Supporting Information

Stereoselective Synthesis of trans-Aziridines via Intramolecular Oxidative $C(sp^3)$ -H Amination of β -amino Ketones

Chen Tan,^a Yongguo Liu,^c Xinyuan Liu,^a Huanxin Jia,^a Sihan Huang,^a Kun Xu,^{b*} Jingwen Wang^a and Jiajing Tan^{a*}

- ^a Department of Organic Chemistry, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, China. E-mail: tanjj@mail.buct.edu.cn.
- ^b College of Chemistry and Pharmaceutical Engineering, Nanyang Normal University, Nanyang, Henan 473061, China. E-mail: xukun@nynu.edu.cn
- c Beijing Key Laboratory of Flavor Chemistry, Beijing Technology and Business University (BTBU), Beijing 100048, China.

CONTENTS

1. General Information	S3
2. Experimental Procedures for the Preparation of 1a-1u , 3a-3j , 5	S4
3. Experimental Procedures for the Preparation of Aziridines 2a-2u,	4a-4j
5a-5c	S6
4. Experimental Procedures for the Preparation of Aziridines 7a-7q.	S27
5. Scale-up Synthesis	\$37
6. Control Experiments	S39
7. References	S40
8. ¹ H NMR and ¹³ C NMR Spectra of the Products	S41

1. General Information

All reactions were carried out in pressure tubes, Schlenk tubes or roundbottomed flask The reactions monitored bv thin-laver were chromatography on silica gel 60-F254 coated 0.2 mm plates. Visualization was accomplished by UV light (254 nm). The crude products were purified by flash column chromatography using silica gel (normal phase, 200-300 mesh). Melting points (uncorrected) were obtained from a RY-1 melting point instrument (from NanBei Instrument). ¹H NMR spectra were recorded on a 400 MHz spectrometer at ambient temperature. Data were reported as follows: (1) chemical shift in parts per million (δ , ppm) from $CDCl_3$ (7.26 ppm); (2) multiplicity (s = singlet, br = broad, d = doublet, t = triplet, q = quartet, and m = multiplet); (3) coupling constants (Hz). ^{13}C NMR spectra were recorded on a 100 MHz spectrometer at ambient temperature. Chemical shifts were reported in ppm from CDCl₃ (77.16 ppm). HR-MS analyses were carried out using a time-of-flight (TOF)-MS instrument with an electrospray ionization (ESI) source. All commercial materials were used as received unless otherwise noted.

2. Experimental Procedures for the Preparation of 1a-1p, 3a-3j, 5a-5c

2.1. General procedure 1:



Scheme S1. General procedure for preparation of 1a-1o, 3a-3j.

The substituted aryl methyl ketone (1.0 mmol), an aqueous solution of 10% sodium hydroxide (2.5 mmol) and ethanol (5 mL) were charged into a 50 mL flask, and the mixture was stirred at room temperature for 10 min, followed by addition of substituted aromatic aldehyde (1.05 mmol). The reaction mixture was then stirred at room temperature and monitored using TLC until all reactants disappeared. The mixture was extracted with ethyl acetate three times, and the combined organic phase was dried over sodium sulfate and concentrated under vacuum. The residue was recrystallized from anhydrous ethanol.

FeCl₃· $6H_2O$ (10 mol%) and the enones (1 equiv.) were dissolved in dichloromethane (10 M). Me₃SiCl (1.1 equiv.) was added. Then carbamates (1.2 equiv.) was added in one portion. The yellow solution was stirred at room temperature and conversion was monitored by TLC. After completion of the reaction, the mixtures were quenched with 5ml saturated aqueous sodium hydrogen carbonate, and the aqueous layer was extracted with dichloromethane. The combined organic layers were dried over

 Na_2SO_4 , filtered, and evaporated *in vacuo*. The crude product was further purified by column chromatography on silica gel (PE/EA = 10:1 to 5:1) to afford the title compound as a white solid.^{S1}

2.2. General procedure 2:



Scheme S2. General procedure for preparation of 1p-1u, 5a-5c.

