosphinyl imines that undergo aziridination by α-phosphonyloxy enolate via aza-Darzens reaction (Scheme 1a). Instead, these *N*-sulfonyl imines undergo Mannich addition to give α-phosphonyloxy-β-amino esters (Scheme 1b).[10] As we failed in our efforts to use phosphite to promote aziridination of *N*-sulfonyl imines with α-ketoesters, we speculated that we might achieve this transformation using trivalent phosphorus reagents in a polar-reversal strategy involving the keto group (Scheme 1d).

Adding trivalent phosphorus reagents to 1,2-dicarbonyl compounds generates Kukhtin−Ramirez adducts, which are normally depicted as dioxaphospholenes or the equivalent oxyphosphonium enolates.[11−13] These dipolar adducts are reactive intermediates that undergo nucleophilic addition to a range of electrophiles including proton sources,[14−17] alkyl halides,[18] carbonyl compounds,[19−24] nitroso compounds,[25] diazenes,[26] and 1,4-Michael acceptors[27−33] (Scheme 1c).

Scheme 1. Imine Aziridination by Kukhtin−Ramirez Adducts



Received: November 4, 2016
Published: December 12, 2016

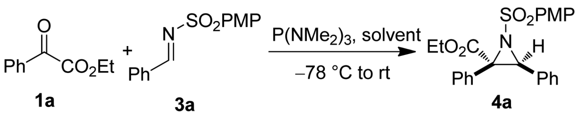
DOI: 10.1021/acs.joc.6b02669
J. Org. Chem. 2017, 82, 811−818

Kukhtin–Ramirez adducts react with carbonyl compounds to form epoxidation products,[19−24] similar to the products formed by Darzens reagents.[34,35]

We predicted that we could use azomethines to trap the zwitterion intermediates in an aza-Darzens-like transformation of Kukhtin–Ramirez adducts (Scheme 1d).[36−38] Such an approach could provide efficient access to aziridine-2-carboxylates, which are important precursors in the synthesis of useful nitrogen-containing compounds.[39−41]

First we examined the reactivity of *N-para*-methoxyphenylsulfonyl (*N*-SO$_2$PMP) imines under conditions of Kukhtin–Ramirez-like condensation. To our delight, the commonly used phosphorus(III) reagent P(NMe$_2$)$_3$ effectively promoted aziridination of the *N*-sulfonyl imine by *α*-ketoester: in the presence of P(NMe$_2$)$_3$ (2.0 equiv), ethyl benzoylformate (**1a**, 2.0 equiv), and *N*-benzylidene-4-methoxybenzenesulfonamide (**3a**, 1.0 equiv) in THF generated aziridine **4a** in 87% yield with 90:10 dr (Scheme 2). Screening solvents showed that both

Scheme 2. Initial Results for the Coupling of *α*-Ketoesters with *N*-Sulfonyl Imines



solvent	THF	CH_2Cl_2	Et_2O	toluene
dr	90:10	69:31	94:6	94:6

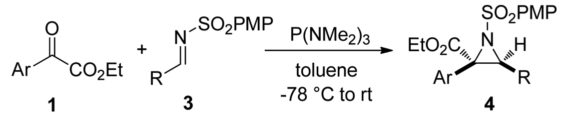
toluene and Et$_2$O raised the diastereoselectivity ratio to 94:6, compared to 69:31 in dicholoromethane. Toluene was chosen as solvent because of the low solubility of imine in ether.

Diastereocontrol was further improved by using an imine with a bulky *N*-sulfonyl substitution: 4-MeC$_6$H$_4$C═NSO$_2$*t*-Bu underwent aziridination in THF, giving the corresponding products in 99% yield with 30:1 dr, albeit as an inseparable mixture of diastereomers. Since most of the *N*-SO$_2$PMP aziridines described here can be obtained as pure diastereomers via silica gel chromatography, we used *N*-SO$_2$PMP imines to investigate the imine substrate scope of our reaction. Activated imines with electron-withdrawing *N*-substitutions such as, diphenylphosphinyl (DPP) and *tert*-butoxycarbonyl (Boc), were suitable substrates for aziridination. In dichloromethane, *p*-MeC$_6$H$_4$CH═NP(O)Ph$_2$ gave the corresponding *trans*-aziridine in 94% yield with 19:1 dr, while PhCH═NC(O)O*t*-Bu gave the *trans*-aziridine in 86% yield with 1.6:1 dr. The dr for these imines was not optimized further.

Chiral *N*-sulfinyl imines such as (R_S)-PhCH═NS(O)*t*-Bu and *N*-aryl imines, such as PhCH═NPMP, were inert under our reaction conditions. Instead, Kukhtin–Ramirez adducts caused epoxidation of the keto group in the *α*-ketoester.[30]

Using optimal reaction conditions, various *N*-SO$_2$PMP imines and *α*-ketoesters were used in the P(NMe$_2$)$_3$-mediated coupling reaction (Table 1). In most cases, the desired products were obtained in high yields. Steric hindrance due to substituents on these substrates significantly influenced the diastereoselectivity of the aziridination products. *N*-SO$_2$PMP imines derived from *ortho*-substituted aryl aldehydes gave diastereoselectivities up to 99:1 dr (Table 1, entries 5 and 9), while aryl *α*-ketoesters containing *ortho*-substituted aryl groups gave desired products in low yields of 15% for **4p** and 47% for **4t** (entries 16 and 20), with poor diastereocontrol involving inversion of the configuration of the major **4p** diastereomer.[42]

Table 1. P(NMe$_2$)$_3$-Mediated Reaction of *N*-SO$_2$PMP Imines and *α*-Ketoesters[a]



entry	ketoester **1** (Ar)	imine **3** (R)	**4**, yield(%)[b], dr[c]
1	**1a** (Ph)	**3a** (Ph)	**4a**, 87(83)[d], 94:6(94:6)[d]
2	**1a** (Ph)	**3b** (4-MeOC$_6$H$_4$)	**4b**, 91, 97:3
3	**1a** (Ph)	**3c** (4-MeC$_6$H$_4$)	**4c**, 90, 96:4
4	**1a** (Ph)	**3d** (3-MeC$_6$H$_4$)	**4d**, 89, 93:7
5	**1a** (Ph)	**3e** (2-MeC$_6$H$_4$)	**4e**, 99, > 99:1
6	**1a** (Ph)	**3f** (4-BrC$_6$H$_4$)	**4f**, 87, 89:11
7	**1a** (Ph)	**3g** (4-ClC$_6$H$_4$)	**4g**, 82, 88:12
8	**1a** (Ph)	**3h** (2-thienyl)	**4h**, 52, 87:13
9	**1a** (Ph)	**3i** (1-naphthyl)	**4i**, 88, 99:1
10	**1a** (Ph)	**3j** (*i*-butyl)[e]	**4j**, 35, 36:64
11	**1a** (Ph)	**3k** (cyclohexyl)[f]	**4k**, 44, 45:55
12	**1a** (Ph)	**3l** (*t*-Bu)[f]	**4l**, 71, 95:5
13	**1b** (4-MeOC$_6$H$_4$)	**3a** (Ph)	**4m**, 62, 63:37
14	**1c** (4-MeC$_6$H$_4$)	**3a** (Ph)	**4n**, 80, 85:15
15	**1d** (3-MeC$_6$H$_4$)	**3a** (Ph)	**4o**, 90, 92:8
16	**1e** (2-MeC$_6$H$_4$)	**3a** (Ph)	**4p**, 15, 27:73
17	**1f** (4-BrC$_6$H$_4$)	**3a** (Ph)	**4q**, 97, 98:2
18	**1g** (4-ClC$_6$H$_4$)	**3a** (Ph)	**4r**, 93, 97:3
19	**1h** (3-ClC$_6$H$_4$)	**3a** (Ph)	**4s**, 96, 97:3
20	**1i** (2-ClC$_6$H$_4$)	**3a** (Ph)	**4t**, 47, 55:45
21	**1j** (2-naphthyl)	**3a** (Ph)	**4u**, 93, 94:6
22	**1g** (4-ClC$_6$H$_4$)	**3g** (4-ClC$_6$H$_4$)	**4v**, 94[g], 91:9
23	**1g** (4-ClC$_6$H$_4$)	**3c** (4-MeC$_6$H$_4$)	**4w**, 95, 98:2

[a]**1** (0.80 mmol), **3** (0.40 mmol), and P(NMe$_2$)$_3$ (0.80 mmol) in anhydrous toluene under argon unless otherwise noted. [b]Isolated yield of *trans* products. [c]Ratios of *trans*/*cis* products were determined by ^{1}H NMR analysis of crude reaction mixtures. [d]1.46-g synthesis of **4a**. [e]The corresponding *α*-amido sulfone was used. [f]*N*-Ts imine was used. [g]Isolated yield of a diastereomer mixture.

