Supporting Information

Novel Synthesis of *gem*-Dichloroaziridines from Imines via the KF/Al₂O₃-Promoted Generation of Dichlorocarbene from Chloroform

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Table of Contents

General Experimental Procedure	S2
Typical Procedure of Method A for 2a	S2
Typical Procedure of Method B for 3g	S3
Reaction Conditions for 2a-h , 3g and 3h	S3
2,2-Dichloroaziridines 2a-c and	
<i>N</i> -benzyl- α -chlorophenylacetamide (3g)	S4
Spectral and Physical Data for 2d-f and 3h	S5

General Experimental Procedure

Chloroform and acetonitrile from commercial sources were used without further purification in method A. Chloroform and acetonitrile, distilled over P₂O₅ and CaH₂ respectively, were used in method B. KF/Al₂O₃ (potassium fluoride, 40 wt. % on alumina) was purchased from Aldrich Chemical Co., Inc. It contained 9.6% water and was used without further treatment. *N*-Benzylideneaniline (**1a**) and *N*-benzylidenebenzylamine (**1g**) were purchased and other imines were prepared by a literature method.¹ Melting points are uncorrected. ¹H and ¹³C NMR spectra were recorded at 300 and 75 MHz, respectively. Chemical shifts are reported in ppm relative to tetramethylsilane (δ-units). Mass and exact mass spectra were recorded in the EI mode. Column chromatography and gel permeation liquid chromatography for further purification were carried out on silica gel 60 and GPC K-2001 and 2002, respectively.

Typical Procedure of Method A; 2,2-Dichloro-1,3-diphenylaziridine (**2a**)

To a suspension of KF/Al₂O₃ (2 g) and **1a** (90.6 mg, 0.5 mmol) in acetonitrile (3.0 mL), chloroform (120.0 μL, 1.5 mmol) was added slowly. The reaction mixture was stirred

for 1.5 h at room temperature. The $\text{KF}/\text{Al}_2\text{O}_3$ was removed by filtration and washed with ether. The combined filtrate was evaporated and purified by recrystallization from hexane to give **2a** (102.9 mg, 77%).

Typical Procedure of Method B; *N*-Benzyl- α -chlorophenylacetamide (**3g**)

To a suspension of $\text{KF}/\text{Al}_2\text{O}_3$ (2 g) and **1g** (39.0 mg, 0.2 mmol) in distilled acetonitrile (6.0 mL), water (54.0 μL , 3.0 mmol) was added and distilled chloroform (320.0 μL , 4.0 mmol) was then added slowly under an Ar atmosphere. The reaction mixture was stirred for 0.5 h at room temperature. The $\text{KF}/\text{Al}_2\text{O}_3$ was removed by filtration and washed with ether. After evaporation of the combined filtrate, **2g** was obtained in 56% NMR yield. The resulting mixture was allowed to stand for a few days and was then purified by column chromatography (hexane/ethyl acetate) to give **3g** (24.4 mg, 47%).

Reaction Conditions for **2a-h**, **3g** and **3h**

SCHEME S1. $\text{KF}/\text{Al}_2\text{O}_3$ -Promoted Dichloroaziridination of Various Imines

TABLE S1. Reaction Conditions

starting material	1 (mmol)	KF/Al ₂ O ₃ (g)	CHCl ₃ (mmol)	MeCN (mL)	H ₂ O (mmol)	time (h)	product	2 or 3	
								(mg)	(%)
1a	0.5	1	0.75	3	1.5	15	2a	112.2	85
1b	0.5	1.2	0.9	3.6	1.8	15	2b	124.2	79
1c	0.5	1.2	0.9	3.6	1.8	15	2c	122.8	69
1d	0.5	2	1.5	6	3	15	2d	67.6	42
1e	0.5	2.5	1.88	7.5	3.75	15	2e	70.8	49
1f	0.1	1.6	0.3	0.6 ^a	1.2	15	2f	24.0	66
1g	0.2	2	4	6	3	0.5	(2g)	51.9	56)
							3g	24.4	47
							(2h)	56.4	29)
1h	0.2	2	4	6	3	0.25	3h	14.5	29

^a CH₂Cl₂ (1 mL) was added.

2,2-Dichloroaziridines 2a-c and N-benzyl-α-chlorophenylacetamide (3g)

2,2-Dichloro-1,3-diphenylaziridine

(**2a**),²

2,2-dichloro-1-(1-naphthyl)-3-phenylaziridine (2b),³
1-benzyl-2,2-dichloro-3,3-diphenylaziridine (2c)³ and
N-benzyl- α -chlorophenylacetamide (3g)⁴ were identified by comparison of their data (¹H
NMR, IR and mp) with those in the literature.

Spectral and Physical Data for 2d-f and 3h

2,2-Dichloro-3-(4-methoxycarbonylphenyl)-1-phenylaziridine (2d)

Yield: 42%; pale yellow solid; mp: 137-138.5 °C.

IR (KBr): ν = 3061, 3038, 2947, 1716, 1599, 1496, 1287, 889 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 8.10 (d, 2 H, *J* = 8.3 Hz), 7.59 (d, 2 H, *J* = 8.3 Hz),
7.05-7.40 (m, 5 H), 3.94 (s, 3 H), 3.74 (s, 1 H).