To a solution of the aminal (0.10 mmol) and trimethyl((1-phenylvinyl)oxy)silane (21 mg, 0.11 mmol) in ichloromethane (1.0 mL) was added copper(II) trifluoromethanesulfonate (3.6 mg, 0.010 mmol) at room temperature. After stirring for 24 h, the crude product was further purified by column chromatography on silica gel (PE/EA = 10:1 to 5:1) to afford the title compound as a white solid.^{S2}

3. Experimental Procedures for the Preparation of Aziridines 2a-2z,

4a-4c

General procedure 3:



Scheme S3. General procedure for preparation of 2a-2z, 4a-4c.

A 10 mL pressure tube was charged with Chalcone (0.2 mmol, 1.0 equiv.), KI (0.16 mmol, 26.6 mg, 0.8 equiv.), K_2CO_3 (0.24 mmol, 34.6 mg, 1.2 equiv.), THF (1.6 mL) and methanol (0.4 mL), then TBHP (4.5 mol/L in *n*-Hexane, 1.0 mmol, 200 µL, 4.5 equiv.) was added to the reaction mixture slowly, The reaction mixture was stirred at room temperate for 1 hour. The resultant solution was quenched with aqueous saturated sodium thiosulfate solution (4 mL), H₂O (10 mL) and extracted with ethyl acetate (3×30 mL), dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The crude product was further purified by column chromatography on silica gel (PE/DCM/EA = 30:5:1 to 25:5:1) to afford the title compound as a colorless oil.

trans-Ethyl-2-benzoyl-3-phenylaziridine-1-carboxylate (2a)



Rf = 0.6 (PE/DCM/EA = 12:5:1).*Color and State*: Colorless oil.*Mass and Yield*: 47 mg, 80% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, J = 7.4 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.7 Hz, 2H), 7.42 – 7.32 (m, 5H), 4.31 – 4.21 (m, 2H), 4.05 (d, J = 2.4 Hz, 1H), 3.91 (d, J = 2.3 Hz, 1H), 1.27 (t, J = 7.1 Hz, 3H).
¹³C NMR (100 MHz, CDCl₃) δ 192.28, 160.52, 136.54, 135.96, 134.15, 129.02, 128.83, 128.65, 128.61, 126.57, 62.94, 47.55, 47.31, 14.46.
HR-MS (ESI, [M+H]⁺) calcd for C₁₈H₁₈NO₃⁺ 296.1281, found 296.1283.

trans-Ethyl-2-benzoyl-3-(o-tolyl)aziridine-1-carboxylate (2b)



Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: Colorless oil.

Mass and Yield: 36 mg, 58% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 8.09 – 8.03 (m, 2H),

7.67 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.7 Hz, 2H), 7.48 – 7.42 (m, 1H), 7.31 – 7.24 (m, 2H), 7.22 – 7.17 (m, 1H), 4.35 – 4.25 (m, 2H), 4.03 (d, J = 2.6 Hz, 1H), 4.01 (d, J = 2.4 Hz, 1H), 2.35 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 192.46, 160.84, 136.85, 136.41, 134.18, 130.13, 129.05, 128.54, 128.38, 126.37, 125.79, 62.88, 46.27, 46.09, 19.13, 14.45.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{19}H_{20}NO_3^+$ 310.1438, found 310.1445.

trans-Ethyl-2-benzoyl-3-(2-bromophenyl)aziridine-1-carboxylate (2c)



Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: Colorless oil.

Mass and Yield: 59 mg, 79% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, J = 7.4 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.52 (ddd, J = 8.9, 7.5, 5.6 Hz, 4H), 7.34 (t, J = 7.5 Hz, 1H), 7.21 (td, J = 7.8, 1.4 Hz, 1H), 4.33 – 4.24 (m, 2H), 4.06 (d, J = 2.3 Hz, 1H), 3.95 (d, J = 2.5 Hz, 1H), 1.29 (t, J = 7.1 Hz, 3H).
¹³C NMR (100 MHz, CDCl₃) δ 192.14, 160.60, 136.43, 135.73, 134.13, 132.46, 129.94, 128.97, 128.67, 128.33, 127.78, 123.72, 63.02, 48.15,

46.13, 14.47.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{18}H_{17}BrNO_3^+$ 374.0386, found 374.0396.

trans-Ethyl-2-benzoyl-3-(2-chlorophenyl)aziridine-1-carboxylate (2d)



Rf = 0.6 (PE/DCM/EA = 12:5:1). *Color and State*: Colorless oil.