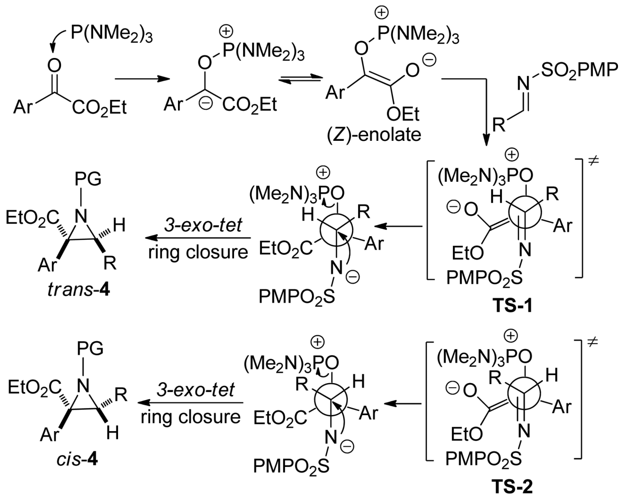
Alkyl *N*-Ts imines were suitable coupling partners, although low to moderate product yields were achieved (entries 10−12). We failed in our attempts to extend the reaction to alkyl-substituted *α*-ketoesters, such as ethyl 2-cyclohexyl-2-oxoacetate and ethyl pyruvate; in these cases, no desired aziridination products were observed.

The relative configuration of aziridine-2-carboxylate **4c** was assigned to be *trans* by X-ray crystallographic analysis,[43] and the configurations of other products were assigned by analogy. We propose the following rationalization for the observed stereoselectivity of C−C bond formation by (*E*)-imine and (*Z*)-enolate[44] generated through oxophilic addition of P(NMe$_2$)$_3$ to *α*-ketoesters. Transition state **TS-1** minimizes repulsion among the R group of the imine and the oxyphosphonium and ester groups of the enolate (Scheme 3). Subsequent intramolecular substitution of the resulting zwitterion causes 3-*exo-tet* ring closure, providing the *trans*-aziridine product. Consistent with this stereochemical rationalization, we observed excellent *trans*-selectivity for products derived from imines with a sterically hindered R group (Table 1, entries 5 and 9). In contrast, when the enolate carries a bulky aryl group, the reaction pathway tends to proceed via transition state **TS-2** to afford *cis*-product, reducing dr. This was the case for products **4p** and **4t**.

We demonstrated the different reactivity of *N-para*-methoxyphenylsulfonyl aziridine and *N*-diphenylphosphinyl

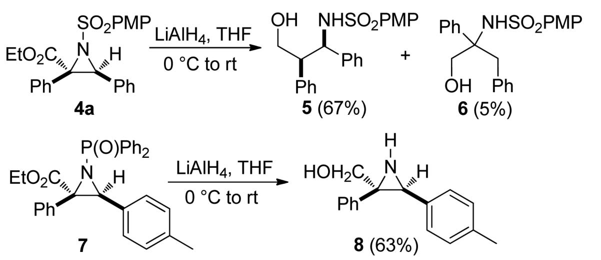
DOI: 10.1021/acs.joc.6b02669
J. Org. Chem. 2017, 82, 811−818

Scheme 3. Stereochemical Rationalization



aziridine-2-carboxylates by reducing them using metal hydride reagent (Scheme 4).[45,46] Treatment of *N*-SO_2PMP aziridine **4a**

Scheme 4. Different Reactions of *N*-DPP and *N*-SO_2PMP Aziridines with $LiAlH_4$



with lithium aluminum hydride led to ring opening, giving *syn*-1,3-amino alcohol **5** in 67% yield,[47] together with 1,2-amino alcohol **6** in 5% yield. Under the same reaction conditions, the phosphinyl group could be removed from *N*-DPP aziridine **7**, affording aziridine containing free N−H.

In summary, we have described a novel protocol for aziridination of *N*-sulfonyl imines using *α*-ketoesters. This $P(NMe_2)_3$-mediated coupling reaction is the first report of Kukhtine−Ramirez adducts captured by imines, and it may serve as a useful complement for aziridination involving phosphites.[10]

■ EXPERIMENTAL SECTION

General Methods. All commercially available reagents were used without further purification unless otherwise stated. THF, Et_2O, and toluene were freshly distilled from sodium-benzophenone under argon atmosphere. DCM was distilled over CaH_2. All reactions were carried out under an argon atmosphere in flame-dried glassware under positive pressure of argon with magnetic stirring using standard Schlenk techniques. Column chromatography was performed on silica gel (200−300 mesh). Visualization on TLC (analytical thin layer chromatography) was achieved by the use of UV light (254 nm) and treatment with aqueous ceric ammonium molybdate followed by heating. ^{1}H NMR spectra were recorded on a 400 or 600 MHz NMR spectrometer and ^{13}C NMR spectra were recorded on 100 or 150 MHz with solvent resonance as the internal standard (^{1}H NMR: $CDCl_3$ at 7.26 ppm, C_6D_6 at 7.16 ppm; ^{13}C NMR: $CDCl_3$ at 77.1 ppm, C_6D_6 at 128.0 ppm). NMR data are reported as follows: chemical shift, multiplicity (br = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz) and integration. High-resolution mass spectra (HRMS) were recorded using electron spray ionization (ESI) with a time-of-flight mass analyzer. *α*-Ketoesters **1**,[48] *N*-sulfonyl imines **3**[49,50] were prepared according to the literature procedures.

General Procedure for Preparing Product 4. A solution of *α*-ketoester **1** (2.0 equiv) and *N*-sulfonyl imine **3** (1.0 equiv) in toluene was cooled to −78 °C, and $P(NMe_2)_3$ (2.0 equiv) was added dropwise to the solution via syringe. After 15 min at −78 °C, the reaction mixture was allowed to stand at room temperature for 2 h with stirring. Water was added, and the reaction was extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography using silica gel.

Procedure for Preparing 1 g of 4a. General procedure was followed by using *α*-ketoester **1a** (1.4250 g, 8.00 mmol), *N*-sulfonyl imine **3a** (1.1010 g, 4.00 mmol), $P(NMe_2)_3$ (1.3060 g, 8.00 mmol), and toluene (40 mL). The crude product was purified by flash column chromatography (petroleum ether/ethyl acetate = 7/1), achieving 1.46 g (83% yield) of *trans*-**4a** as a white solid and 30.0 mg (1.7% yield) of *cis*-**4a** as a white solid. Analytical data for *cis*-**4a**: R_f = 0.28 (petroleum ether/ethyl acetate =6/1), mp 134−135 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.77 (dd, *J* = 7.2, 2.0 Hz, 2H), 7.59−7.53 (m, 2H), 7.45−7.37 (m, 3H), 7.34−7.25 (m, 5H), 6.90 (dd, *J* = 7.2, 2.0 Hz, 2H), 4.70 (s, 1H), 3.95−3.86 (m, 1H), 3.85 (s, 3H), 3.78−3.70 (m, 1H), 0.73 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 165.9, 163.6, 132.4, 130.71, 130.69, 130.4, 130.2, 129.8, 128.53, 128.49, 127.1, 114.2, 61.8, 61.4, 55.8, 48.6, 13.7; HRMS (ESI-TOF) (*m/z*) $[M+Na]^+$ calcd for $C_{24}H_{23}NNaO_5S$ 460.1189, found 460.1195.