¹³C NMR (75 MHz, CDCl₃): δ = 166.6, 144.5, 137.9, 130.7, 129.7, 129.2, 127.9, 124.5,
119.7, 75.0, 54.2, 52.2.

MS (EI, 70 eV): *m/z* (%) = 325 [*M*⁺ (C₁₆H₁₃³⁷Cl₂NO₂), 7], 323 [*M*⁺ (C₁₆H₁₃³⁵Cl³⁷ClNO₂),
43], 321 [*M*⁺ (C₁₆H₁₃³⁵Cl₂NO₂), 66], 286 (100), 251 (92), 227 (46), 183 (78), 138 (63),
77 (52).

Anal. Calcd for C₁₆H₁₃Cl₂NO₂: C, 59.65; H, 4.07; N, 4.35. Found: C, 59.38; H, 4.21; N,
4.31.

2,2-Dichloro-3-(4-cyanophenyl)-1-phenylaziridine (2e)

Yield: 49%; colorless oil.

IR (neat): $\nu = 3066, 2229, 1597, 1493, 1390, 887, 760 \text{ cm}^{-1}$.

^1H NMR (300 MHz, CDCl_3): $\delta = 7.72$ (d, 2 H, $J = 8.3 \text{ Hz}$), 7.63 (d, 2 H, $J = 8.3 \text{ Hz}$), 7.03 - 7.45 (m, 5 H), 3.73 (s, 1 H).

^{13}C NMR (75 MHz, CDCl_3): $\delta = 144.2, 138.2, 132.2, 129.2, 128.6, 124.8, 119.7, 118.4, 112.8, 74.8, 53.8$.

MS (EI, 70 eV): m/z (%) = 292 [M^+ ($\text{C}_{15}\text{H}_{10}^{37}\text{Cl}_2\text{N}_2$), 4], 290 [M^+ ($\text{C}_{15}\text{H}_{10}^{35}\text{Cl}^{37}\text{ClN}_2$), 23], 288 [M^+ ($\text{C}_{15}\text{H}_{10}^{35}_2\text{ClN}_2$), 37], 253 (100), 218 (69), 150 (58), 138 (25), 77 (45).

Anal. Calcd for $\text{C}_{15}\text{H}_{10}\text{Cl}_2\text{N}_2$: C, 62.31; H, 3.49; N, 9.69. Found: C, 62.35; H, 3.33; N, 9.40.

2,2-Dichloro-1-phenyl-3-(4-styrylphenyl)aziridine (2f)

Yield: 66%; white solid; mp: 148-149.5 °C.

IR (KBr): $\nu = 3022, 1597, 1493, 1268, 886, 753, 692, 573 \text{ cm}^{-1}$.

^1H NMR (300 MHz, CDCl_3): $\delta = 7.06$ - 7.59 (m, 16 H), 3.71 (s, 1 H).

^{13}C NMR (75 MHz, CDCl_3): $\delta = 144.9, 138.1, 137.1, 132.2, 129.5, 129.1, 128.7, 128.2, 128.0, 127.8, 126.6, 126.5, 124.3, 119.7, 75.4, 54.5$.

MS (EI, 70 eV): m/z (%) = 369 [M^+ ($\text{C}_{22}\text{H}_{17}^{37}\text{Cl}_2\text{N}$), 10], 367 [M^+ ($\text{C}_{22}\text{H}_{17}^{35}\text{Cl}^{37}\text{ClN}$), 54], 365 [M^+ ($\text{C}_{22}\text{H}_{17}^{35}_2\text{Cl}_2\text{N}$), 82], 330 (80), 295 (59), 283 (19), 227 (100), 191 (43), 138 (20), 77 (17).

Exact Mass calcd for $\text{C}_{22}\text{H}_{17}^{35}\text{Cl}_2\text{N}$: 365.0738. Found: 365.0718.

N-n-Octyl- α -chlorophenylacetamide (3h)

Yield: 29%; colorless oil.

IR (neat): $\nu = 3289, 3083, 2927, 2855, 1658, 1557 \text{ cm}^{-1}$.

^1H NMR (300 MHz, CDCl_3): $\delta = 7.33\text{--}7.44$ (m, 5 H), 6.70 (br s, 1 H), 5.36 (s, 1 H), 3.29–3.35 (m, 2 H), 1.27–1.57 (m, 12 H), 0.88 (t, 3 H, $J = 7.0 \text{ Hz}$).

^{13}C NMR (75 MHz, CDCl_3): $\delta = 167.2, 137.3, 129.0, 128.9, 127.8, 61.9, 40.2, 31.8, 29.3, 29.2, 26.8, 22.6, 14.1$.

MS (EI, 70 eV): m/z (%) = 283 [M^+ ($\text{C}_{16}\text{H}_{24}^{37}\text{ClNO}$), 11], 281 [M^+ ($\text{C}_{16}\text{H}_{24}^{35}\text{ClNO}$), 33], 156 (73), 126 (57), 91 (27), 71 (100), 57 (86).

Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{ClNO}$: C, 68.19; H, 8.58; N, 4.97. Found: C, 67.93; H, 8.77; N, 5.02.

References

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¹³C-NMR Spectra for 2a

¹³C-NMR Spectra for 2b

¹³C-NMR Spectra for 2c

¹³C-NMR Spectra for 2f

¹³C-NMR Spectra for 3g