Mass and Yield: 60 mg, 91% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 8.09 – 8.02 (m, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 3H), 7.42 – 7.36 (m, 1H), 7.34 – 7.28 (m, 2H), 4.36 – 4.27 (m, 2H), 4.15 (d, *J* = 2.4 Hz, 1H), 3.99 (d, *J* = 2.5 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 192.14, 160.61, 136.40, 134.13, 134.07, 129.65, 129.31, 128.98, 128.61, 127.91, 127.20, 63.01, 46.13, 45.73,

14.46.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{18}H_{17}CINO_3^+$ 330.0891, found 330.0879.

trans-Ethyl 2-benzoyl-3-(2-(trifluoromethyl)phenyl)aziridine-1carboxylate (2e)



Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: Colorless oil.

Mass and Yield: 63 mg, 87% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 7.99 (d, J = 7.4 Hz,

2H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.67 – 7.56 (m, 3H), 7.52 – 7.41 (m, 3H), 4.29 (q, 2H), 4.19 (br, 1H), 3.99 (d, *J* = 2.5 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 191.74, 160.51, 136.40, 134.46, 134.15, 132.46, 128.95, 128.85 (q, J = 31.2 Hz), 128.58, 128.46, 127.86, 125.91 (q, J = 5.5 Hz), 124.26 (q, J = 273.8 Hz), 63.05, 46.42, 44.75, 14.43.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{19}H_{17}F_3NO_3^+$ 364.1155, found 364.1150.

trans-Ethyl-2-benzoyl-3-(3-methoxyphenyl)aziridine-1-carboxylate (2f)



$$Rf = 0.6 (PE/DCM/EA = 12:5:1).$$

Color and State: Colorless oil.

Mass and Yield: 57 mg, 88% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 7.31 – 7.26 (m, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 2.2 Hz, 1H), 6.88 (dd, *J* = 7.9, 2.2 Hz, 1H), 4.30 – 4.21 (m, 2H), 4.04 (d, *J* = 2.4 Hz, 1H), 3.88 (d, *J* = 2.3 Hz, 1H), 3.82 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 192.23, 160.47, 160.14, 137.56, 136.52, 134.16, 129.91, 129.03, 128.61, 119.04, 114.60, 111.47, 62.96, 55.47, 47.49, 47.32, 14.46.

HR-MS (ESI, $[M+H]^+$) calcd for C₁₉H₂₀NO₄⁺ 326.1387, found 326.1389.

trans-Ethyl-2-benzoyl-3-(3-chlorophenyl)aziridine-1-carboxylate (2g)



Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: Colorless oil.

Mass and Yield: 59 mg, 90% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 8.03 – 7.96 (m, 2H),

7.63 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.7 Hz, 2H), 7.38 (d, J = 1.0 Hz, 1H), 7.33 – 7.27 (m, 3H), 4.31 – 4.20 (m, 2H), 4.02 (d, J = 2.4 Hz, 1H), 3.88 (d, J = 2.3 Hz, 1H), 1.26 (t, J = 7.1 Hz, 3H).

¹³C NMR δ 191.80, 160.10, 138.00, 136.28, 134.79, 134.18, 130.02, 128.97, 128.69, 128.50, 126.43, 124.87, 62.91, 47.06, 46.43, 14.34.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{18}H_{17}CINO_3^+$ 330.0891, found

330.0902.

trans-Ethyl-2-benzoyl-3-(3-bromophenyl)aziridine-1-carboxylate (2h)



Rf = 0.6 (PE/DCM/EA = 12:5:1).*Color and State*: Colorless oil.*Mass and Yield*: 69 mg, 93% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 8.02 (d, J = 7.4 Hz,

2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.58 – 7.46 (m, 4H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.26 (t, *J* = 7.8 Hz, 1H), 4.33 – 4.23 (m, 2H), 4.04 (d, *J* = 2.4 Hz, 1H), 3.89 (d, *J* = 2.3 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 191.78, 160.07, 138.21, 136.27, 134.18, 131.63, 130.24, 129.32, 128.95, 128.50, 125.32, 122.91, 62.94, 47.11, 46.34, 14.32.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{18}H_{17}BrNO_3^+$ 374.0386, found 374.0393.

trans-Ethyl-2-benzoyl-3-(p-tolyl)aziridine-1-carboxylate (2i)



Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: Colorless oil.