*Ethyl 1-((4-Methoxyphenyl)sulfonyl)-2,3-diphenylaziridine-2-carboxylate (**4a**).* According to the general procedure, the reaction of *α*-ketoester **1a** (35.6 mg, 0.20 mmol), imine **3a** (27.5 mg, 0.10 mmol), and $P(NMe_2)_3$ (32.6 mg, 0.20 mmol) generated product **4a** with a diastereomeric ratio of 94:6. Column chromatography (petroleum ether/ethyl acetate = 8/1) afforded *trans*-**4a** (white solid, 37.9 mg, 87% yield). Analytical data for *trans*-**4a**: R_f = 0.30 (petroleum ether/ethyl acetate = 6/1), mp 110−111 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.04 (d, *J* = 8.8 Hz, 2H), 7.06−7.00 (m, 10H), 6.99−6.94 (m, 2H), 4.88 (s, 1H), 4.39−4.26 (m, 2H), 3.88 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 166.9, 163.8, 132.1, 131.9, 131.0, 130.3, 128.4, 128.3, 128.2, 128.1, 128.0, 127.4, 114.4, 62.9, 60.8, 55.8, 50.5, 13.9; HRMS (ESI-TOF) (*m/z*) $[M+Na]^+$ calcd for $C_{24}H_{23}NNaO_5S$ 460.1189, found 460.1189.

*Ethyl 3-(4-Methoxyphenyl)-1-((4-methoxyphenyl)sulfonyl)-2-phenylaziridine-2-carboxylate (**4b**).* According to the general procedure, the reaction of *α*-ketoester **1a** (142.5 mg, 0.80 mmol), imine **3b** (122.1 mg, 0.40 mmol), and $P(NMe_2)_3$ (130.6 mg, 0.80 mmol) generated product **4b** with a diastereomeric ratio of 97:3. Column chromatography (petroleum ether/ethyl acetate = 6/1) afforded *trans*-**4b** (white solid, 170.2 mg, 91% yield). Analytical data for *trans*-**4b**: R_f = 0.30 (petroleum ether/ethyl acetate =5/1), mp 96−97 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.02 (dd, *J* = 7.2, 2.0 Hz, 2H), 7.18−7.07 (m, 5H), 7.01 (dd, *J* = 7.2, 2.0 Hz, 2H), 6.86 (dd, *J* = 6.8, 2.0 Hz, 2H), 6.59 (dd, *J* = 6.8, 2.0 Hz, 2H), (m, 2H), 4.82 (s, 1H), 4.40−4.23 (m, 2H), 3.88 (s, 3H), 3.66 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 167.0, 163.7, 159.5, 132.3, 131.2, 130.2, 128.7, 128.4, 128.3, 128.2, 124.0, 114.4, 113.5, 62.9, 60.8, 55.8, 55.2, 50.3, 14.0; HRMS (ESI-TOF) (*m/z*) $[M+Na]^+$ calcd for $C_{25}H_{25}NNaO_6S$ 490.1295, found 490.1301.

*Ethyl 1-((4-Methoxyphenyl)sulfonyl)-2-phenyl-3-(p-tolyl)-aziridine-2-carboxylate (**4c**).* According to the general procedure, the reaction of *α*-ketoester **1a** (71.2 mg, 0.40 mmol), imine **3c** (57.9 mg, 0.20 mmol), and $P(NMe_2)_3$ (65.2 mg, 0.40 mmol) generated product **4c** with a diastereomeric ratio of 96:4. Column chromatography (petroleum ether/ethyl acetate = 8/1) afforded *trans*-**4c** (white solid, 80.8 mg, 90% yield). Analytical data for *trans*-**4c**: R_f = 0.30 (petroleum ether/ethyl acetate = 6:1), mp 107−108 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.03 (d, *J* = 8.8 Hz, 2H), 7.17−7.08 (m, 5H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.88−6.81 (m, 4H), 4.84 (s, 1H), 4.39−4.25 (m, 2H), 3.87 (s, 3H), 2.17 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H); ^{13}C

DOI: 10.1021/acs.joc.6b02669
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NMR (150 MHz, $CDCl_3$): δ 167.0, 163.7, 137.8, 132.3, 131.2, 130.2, 128.9, 128.7, 128.3, 128.2, 127.3, 114.4, 62.9, 60.8, 55.8, 50.6, 21.2, 13.9; HRMS (ESI-TOF) (*m*/*z*) $[M+Na]^+$ calcd for $C_{25}H_{25}NNaO_5S$ 474.1346, found 474.1351.

*Ethyl 1-((4-Methoxyphenyl)sulfonyl)-2-phenyl-3-(m-tolyl)-aziridine-2-carboxylate (**4d**).* According to the general procedure, the reaction of α-ketoester **1a** (71.2 mg, 0.40 mmol), imine **3d** (57.9 mg, 0.20 mmol), and $P(NMe_2)_3$ (65.2 mg, 0.40 mmol) generated product **4d** with a diastereomeric ratio of 93:7. Column chromatography (petroleum ether/ethyl acetate = 6/1) afforded *trans*-**4d** (colorless oil, 80.7 mg, 89% yield). Analytical data for *trans*-**4d**: R_f = 0.20 (petroleum ether/ethyl acetate = 6/1); ^1H NMR (400 MHz, $CDCl_3$): δ 8.08−8.01 (m, 2H), 7.16−7.07 (m, 5H), 7.04−6.99 (m, 2H), 6.95−6.87 (m, 2H), 6.80 (s, 1H), 6.70 (d, *J* = 7.2 Hz, 1H), 4.83 (s, 1H), 4.39−4.26 (m, 2H), 3.88 (s, 3H), 2.14 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 163.8, 137.6, 132.2, 131.8, 131.1, 130.3, 128.9, 128.35, 128.29, 128.1, 127.9, 124.4, 114.4, 62.9, 60.8, 55.8, 50.5, 21.3, 14.0; HRMS (ESI-TOF) (*m*/*z*) $[M+Na]^+$ calcd for $C_{25}H_{25}NNaO_5S$ 474.1346, found 474.1340.

*Ethyl 1-((4-Methoxyphenyl)sulfonyl)-2-phenyl-3-(o-tolyl)-aziridine-2-carboxylate (**4e**).* According to the general procedure, the reaction of α-ketoester **1a** (71.2 mg, 0.40 mmol), imine **3e** (57.9 mg, 0.20 mmol), and $P(NMe_2)_3$ (65.2 mg, 0.40 mmol) generated product **4e** with a diastereomeric ratio of >99:1. Column chromatography (petroleum ether/ethyl acetate = 7/1) afforded *trans*-**4e** (colorless oil, 90.2 mg, 99% yield). Analytical data for *trans*-**4e**: R_f = 0.30 (petroleum ether/ethyl acetate = 6/1); ^1H NMR (400 MHz, $CDCl_3$): δ 8.07 (dd, *J* = 7.2, 2.0 Hz, 2H), 7.09 (s, 5H), 7.04 (dd, *J* = 7.2, 2.0 Hz, 2H), 7.00−6.95 (m, 2H), 6.85−6.78 (m, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 4.89 (s, 1H), 4.45−4.30 (m, 2H), 3.89 (s, 3H), 2.46 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 163.9, 136.5, 132.0, 130.8, 130.4, 130.1, 129.6, 128.3, 128.1, 127.9, 127.5, 126.8, 125.4, 114.4, 62.9, 60.2, 55.8, 49.9, 19.2, 14.0; HRMS (ESI-TOF) (*m*/*z*) $[M+Na]^+$ calcd for $C_{25}H_{25}NNaO_5S$ 474.1346, found 474.1350.