Mass and Yield: 28 mg, 45% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.02 – 7.97 (m, 2H),

7.62 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H),

7.18 (d, J = 8.0 Hz, 2H), 4.30 – 4.20 (m, 2H), 4.03 (d, J = 2.5 Hz, 1H), 3.86 (d, J = 2.4 Hz, 1H), 2.36 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H).
¹³C NMR (100 MHz, CDCl₃) δ 192.32, 160.56, 138.54, 136.54, 134.08, 132.95, 129.49, 128.98, 128.56, 126.45, 62.86, 47.57, 47.34, 21.34, 14.45.
HR-MS (ESI, [M+H]⁺) calcd for C₁₉H₂₀NO₃⁺ 310.1438, found 310.1443.

trans-Ethyl-2-benzoyl-3-(4-fluorophenyl)aziridine-1-carboxylate (2j)



Rf = 0.6 (PE/DCM/EA = 12:5:1). Color and State: Colorless oil. Mass and Yield: 48 mg, 77% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.03 – 7.95 (m, 2H),

7.63 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.41 – 7.32 (m, 2H), 7.06 (dd, *J* = 12.0, 5.3 Hz, 2H), 4.32 – 4.18 (m, 2H), 4.01 (d, *J* = 2.4 Hz, 1H), 3.88 (d, *J* = 2.3 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 192.08, 162.96 (d, *J* = 247.4 Hz), 160.38, 136.46, 134.19, 131.75 (d, *J* = 3.1 Hz), 128.25 (d, *J* = 8.3 Hz), 115.80 (d, *J* = 21.8 Hz), 62.96, 47.26, 46.75, 14.42.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{18}H_{17}FNO_3^+$ 314.1187, found 314.1196.

trans-Ethyl-2-benzoyl-3-(4-chlorophenyl)aziridine-1-carboxylate (2k)



Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: Colorless oil.

Mass and Yield: 59 mg, 89% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 8.02 – 7.97 (m, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.7 Hz, 2H), 7.37 – 7.30 (m, 4H), 4.30 – 4.20 (m, 2H), 4.00 (d, J = 2.4 Hz, 1H), 3.87 (d, J = 2.4 Hz, 1H), 1.26 (t, J = 7.1 Hz, 4H). ¹³**C NMR** (100 MHz, CDCl₃) δ 191.97, 160.30, 136.42, 134.52, 134.24, 129.05, 129.02, 129.02, 128.58, 127.90, 63.01, 47.27, 46.68, 14.43. **HR-MS** (ESI, [M+H]⁺) calcd for C₁₈H₁₇ClNO₃⁺ 330.0891, found 330.0897.

trans-Ethyl-2-benzoyl-3-(4-bromophenyl)aziridine-1-carboxylate (2l)



Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: Colorless oil.

Mass and Yield: 64 mg, 85% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.04 – 7.98 (m, 2H),

7.65 (t, *J* = 7.4 Hz, 1H), 7.53 (dd, *J* = 8.0, 6.8 Hz, 4H), 7.33 – 7.26 (m, 2H), 4.28 (dtt, *J* = 10.7, 7.1, 3.5 Hz, 2H), 4.03 (d, *J* = 2.4 Hz, 1H), 3.89 (d, *J* = 2.3 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 191.91, 160.25, 136.37, 135.03, 134.23, 132.04, 131.93, 129.03, 128.55, 128.19, 122.60, 62.99, 47.19, 46.70, 14.41.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{18}H_{17}BrNO_3^+$ 374.0386, found 374.0393.

trans-Ethyl-2-benzoyl-3-(4-(trifluoromethyl)phenyl)aziridine-1-

carboxylate (2m)



Rf = 0.6 (PE/DCM/EA = 12:5:1). *Color and State*: Colorless oil. *Mass and Yield*: 49 mg, 67% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.02 – 7.97 (m, 2H),

7.67 – 7.61 (m, 3H), 7.50 (dd, J = 10.9, 4.8 Hz, 4H), 4.30 – 4.21 (m, 2H), 4.04 (d, J = 2.4 Hz, 1H), 3.96 (d, J = 2.4 Hz, 1H), 1.27 (t, J = 7.1 Hz, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 191.70, 160.07, 139.90, 136.23, 134.24, 130.70 (q, J = 32.6 Hz), 128.98, 128.49, 126.85, 125.69 (q, J = 3.5 Hz), 123.98 (q, J = 272.1 Hz). 63.00, 47.14, 46.39, 14.29.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{19}H_{17}F_3NO_3^+$ 364.1155, found 346.1148.

trans-Ethyl 2-benzoyl-3-(naphthalen-1-yl)aziridine-1-carboxylate (2n)



Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: Colorless oil.

Mass and Yield: 62 mg, 90% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 8.02 (d, J = 7.4 Hz,

2H), 7.91 (s, 1H), 7.88 – 7.81 (m, 3H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.53 – 7.45 (m, 5H), 4.34 – 4.25 (m, 2H), 4.14 (d, *J* = 2.4 Hz, 1H), 4.08 (d, *J* = 2.4 Hz,

1H), 1.29 (t, J = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 192.19, 160.55, 136.53, 134.15, 133.48, 133.38, 133.30, 129.03, 128.74, 128.60, 128.02, 127.92, 126.70, 126.51, 126.18, 123.67, 62.99, 47.78, 47.50, 14.48.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{22}H_{20}NO_3^+$ 346.1438, found 346.1445.

trans-Ethyl 2-benzoyl-3-(naphthalen-2-yl)aziridine-1-carboxylate (20)



Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: Colorless oil.

Mass and Yield: 53 mg, 76% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 8.04 (dd, J = 9.2, 8.0

Hz, 3H), 7.92 – 7.83 (m, 2H), 7.71 – 7.61 (m, 2H), 7.55 – 7.45 (m, 5H), 4.50 (d, *J* = 2.1 Hz, 1H), 4.37 – 4.27 (m, 2H), 4.12 (d, *J* = 2.6 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 192.62, 160.97, 136.49, 134.22, 133.49,
131.83, 131.68, 129.04, 128.96, 128.90, 128.63, 126.83, 126.21, 125.59,
124.21, 122.89, 62.96, 46.27, 45.98, 14.47.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{22}H_{20}NO_3^+$ 346.1438, found 346.1439.

trans-Ethyl 2-benzoyl-3-(tert-butyl)aziridine-1-carboxylate (2p)



Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: Colorless oil.

Mass and Yield: 42 mg, 78% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.00 – 7.95 (m, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 4.20 (q, J = 7.1 Hz, 2H), 3.94 (d, J = 2.8 Hz, 1H), 2.71 (d, J = 2.8 Hz, 1H), 1.23 (t, J = 7.1 Hz, 3H), 1.00 (s, 9H).
¹³C NMR (100 MHz, CDCl₃) δ 193.62, 161.23, 136.62, 133.86, 128.95, 128.27, 62.47, 55.87, 40.50, 31.20, 26.53, 14.40.
HR-MS (ESI, [M+H]⁺) calcd for C₂₂H₂₀NO₃⁺ 276.1594, found 276.1599.

trans-Ethyl-2-benzoyl-3-cyclohexylaziridine-1-carboxylate (2q)



Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: Colorless oil.

Mass and Yield: 51 mg, 85% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 8.00 (d, J = 7.5 Hz,

2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.90 (d, *J* = 2.7 Hz, 1H), 2.70 (dd, *J* = 7.2, 2.7 Hz, 1H), 1.94 – 1.88 (m, 1H), 1.82 – 1.71 (m, 3H), 1.70 – 1.60 (m, 1H), 1.35 (tt, *J* = 9.0, 6.6 Hz, 1H), 1.27 – 1.10 (m, 8H).