*Ethyl 3-(4-Bromophenyl)-1-((4-methoxyphenyl)sulfonyl)-2-phenylaziridine-2-carboxylate (**4f**).* According to the general procedure, the reaction of α-ketoester **1a** (71.2 mg, 0.40 mmol), imine **3f** (70.8 mg, 0.20 mmol), and $P(NMe_2)_3$ (65.2 mg, 0.40 mmol) generated product **4f** with a diastereomeric ratio of 89:11. Column chromatography (petroleum ether/ethyl acetate = 7:1) afforded *trans*-**4f** (white solid, 89.8 mg, 87% yield). Analytical data for *trans*-**4f**: R_f = 0.28 (petroleum ether/ethyl acetate = 6/1), mp 87−88 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.02 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.21−7.12 (m, 5H), 7.10−7.05 (m, 2H), 7.02 (dd, *J* = 6.8, 2.0 Hz, 2H), 6.83 (d, *J* = 8.0 Hz, 2H), 4.80 (s, 1H), 4.38−4.25 (m, 2H), 3.88 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.6, 163.9, 131.8, 131.2, 131.1, 130.8, 130.3, 129.1, 128.6, 128.4, 128.2, 122.3, 114.4, 63.0, 60.9, 55.8, 49.7, 13.9; HRMS (ESI-TOF) (*m*/*z*) $[M+Na]^+$ calcd for $C_{24}H_{22}BrNNaO_5S$ 538.0294, found 538.0298.

*Ethyl 3-(4-Chlorophenyl)-1-((4-methoxyphenyl)sulfonyl)-2-phenylaziridine-2-carboxylate (**4g**).* According to the general procedure, the reaction of α-ketoester **1a** (71.2 mg, 0.40 mmol), imine **3g** (62.0 mg, 0.20 mmol), and $P(NMe_2)_3$ (65.2 mg, 0.40 mmol) generated product **4g** with a diastereomeric ratio of 88:12. Column chromatography (petroleum ether/ethyl acetate = 7/1) afforded *trans*-**4g** (white solid, 77.7 mg, 82% yield). Analytical data for *trans*-**4g**: R_f = 0.25 (petroleum ether/ethyl acetate = 6/1), mp 95−96 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.02 (dd, *J* = 7.2, 2.0 Hz, 2H), 7.18−7.11 (m, 3H), 7.09−6.99 (m, 6H), 6.89 (dd, *J* = 7.2, 2.0 Hz, 2H), 4.82 (s, 1H), 4.38−4.25 (m, 2H), 3.89 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 163.9, 134.1, 131.8, 130.8, 130.6, 130.3, 128.8, 128.6, 128.4, 128.3, 128.2, 114.5, 63.1, 61.0, 55.8, 49.7, 13.9; HRMS (ESI-TOF) (*m*/*z*) $[M+Na]^+$ calcd for $C_{24}H_{22}ClNNaO_5S$ 494.0799, found 494.0818.

*Ethyl 1-((4-Methoxyphenyl)sulfonyl)-2-phenyl-3-(thiophen-2-yl)-aziridine-2-carboxylate (**4h**).* According to the general procedure, the reaction of α-ketoester **1a** (71.2 mg, 0.40 mmol), imine **3h** (56.3 mg, 0.20 mmol), and $P(NMe_2)_3$ (65.2 mg, 0.40 mmol) generated product **4h** with a diastereomeric ratio of 87:13. Column chromatography (petroleum ether/ethyl acetate = 5/1) afforded *trans*-**4h** (yellow oil, 46.4 mg, 52% yield). Analytical data for *trans*-**4h**: R_f = 0.25 (petroleum ether/ethyl acetate = 5/1); ^1H NMR (400 MHz, C_6D_6): δ 8.06 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.53−7.43 (m, 2H), 6.99−6.93 (m, 2H), 6.93−6.88 (m, 1H), 6.66−6.61 (m, 1H), 6.49−6.42 (m, 3H), 6.36−6.31 (m, 1H), 5.41 (s, 1H), 4.30−4.20 (m, 1H), 4.16−4.06 (m, 1H), 2.97 (s, 3H), 1.06 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ 166.8, 163.8, 136.1, 133.2, 131.8, 130.6, 128.9, 128.5, 126.7, 126.2, 114.4, 63.0, 62.0, 54.9, 47.9, 13.8; HRMS (ESI-TOF) (*m*/*z*) $[M+H]^+$ calcd for $C_{22}H_{22}NO_5S_2$ 444.0934, found 444.0930.

*Ethyl 1-((4-Methoxyphenyl)sulfonyl)-3-(naphthalen-1-yl)-2-phenylaziridine-2-carboxylate (**4i**).* According to the general procedure, the reaction of α-ketoester **1a** (142.5 mg, 0.80 mmol), imine **3i** (130.2 mg, 0.40 mmol), and $P(NMe_2)_3$ (130.6 mg, 0.80 mmol) generated product **4i** with a diastereomeric ratio of 99:1. Column chromatography (petroleum ether/ethyl acetate = 7/1) afforded *trans*-**4i** (white solid, 172.1 mg, 88% yield). Analytical data for *trans*-**4i**: R_f = 0.45 (petroleum ether/ethyl acetate = 5/1), mp 67−68 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, *J* = 8.4 Hz, 1H), 8.16−8.07 (m, 2H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.65−7.56 (m, 2H), 7.51−7.45 (m, 1H), 7.12−7.02 (m, 5H), 7.01−6.91 (m, 4H), 5.34 (s, 1H), 4.50−4.35 (m, 2H), 3.88 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 164.0, 133.1, 131.9, 131.6, 130.6, 130.5, 128.6, 128.5, 128.3, 127.9, 127.7, 127.5, 126.8, 126.1, 125.0, 124.7, 123.4, 114.5, 63.1, 60.6, 55.8, 49.7, 14.0; HRMS (ESI-TOF) (*m*/*z*) $[M+Na]^+$ calcd for $C_{28}H_{25}NNaO_5S$ 510.1346, found 510.1349.