¹³C NMR (100 MHz, CDCl₃) δ 193.53, 161.15, 136.64, 133.86, 128.94, 128.36, 62.50, 51.73, 42.33, 39.97, 30.31, 29.92, 26.19, 25.72, 25.62, 14.42.

HR-MS (ESI, $[M+H]^+$) calcd for C₁₈H₂₄NO₃⁺ 302.1751, found 302.1760.

trans-Ethyl-2-benzoyl-3-isopropylaziridine-1-carboxylate (2r)



Rf = 0.3 (PE /EA = 20:1).
Color and State: Colorless oil.
Mass and Yield: 26 mg, 52% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 8.03 – 7.98 (m, 2H), 7.62 (ddd, J = 6.9, 2.3, 1.2 Hz, 1H), 7.55 – 7.48 (m, 2H), 4.21 (tt, J = 7.1, 3.6 Hz, 2H), 3.88 (d, J = 2.7 Hz, 1H), 2.71 (dd, J = 7.2, 2.7 Hz, 1H), 1.70 (dq, J = 13.7, 6.8 Hz, 1H), 1.24 (t, J = 7.1 Hz, 3H), 1.11 (d, J = 6.7 Hz, 3H), 1.02 (d, J = 6.8 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 193.51, 161.12, 136.68, 133.91, 128.98, 128.39, 62.56, 52.74, 42.45, 30.67, 19.74, 19.26, 14.44.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{15}H_{20}NO_3^+$ 262.1438, found 262.1437.





Rf = 0.7 (PE/DCM/EA = 12:5:1).*Color and State*: Colorless oil.*Mass and Yield*: 20 mg, 69% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.03 – 7.99 (m, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.7 Hz, 2H), 4.24 – 4.16 (m, 2H), 3.82 (d, J = 2.7 Hz, 1H), 2.87 (td, J = 6.1, 2.7 Hz, 1H), 1.72 – 1.49 (m, 4H), 1.34 (dt, J = 8.4, 5.2 Hz, 4H), 1.24 – 1.22 (m, 3H), 0.88 (t, J = 7.0 Hz, 3H).
¹³C NMR (100 MHz, CDCl₃) δ 193.56, 161.14, 136.69, 133.92, 128.96,

128.48, 62.61, 46.82, 43.66, 31.74, 31.45, 26.53, 22.65, 14.46, 14.11. **HR-MS** (ESI, [M+H]⁺) calcd for C₁₇H₂₄NO₃⁺ 290.1751, found 290.1748.

trans-Ethyl-2-benzoyl-3-methylaziridine-1-carboxylate (2t)



Rf = 0.4 (PE/EA = 20:1).*Color and State*: Colorless oil.*Mass and Yield*: 38 mg, 81% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 8.05 – 7.98 (m, 2H), 7.62 (ddd, *J* = 6.9, 2.3, 1.1 Hz, 1H), 7.50 (dd, *J* = 10.6, 4.7 Hz, 2H), 4.25 – 4.15 (m, 2H), 3.76 (t, *J* = 2.4 Hz, 1H), 2.93 (dq, *J* = 8.2, 2.8 Hz, 1H), 1.44 (d, *J* = 5.5 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 193.53, 161.05, 136.62, 133.92, 128.93, 128.50, 62.64, 44.49, 41.99, 17.06, 14.45.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{13}H_{16}NO_3^+$ 234.1125, found 234.1124.

trans-Ethyl-2-benzoyl-3-benzylaziridine-1-carboxylate (2u)



Rf = 0.6 (PE/DCM/EA = 12:5:1). *Color and State*: Colorless oil.

Mass and Yield: 54 mg, 88% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 7.83 (d, *J* = 7.4 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.27 – 7.14 (m, 5H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.77 (d, *J* = 2.2 Hz, 1H), 3.16 – 3.04 (m, 2H), 2.80 (dd, *J* = 16.6, 8.0 Hz,

1H), 1.15 (t, J = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 193.23, 160.88, 136.91, 136.55, 133.93, 128.98, 128.92, 128.77, 128.41, 127.01, 62.68, 46.36, 43.16, 37.67, 14.40.
HR-MS (ESI, [M+H]⁺) calcd for C₁₉H₂₀NO₃⁺ 310.1438, found 310.1446.



Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: Colorless oil.

Mass and Yield: 59 mg, 95 % yield.

¹**H NMR** (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.2 Hz, 2H), 4.15 (pd, *J* = 7.6, 3.5 Hz, 2H), 3.93 (d, *J* = 2.4 Hz, 1H), 3.79 (d, *J* = 2.4 Hz, 1H), 2.33 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 191.66, 160.56, 145.22, 136.04, 134.05, 129.66, 128.76, 128.71, 128.55, 126.53, 62.83, 47.31, 47.20, 21.87, 14.42.
HR-MS (ESI, [M+H]⁺) calcd for C₁₉H₂₀NO₃⁺ 310.1438, found 310.1426.

trans-Ethyl-2-(4-methoxybenzoyl)-3-phenylaziridine-1-carboxylate (4b)



Rf = 0.6 (PE/DCM/EA = 12:5:1). *Color and State*: Colorless oil. *Mass and Yield*: 63 mg, 97% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.01 – 7.97 (m, 2H), 7.43 – 7.29 (m, 5H),

6.98 – 6.93 (m, 2H), 4.29 – 4.19 (m, 2H), 4.00 (d, J = 2.5 Hz, 1H), 3.88 (d, J = 2.5 Hz, 1H), 3.87 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H).
¹³C NMR (100 MHz, CDCl₃) δ 190.31, 164.41, 160.63, 136.13, 131.02, 129.61, 128.75, 128.51, 126.53, 114.19, 62.80, 55.68, 47.09, 47.04, 14.43.
HR-MS (ESI, [M+H]⁺) calcd for C₁₉H₂₀NO₄⁺ 326.1387, found 326.1387.

trans-Ethyl-2-(4-fluorobenzoyl)-3-phenylaziridine-1-carboxylate (4c)



Rf = 0.6 (PE/DCM/EA = 12:5:1). Color and State: Colorless oil.

Mass and Yield: 46 mg, 74% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 8.06 – 8.01 (m, 2H), 7.40 – 7.31 (m, 5H), 7.20 – 7.13 (m, 2H), 4.29 – 4.19 (m, 2H), 4.00 (d, *J* = 2.5 Hz, 1H), 3.90 (d, *J* = 2.4 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 190.67, 166.38 (d, J = 256.7 Hz), 160.35, 135.77, 132.99, 131.34 (d, J = 9.5 Hz), 128.83, 126.52, 116.23 (d, J = 22.1 Hz), 62.93, 47.49, 47.05, 14.41.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{18}H_{17}FNO_3^+$ 314.1187, found 314.1118.

trans-Ethyl-2-(4-bromobenzoyl)-3-phenylaziridine-1-carboxylate (4d)



Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: Colorless oil.

Mass and Yield: 35 mg, 47% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 7.88 – 7.84 (m, 2H), 7.67 – 7.61 (m, 2H), 7.40 – 7.33 (m, 5H), 4.29 – 4.20 (m, 2H), 3.98 (d, *J* = 2.4 Hz, 1H), 3.90 (d, *J* = 2.4 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 191.26, 160.18, 135.60, 135.10, 132.26, 129.92, 128.75, 128.63, 126.42, 62.88, 47.55, 46.95, 14.33.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{18}H_{17}BrNO_3^+$ 374.0386, found 374.0378.

trans-Ethyl-2-(3-methylbenzoyl)-3-phenylaziridine-1-carboxylate (4e)



Rf = 0.6 (PE/DCM/EA = 12:5:1).*Color and State*: Colorless oil.*Mass and Yield*: 57 mg, 85% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 7.80 (d, *J* = 8.6 Hz, 2H), 7.45 – 7.29 (m, 7H), 3.51 (d, *J* = 5.7 Hz, 1H), 3.18 (d, *J* = 7.1 Hz, 1H), 2.67 (br, 1H), 2.41 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 196.00, 138.84, 138.56, 136.09, 134.74,
128.86, 128.80, 128.66, 127.96, 126.36, 125.74, 44.19, 43.65, 21.44.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{19}H_{20}NO_3^+$ 310.1438, found 310.1438.

trans-Ethyl-2-(3-bromobenzoyl)-3-phenylaziridine-1-carboxylate (4f)



Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: Colorless oil.