*Ethyl 3-Isobutyl-2-phenyl-1-tosylaziridine-2-carboxylate (**4j**).* 4-Methyl-*N*-(3-methyl-1-tosylbutyl)benzenesulfonamide (158.2 mg, 0.4 mmol, 1.0 equiv, dissolved in 2.0 mL toluene) and K_2CO_3 (110.6 mg, 0.80 mmol, 2.0 equiv) were added to a flame-dried Schlenk flask equipped with a magnetic stirring bar and purged with argon. After stirring at rt for 30 min, the mixture was cooled to −78 °C. Then $P(NMe_2)_3$ (130.6 mg, 0.80 mmol, 2.0 equiv, dissolved in 2.0 mL toluene) and α-ketoester **1a** (142.5 mg, 0.80 mmol, 2.0 equiv, dissolved in 2.0 mL toluene) were added dropwise to the solution via syringe. After 15 min, the reaction mixture was warmed to room temperature and stirred for 2 h. After quenching with 2.0 mL water the reaction mixture was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The product **4j** was achieved with a diastereomeric ratio of 36:64. Column chromatography (petroleum ether/ethyl acetate = 12/1) afforded *trans*-**4j** (white solid, 55.6 mg, 35% yield) and *cis*-**4j** (colorless oil, 100.3 mg, 63% yield). Analytical data for *trans*-**4j**: R_f = 0.50 (petroleum ether/ethyl acetate =10/1), mp 77−78 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.99−7.91 (m, 2H), 7.37−7.33 (m, 2H), 7.31−7.27 (m, 3H), 7.25−7.20 (m, 2H), 4.32−4.22 (m, 2H), 3.81 (dd, *J* = 7.6, 1.2 Hz, 1H), 2.46 (s, 3H), 1.56−1.46 (m, 1H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.14−1.06 (m, 1H), 0.90−0.83 (m, 4H), 0.79 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 144.5, 136.7, 133.2, 129.7, 128.52, 128.46, 128.1, 127.7, 62.7, 58.9, 48.3, 36.6, 26.5, 22.9, 22.1, 21.8, 13.9; HRMS (ESI-TOF) (*m*/*z*) $[M+Na]^+$ calcd for $C_{22}H_{27}NNaO_4S$ 424.1553, found 424.1563. Analytical data for *cis*-**4j**: R_f = 0.45 (petroleum ether/ethyl acetate =10/1); ^1H NMR (400 MHz, $CDCl_3$): δ 7.73−7.62 (m, 2H), 7.39−7.29 (m, 5H), 7.26−7.21 (m, 2H), 4.25−4.09 (m, 2H), 3.69−3.62 (m, 1H), 2.42 (s, 3H), 1.71−1.62 (m, 1H), 1.55−1.46 (m, 1H), 1.42−1.33 (m, 1H), 1.19 (t, *J* = 7.2 Hz, 3H), 0.99−0.91 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 144.3, 136.4, 131.0, 130.1, 129.6, 129.4, 128.4, 128.2, 62.1, 58.9, 46.3, 37.7, 26.6, 23.0, 22.3, 21.8, 14.2; HRMS (ESI-TOF) (*m*/*z*) $[M+Na]^+$ calcd for $C_{22}H_{27}NNaO_4S$ 424.1553, found 424.1555.

*Ethyl 3-Cyclohexyl-2-phenyl-1-tosylaziridine-2-carboxylate (**4k**).* According to the general procedure, the reaction of α-ketoester **1a** (142.5 mg, 0.80 mmol), imine **3k** (106.1 mg, 0.40 mmol), and $P(NMe_2)_3$ (130.6 mg, 0.80 mmol) generated product **4k** with a diastereomeric ratio of 45:55. Column chromatography (petroleum ether/ethyl acetate = 12/1) afforded *trans*-**4k** (white solid, 75.6 mg, 44% yield) and *cis*-**4k** (white solid, 85.1 mg, 50% yield). Analytical data for *trans*-**4k**: R_f = 0.30 (petroleum ether/ethyl acetate =10/1), mp 111−112 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.00−7.90 (m, 2H),

DOI: 10.1021/acs.joc.6b02669
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7.35 (d, J = 8.0 Hz, 2H), 7.31−7.24 (m, 5H), 4.32−4.21 (m, 2H), 3.49 (d, J = 9.6 Hz, 1H), 2.45 (s, 3H), 1.62−1.44 (m, 4H), 1.40−1.32 (m, 1H), 1.27 (t, J = 7.2 Hz, 3H), 1.17−0.78 (m, 5H), 0.64−0.53 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 144.5, 136.6, 133.3, 129.7, 128.50, 128.45, 128.3, 127.6, 62.7, 59.4, 54.1, 35.8, 30.6, 29.0, 26.0, 25.3, 25.1, 21.8, 13.9; HRMS (ESI-TOF) (m/z) $[M+Na]^+$ calcd for $C_{24}H_{29}NNaO_4S$ 450.1710, found 450.1716. Analytical data for *cis*-**4k**: R_f = 0.22 (petroleum ether/ethyl acetate =10/1), mp 97−98 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72−7.61 (m, 2H), 7.40−7.28 (m, 5H), 7.23 (d, J = 8.0 Hz, 2H), 4.32−4.20 (m, 1H), 4.13−4.02 (m, 1H), 3.31 (d, J = 9.6 Hz, 1H), 2.42 (s, 3H), 1.98−1.87 (m, 1H), 1.80−1.70 (m, 1H), 1.68−1.59 (m, 2H), 1.48−1.40 (m, 1H), 1.31−1.08 (m, 8H), 1.04−0.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 144.3, 136.0, 131.2, 130.3, 129.5, 129.4, 128.5, 128.4, 62.0, 59.2, 52.4, 37.8, 30.9, 29.7, 26.1, 25.4, 25.3, 21.8, 14.2; HRMS (ESI-TOF) (m/z) $[M+Na]^+$ calcd for $C_{24}H_{29}NNaO_4S$ 450.1710, found 450.1724.

*Ethyl 3-(tert-Butyl)-2-phenyl-1-tosylaziridine-2-carboxylate (**4l**).* According to the general procedure, the reaction of α-ketoester **1a** (142.5 mg, 0.80 mmol), imine **3l** (95.7 mg, 0.40 mmol), and $P(NMe_2)_3$ (130.6 mg, 0.80 mmol) generated product **4l** with a diastereomeric ratio of 95:5. Column chromatography (petroleum ether/ethyl acetate = 15/1) afforded *trans*-**4l** (white solid, 113.5 mg, 71% yield). Analytical data for *trans*-**4l**: R_f = 0.35 (petroleum ether/ethyl acetate =15/1), mp 107−108 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.33−7.25 (m, 5H), 4.30−4.18 (m, 2H), 3.55 (s, 1H), 2.46 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H), 0.62 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 144.6, 136.6, 133.8, 129.7, 128.4, 128.0, 62.7, 59.0, 57.3, 31.9, 27.2, 21.8, 13.8; HRMS (ESI-TOF) (m/z) $[M+Na]^+$ calcd for $C_{22}H_{27}NNaO_4S$ 424.1553, found 424.1550.

*Ethyl 2-(4-Methoxyphenyl)-1-((4-methoxyphenyl)sulfonyl)-3-phenylaziridine-2-carboxylate (**4m**).* According to the general procedure, the reaction of α-ketoester **1b** (166.6 mg, 0.80 mmol), imine **3a** (110.1 mg, 0.40 mmol), and $P(NMe_2)_3$ (130.6 mg, 0.80 mmol) generated product **4m** with a diastereomeric ratio of 63:37. Column chromatography (petroleum ether/ethyl acetate = 6/1) afforded *trans*-**4m** (pale yellow solid, 115.7 mg, 62% yield) and *cis*-**4m** (pale yellow solid, 50.2 mg, 27% yield). Analytical data for *trans*-**4m**: R_f = 0.25 (petroleum ether/ethyl acetate = 5/1), mp 86−87 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (dd, J = 6.8, 2.0 Hz, 2H), 7.13−7.05 (m, 3H), 7.03−6.95 (m, 6H), 6.64 (dd, J = 6.8, 2.0 Hz, 2H), 4.83 (s, 1H), 4.38−4.25 (m, 2H), 3.88 (s, 3H), 3.68 (s, 3H), 1.32 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.1, 163.8, 159.5, 132.1, 131.1, 130.3, 129.6, 128.1, 128.0, 127.5, 124.2, 114.4, 113.7, 62.9, 60.5, 55.8, 55.2, 50.4, 14.0; HRMS (ESI-TOF) (m/z) $[M+Na]^+$ calcd for $C_{25}H_{25}NNaO_6S$ 490.1295, found 490.1300. Analytical data for *cis*-**4m**: R_f = 0.22 (petroleum ether/ethyl acetate =5:1), mp 104−105 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (dd, J = 6.8, 2.0 Hz, 2H), 7.47 (dd, J = 6.8, 2.0 Hz, 2H), 7.33−7.23 (m, 5H), 6.91 (d, J = 8.4 Hz, 4H), 4.68 (s, 1H), 3.92−3.81 (m, 7H), 3.78−3.69 (m, 1H), 0.73 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.1, 163.6, 160.6, 132.5, 131.4, 130.9, 130.3, 128.5, 127.1, 122.6, 114.1, 113.9, 61.7, 61.0, 55.7, 55.4, 48.8, 13.7; HRMS (ESI-TOF) (m/z) $[M+Na]^+$ calcd for $C_{25}H_{25}NNaO_6S$ 490.1295, found 490.1298.

*Ethyl 1-((4-Methoxyphenyl)sulfonyl)-3-phenyl-2-(p-tolyl)-aziridine-2-carboxylate (**4n**).* According to the general procedure, the reaction of α-ketoester **1c** (153.8 mg, 0.80 mmol), imine **3a** (110.1 mg, 0.40 mmol), and $P(NMe_2)_3$ (130.6 mg, 0.80 mmol) generated product **4n** with a diastereomeric ratio of 85:15. Column chromatography (petroleum ether/ethyl acetate = 7/1) afforded *trans*-**4n** (colorless oil, 145.1 mg, 80% yield). Analytical data for *trans*-**4n**: R_f = 0.45 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (dd, J = 6.8, 2.0 Hz, 2H), 7.11−7.05 (m, 3H), 7.03−6.95 (m, 6H), 6.92 (d, J = 8.0 Hz, 2H), 4.86 (s, 1H), 4.39−4.25 (m, 2H), 3.87 (s, 3H), 2.20 (s, 3H), 1.32 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.0, 163.8, 138.1, 132.1, 131.1, 130.3, 129.1, 128.9, 128.1, 128.02, 127.99, 127.5, 114.3, 62.8, 60.8, 55.7, 50.4, 21.3, 13.9; HRMS (ESI-TOF) (m/z) $[M+Na]^+$ calcd for $C_{25}H_{25}NNaO_5S$ 474.1346, found 474.1358.

*Ethyl 1-((4-Methoxyphenyl)sulfonyl)-3-phenyl-2-(m-tolyl)-aziridine-2-carboxylate (**4o**).* According to the general procedure, the reaction of α-ketoester **1d** (76.9 mg, 0.40 mmol), imine **3a** (55.1 mg, 0.20 mmol), and $P(NMe_2)_3$ (65.2 mg, 0.40 mmol) generated product **4o** with a diastereomeric ratio of 92:8. Column chromatography (petroleum ether/ethyl acetate = 7/1) afforded *trans*-**4o** (colorless oil, 81.5 mg, 90% yield). Analytical data for *trans*-**4o**: R_f = 0.40 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (dd, J = 6.8, 2.0 Hz, 2H), 7.11−7.03 (m, 3H), 7.03−6.92 (m, 6H), 6.91 (s, 1H), 6.87 (d, J = 7.6 Hz, 1H), 4.83 (s, 1H), 4.40−4.25 (m, 2H), 3.88 (s, 3H), 2.17 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 163.8, 137.8, 132.0, 131.9, 131.0, 130.3, 129.2, 128.9, 128.1, 128.01, 127.98, 127.5, 125.3, 114.4, 62.9, 60.9, 55.8, 50.4, 21.4, 14.0; HRMS (ESI-TOF) (m/z) $[M+Na]^+$ calcd for $C_{25}H_{25}NNaO_5S$ 474.1346, found 474.1363.

*Ethyl 1-((4-Methoxyphenyl)sulfonyl)-3-phenyl-2-(o-tolyl)-aziridine-2-carboxylate (**4p**).* According to the general procedure, the reaction of α-ketoester **1e** (153.8 mg, 0.80 mmol), imine **3a** (110.1 mg, 0.40 mmol), and $P(NMe_2)_3$ (130.6 mg, 0.80 mmol) generated product **4p** with a diastereomeric ratio of 27:73. Column chromatography (petroleum ether/ethyl acetate = 7/1) afforded *trans*-**4p** (colorless oil, 27.1 mg, 15% yield) and *cis*-**4p** (white solid, 75.4 mg, 42% yield). Analytical data for *trans*-**4p**: R_f = 0.35 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (dd, J = 7.2, 2.0 Hz, 2H), 7.33 (br s, 1H), 7.13−6.97 (m, 7H), 6.94−6.89 (m, 2H), 6.88−6.80 (m, 1H), 5.01 (s, 1H), 4.40−4.23 (m, 2H), 3.88 (s, 3H), 1.90 (s, 3H), 1.31 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 163.7, 132.0, 131.7, 130.8, 130.5, 130.0, 128.5, 128.3, 127.8, 127.5, 125.7, 114.4, 63.0, 61.2, 55.8, 51.2, 18.9, 14.0; HRMS (ESI-TOF) (m/z) $[M+Na]^+$ calcd for $C_{25}H_{25}NNaO_5S$ 474.1346, found 474.1356. Analytical data for *cis*-**4p**: R_f = 0.33 (petroleum ether/ethyl acetate = 5/1), mp 55−56 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.4 (dd, J = 7.2, 2.0 Hz, 2H), 7.52 (d, J = 7.6 Hz, 1H), 7.36−7.17 (m, 8H), 6.87 (dd, J = 7.2, 2.0 Hz, 2H), 4.66 (s, 1H), 3.92−3.85 (m, 1H), 3.83 (s, 3H), 3.78−3.70 (m, 1H), 2.50 (s, 3H), 0.75 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.0, 163.6, 132.0, 131.2, 130.4, 130.3, 130.1, 129.7, 128.5, 128.4, 127.4, 125.8, 114.2, 61.8, 61.2, 55.7, 48.9, 20.5, 13.7; HRMS (ESI-TOF) (m/z) $[M+Na]^+$ calcd for $C_{25}H_{25}NNaO_5S$ 474.1346, found 474.1364.

*Ethyl 2-(4-Bromophenyl)-1-((4-methoxyphenyl)sulfonyl)-3-phenylaziridine-2-carboxylate (**4q**).* According to the general procedure, the reaction of α-ketoester **1f** (205.7 mg, 0.80 mmol), imine **3a** (110.1 mg, 0.40 mmol), and $P(NMe_2)_3$ (130.6 mg, 0.80 mmol) generated product **4q** with a diastereomeric ratio of 98:2. Column chromatography (petroleum ether/ethyl acetate = 7/1) afforded *trans*-**4q** (white gum, 200.5 mg, 97% yield). Analytical data for *trans*-**4q**: R_f = 0.35 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (dd, J = 6.8, 2.0 Hz, 2H), 7.28−7.23 (m, 2H), 7.15−7.06 (m, 3H), 7.01 (dd, J = 6.8, 2.0 Hz, 2H), 6.98−6.91 (m, 4H), 4.88 (s, 1H), 4.39−4.26 (m, 2H), 3.88 (s, 3H), 1.32 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 163.9, 131.6, 131.42, 131.37, 130.9, 130.2, 130.0, 128.3, 128.2, 127.3, 122.7, 114.5, 63.2, 60.1, 55.8, 50.6, 13.9; HRMS (ESI-TOF) (m/z) $[M+Na]^+$ calcd for $C_{24}H_{22}BrNNaO_5S$ 538.0294, found 538.0303.

*Ethyl 2-(4-Chlorophenyl)-1-((4-methoxyphenyl)sulfonyl)-3-phenylaziridine-2-carboxylate (**4r**).* According to the general procedure, the reaction of α-ketoester **1g** (170.1 mg, 0.80 mmol), imine **3a** (110.1 mg, 0.40 mmol), and $P(NMe_2)_3$ (130.6 mg, 0.80 mmol) generated product **4r** with a diastereomeric ratio of 97:3. Column chromatography (petroleum ether/ethyl acetate = 7/1) afforded *trans*-**4r** (white solid, 175.3 mg, 93% yield). Analytical data for *trans*-**4r**: R_f = 0.33 (petroleum ether/ethyl acetate = 5/1), mp 83−85 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06−7.97 (m, 2H), 7.14−7.06 (m, 5H), 7.05−6.99 (m, 4H), 6.97−6.92 (m, 2H), 4.88 (s, 1H), 4.39−4.26 (m, 2H), 3.88 (s, 3H), 1.32 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.5, 163.9, 134.4, 131.6, 130.95, 130.86, 130.3, 129.7, 128.5, 128.3, 128.2, 127.3, 114.5, 63.1, 60.1, 55.8, 50.7, 13.9; HRMS (ESI-TOF) (m/z) $[M+Na]^+$ calcd for $C_{24}H_{22}ClNNaO_5S$ 494.0799, found 494.0798.

DOI: 10.1021/acs.joc.6b02669
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*Ethyl 2-(3-Chlorophenyl)-1-((4-methoxyphenyl)sulfonyl)-3-phenylaziridine-2-carboxylate (**4s**).* According to the general procedure, the reaction of α-ketoester **1h** (170.1 mg, 0.80 mmol), imine **3a** (110.1 mg, 0.40 mmol), and $P(NMe_2)_3$ (130.6 mg, 0.80 mmol) generated product **4s** with a diastereomeric ratio of 97:3. Column chromatography (petroleum ether/ethyl acetate = 6/1) afforded *trans*-**4s** (yellow oil, 181.6 mg, 96% yield). Analytical data for *trans*-**4s**: R_f = 0.33 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.15−7.00 (m, 8H), 6.98−6.92 (m, 3H), 4.88 (s, 1H), 4.40−4.28 (m, 2H), 3.89 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 163.9, 134.3, 134.1, 131.5, 130.9, 130.3, 129.5, 128.7, 128.6, 128.3, 128.2, 127.3, 126.4, 114.5, 63.2, 60.0, 55.8, 50.8, 14.0; HRMS (ESI-TOF) (*m/z*) $[M+H]^+$ calcd for $C_{24}H_{23}ClNO_5S$ 472.0980, found 472.0988.

*Ethyl 2-(2-Chlorophenyl)-1-((4-methoxyphenyl)sulfonyl)-3-phenylaziridine-2-carboxylate (**4t**).* According to the general procedure, the reaction of α-ketoester **1i** (170.1 mg, 0.80 mmol), imine **3a** (110.1 mg, 0.40 mmol), and $P(NMe_2)_3$ (130.6 mg, 0.80 mmol) generated product **4t** with a diastereomeric ratio of 55:45. Column chromatography (petroleum ether/ethyl acetate = 6/1) afforded *trans*-**4t** (colorless oil, 89.0 mg, 47% yield) and *cis*-**4t** (white solid, 70.2 mg, 37% yield). Analytical data for *trans*-**4t**: R_f = 0.33 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.18−7.07 (m, 3H), 7.06−7.00 (m, 5H), 6.99−6.94 (m, 2H), 5.24 (s, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 3.90 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 163.7, 133.4, 132.2, 131.6, 131.5, 131.3, 129.8, 129.7, 129.0, 128.3, 127.8, 127.4, 126.5, 114.5, 63.2, 60.0, 55.8, 52.6, 14.0; HRMS (ESI-TOF) (*m/z*) $[M+H]^+$ calcd for $C_{24}H_{23}ClNO_5S$ 472.0980, found 472.1006. Analytical data for *cis*-**4t**: R_f = 0.30 (petroleum ether/ethyl acetate = 5/1), mp 57−58 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.47−7.42 (m, 1H), 7.40−7.31 (m, 4H), 7.29−7.23 (m, 3H), 6.93 (dd, *J* = 6.8, 2.0 Hz, 2H), 4.79 (s, 1H), 3.93−3.75 (m, 5H), 0.80 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 163.8, 132.5, 131.8, 130.9, 130.6, 130.5, 130.34, 130.28, 128.6, 128.3, 127.6, 126.8, 114.3, 62.0, 59.7, 55.8, 49.2, 13.7; HRMS (ESI-TOF) (*m/z*) $[M+H]^+$ calcd for $C_{24}H_{23}ClNO_5S$ 472.0980, found 472.0998.

*Ethyl 1-((4-Methoxyphenyl)sulfonyl)-2-(naphthalen-2-yl)-3-phenylaziridine-2-carboxylate (**4u**).* According to the general procedure, the reaction of α-ketoester **1j** (182.6 mg, 0.80 mmol), imine **3a** (110.1 mg, 0.40 mmol), and $P(NMe_2)_3$ (130.6 mg, 0.80 mmol) generated product **4u** with a diastereomeric ratio of 94:6. Column chromatography (petroleum ether/ethyl acetate = 6/1) afforded *trans*-**4u** (yellow solid, 180.6 mg, 93% yield). Analytical data for *trans*-**4u**: R_f = 0.33 (petroleum ether/ethyl acetate = 5/1), mp 58−60 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12−8.05 (m, 2H), 7.73−7.63 (m, 2H), 7.62−7.58 (m, 2H), 7.43−7.38 (m, 2H), 7.21−7.17 (m, 1H), 7.06−6.98 (m, 7H), 4.94 (s, 1H), 4.40−4.26 (m, 2H), 3.88 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 163.9, 133.1, 132.8, 131.9, 131.1, 130.3, 129.6, 128.2, 128.13, 128.07, 127.7, 127.4, 126.5, 126.3, 125.4, 114.4, 63.0, 61.0, 55.8, 50.8, 14.0; HRMS (ESI-TOF) (*m/z*) $[M+Na]^+$ calcd for $C_{28}H_{25}NNaO_5S$ 510.1346, found 510.1350.

*Ethyl 2,3-Bis(4-chlorophenyl)-1-((4-methoxyphenyl)sulfonyl)-aziridine-2-carboxylate (**4v**).* According to the general procedure, the reaction of α-ketoester **1g** (170.1 mg, 0.80 mmol), imine **3g** (123.9 mg, 0.40 mmol), and $P(NMe_2)_3$ (130.6 mg, 0.80 mmol) generated product **4v** with a diastereomeric ratio of 91:9. Column chromatography (petroleum ether/ethyl acetate = 7/1) afforded a mixture of *trans*-**4v** and *cis*-**4v** (white solid, 189.6 mg, 94% yield). Analytical data for *trans*-**4v**: R_f = 0.31 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03−7.96 (m, 2H), 7.15−7.10 (m, 2H), 7.09−7.04 (m, 2H), 7.04−6.97 (m, 4H), 6.90−6.85 (m, 2H), 4.82 (s, 1H), 4.39−4.24 (m, 2H), 3.89 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 164.0, 134.7, 134.4, 131.5, 130.7, 130.5, 130.3, 129.6, 128.7, 128.5, 114.5, 63.3, 60.2, 55.8, 49.9, 13.9; HRMS (ESI-TOF) (*m/z*) $[M+Na]^+$ calcd for $C_{24}H_{21}Cl_2NNaO_5S$ 528.0410, found 528.0398.

*Ethyl 2-(4-Chlorophenyl)-1-((4-methoxyphenyl)sulfonyl)-3-(p-tolyl)aziridine-2-carboxylate (**4w**).* According to the general procedure, the reaction of α-ketoester **1g** (170.1 mg, 0.80 mmol), imine **3c** (115.7 mg, 0.40 mmol), and $P(NMe_2)_3$ (130.6 mg, 0.80 mmol) generated product **4w** with a diastereomeric ratio of 98:2. Column chromatography (petroleum ether/ethyl acetate = 7/1) afforded *trans*-**4w** (white gum, 183.9 mg, 95% yield). Analytical data for *trans*-**4w**: R_f = 0.32 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05−7.96 (m, 2H), 7.15−7.08 (m, 2H), 7.05−6.98 (m, 4H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 2H), 4.84 (s, 1H), 4.38−4.25 (m, 2H), 3.87 (s, 3H), 2.19 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 163.8, 138.1, 134.3, 131.04, 130.97, 130.2, 129.8, 128.9, 128.54, 128.47, 127.2, 114.4, 63.1, 60.0, 55.8, 50.8, 21.2, 13.9; HRMS (ESI-TOF) (*m/z*) $[M+Na]^+$ calcd for $C_{25}H_{24}ClNNaO_5S$ 508.0956, found 508.0957.

*N-(3-Hydroxy-1,2-diphenylpropyl)-4-methoxybenzenesulfonamide (**5**) and N-(1-Hydroxy-2,3-diphenylpropan-2-yl)-4-methoxybenzenesulfonamide (**6**).* THF (5.0 mL) and 171.0 mg $LiAlH_4$ (4.50 mmol, 3.0 equiv) were added to a flame-dried Schlenk flask equipped with a magnetic stirring bar and purged with argon. The mixture was cooled to 0 °C, and 656.3 mg *N*-SO_2PMP aziridine *trans*-**4a** (1.50 mmol, 1.0 equiv, dissolved in 20.0 mL THF) was added to the solution via syringe. The reaction mixture was then stirred at room temperature for 3.5 h. After 10.0 mL saturated aqueous ammonium chloride was slowly added, the reaction mixture was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. Column chromatography (petroleum ether/ethyl acetate = 3/1) afforded **5** (400.0 mg, white solid, 67% yield) and **6** (32.3 mg, white solid, 5% yield). Analytical data for **5**: R_f = 0.35 (petroleum ether/ethyl acetate = 2/1), mp 152−153 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.5 (dd, *J* = 7.2, 2.0 Hz, 2H), 7.28−7.21 (m, 3H), 7.16−7.04 (m, 3H), 6.97−6.91 (m, 2H), 6.83−6.77 (m, 2H), 6.70 (dd, *J* = 7.2, 2.0 Hz, 2H), 4.99 (d, *J* = 8.0 Hz, 1H), 4.77 (t, *J* = 6.8 Hz, 1H), 3.95 (dd, *J* = 11.2, 8.0 Hz, 1H), 3.78 (s, 3H), 3.69 (dd, *J* = 11.2, 5.6 Hz, 1H), 3.10−3.03 (m, 1H), 1.87 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7, 138.9, 136.9, 131.7, 129.3, 129.0, 128.9, 128.2, 127.9, 127.5, 127.2, 113.9, 63.2, 58.4, 55.7, 54.2; HRMS (ESI-TOF) (*m/z*) $[M+Na]^+$ calcd for $C_{22}H_{23}NNaO_4S$ 420.1240, found 420.1249. Analytical data for **6**: R_f = 0.37 (petroleum ether/ethyl acetate =2/1), mp 185−186 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (dd, *J* = 7.2, 2.0 Hz, 2H), 7.16−7.05 (m, 6H), 6.95 (d, *J* = 7.6 Hz, 2H), 6.78−6.73 (m, 4H), 4.93 (s, 1H), 4.23 (d, *J* = 12.0 Hz, 1H), 3.99 (d, *J* = 12.0 Hz, 1H), 3.82 (s, 3H), 3.35 (d, *J* = 12.8 Hz, 1H), 3.07 (d, *J* = 12.8 Hz, 1H), 1.62 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 139.1, 134.9, 133.1, 130.9, 129.4, 128.2, 128.1, 127.5, 127.1, 127.0, 114.0, 65.9, 64.3, 55.8, 45.0; HRMS (ESI-TOF) (*m/z*) $[M+Na]^+$ calcd for $C_{22}H_{23}NNaO_4S$ 420.1240, found420.1270.

*cis-2-Phenyl-3-(p-tolyl)aziridine-2-yl Methanol (**8**).* THF (0.27 mL) and 10.3 mg $LiAlH_4$ (0.27 mmol, 3.0 equiv) were added to a flame-dried Schlenk flask equipped with a magnetic stirring bar and purged with argon. The mixture was cooled to 0 °C, and 43.3 mg *N*-DPP aziridine **7** (0.09 mmol, 1.0 equiv, dissolved in 1.0 mL THF) was added dropwise to the solution via syringe. The reaction mixture was stirred at room temperature for 3.5 h, and then quenched with 1.0 mL saturated aqueous ammonium chloride and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 2/1), achieving 13.5 mg (63% yield) of **8** as a white solid. Analytical data for **8**: R_f = 0.25 (petroleum ether/ethyl acetate = 1/1), mp 148−149 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.22−7.15 (m, 5H), 6.89 (d, *J* = 7.8 Hz, 2H), 6.83 (d, *J* = 7.8 Hz, 2H), 3.97 (d, *J* = 11.4 Hz, 1H), 3.94 (d, *J* = 11.4 Hz, 1H), 3.46 (s, 1H), 2.20 (s, 3H), 1.98 (br s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 136.8, 136.2, 134.0, 129.4, 128.5, 128.2, 127.4, 127.2, 66.8, 50.8, 41.4, 21.1; HRMS (ESI-TOF) (*m/z*) $[M+H]^+$ calcd for $C_{16}H_{18}NO$ 240.1383, found 240.1391.

*cis-3-((4-Methoxyphenyl)sulfonyl)-4,5-diphenyl-1,3-oxazinan-2-one (**9**).* Triphosgene (53.8 mg, 0.18 mmol, 1.0 equiv), TEA (0.45 mL, 3.26 mmol, 18.0 equiv), and DMAP (22.1 mg, 0.18 mmol, 1.0 equiv) were added to a solution of **5** (72.0 mg, 0.18 mmol, 1.0 equiv) in

DOI: 10.1021/acs.joc.6b02669
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DCM (4.0 mL) at 0 °C. The mixture was allowed to be stirred at room temperature overnight. Subsequently, 10.0 mL H_2O was added, and the reaction mixture was extracted with DCM. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. Column chromatography (petroleum ether/ethyl acetate = 3:1) using 200−300 mesh silica gel afforded **9** (52.0 mg, light yellow solid, 68% yield). Analytical data for **9**: R_f = 0.50 (petroleum ether/ethyl acetate = 2:1), mp 205−206 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.31−7.13 (m, 6H), 6.82−6.77 (m, 2H), 6.71−6.65 (m, 4H), 5.76 (dd, *J* = 4.8, 1.6 Hz, 1H), 4.64 (dd, *J* = 12.4, 10.8 Hz, 1H), 4.37 (ddd, *J* = 10.8, 4.8, 1.6 Hz, 1H), 3.86 (dt, *J* = 12.4, 4.8 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.0, 148.6, 134.9, 133.9, 132.2, 129.2, 128.8, 128.6, 128.47, 128.45, 128.34, 128.25, 113.5, 66.9, 63.4, 55.8, 43.3; HRMS (ESI-TOF) (*m*/*z*) $[M+Na]^+$ calcd for $C_{23}H_{21}NNaO_5S$ 446.1033, found 446.1038.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02669.

^{1}H and ^{13}C NMR spectra of all new compounds (PDF)
X-ray crystal structure of compound **4c** (CIF)

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foun-dation of China (21572262, U1403301, and 21372255), the Recruitment Program of Global Experts (Xinjiang Program), and the Director Foundation of XTIPC (2015RC014).

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