Mass and Yield: 64 mg, 85% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 8.12 (t, *J* = 1.7 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.78 – 7.71 (m, 1H), 4.30 – 4.19 (m, 2H), 3.97 (d, *J* = 2.4 Hz, 1H), 3.91 (d, *J* = 2.4 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 191.18, 160.24, 138.16, 136.99, 135.64, 131.57, 130.58, 128.88, 128.80, 127.13, 126.56, 123.41, 63.05, 47.86, 47.09, 14.46.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{18}H_{17}BrNO_3^+$ 374.0386, found 374.0392.

trans-Ethyl-2-(2-methylbenzoyl)-3-phenylaziridine-1-carboxylate (4g)



Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: Colorless oil.

Mass and Yield: 54 mg, 87% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 7.83 – 7.76 (m, 2H), 7.46 – 7.32 (m, 7H), 4.31 – 4.20 (m, 2H), 4.04 (d, *J* = 2.4 Hz, 1H), 3.90 (d, *J* = 2.4 Hz, 1H), 2.42 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 192.40, 160.53, 138.93, 136.56, 136.02, 134.93, 129.07, 128.87, 128.80, 128.60, 126.57, 125.85, 62.89, 47.51, 47.32, 21.46, 14.46.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{19}H_{20}NO_3^+$ 310.1438, found 310.1431

trans-Ethyl-2-(2-chlorobenzoyl)-3-phenylaziridine-1-carboxylate (4h)



Rf = 0.6 (PE/DCM/EA = 12:5:1).*Color and State*: Colorless oil.*Mass and Yield*: 44 mg, 67% yield.

¹**H NMR** δ 7.61 (dt, *J* = 8.6, 3.0 Hz, 1H), 7.49 – 7.36 (m, 9H), 4.34 – 4.27 (m, 2H), 3.96 (d, *J* = 2.4 Hz, 1H), 3.92 (d, *J* = 2.4 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 195.13, 160.16, 137.89, 135.68, 133.16, 130.67, 130.09, 129.14, 128.76, 128.65, 127.36, 126.57, 62.97, 50.45, 48.72, 14.50.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{18}H_{17}CINO_3^+$ 326.1387, found 330.0894.

trans-Ethyl-2-(furan-2-carbonyl)-3-phenylaziridine-1-carboxylate (4i)



Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: Colorless oil.

Mass and Yield: 42 mg, 73% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 7.65 (s, 1H), 7.35 (d, *J* = 7.2 Hz, 6H), 6.63 - 6.57 (m, 1H), 4.31 - 4.15 (m, 2H), 3.95 (s, 1H), 3.91 (s, 1H), 1.26 (t, *J* = 7.0 Hz, 4H).

¹³C NMR (100 MHz, CDCl₃) δ 180.37, 160.18, 152.55, 147.80, 135.81, 128.74, 128.59, 126.53, 119.19, 112.98, 77.48, 77.16, 76.84, 62.93, 47.01,

46.93, 14.40.

HR-MS (ESI, $[M+H]^+$) calcd for C₁₆H₁₆NO₄⁺ 286.1074, found 286.1051.

trans-Ethyl (2R,38)-2-phenyl-3-(thiophene-2-carbonyl)aziridine-1carboxylate (4j)



Rf = 0.6 (PE/DCM/EA = 12:5:1).*Color and State*: Colorless oil.*Mass and Yield*: 56 mg, 92% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 7.86 (dd, *J* = 3.9, 0.9 Hz, 1H), 7.75 (dd, *J* = 4.9, 0.9 Hz, 1H), 7.41 – 7.31 (m, 5H), 7.18 (dd, *J* = 4.8, 4.0 Hz, 1H), 4.24 (dtt, *J* = 10.7, 7.1, 3.5 Hz, 2H), 3.94 (d, *J* = 2.4 Hz, 1H), 3.89 (d, *J* = 2.4 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 184.39, 160.19, 143.37, 135.80, 135.60, 133.46, 128.78, 128.70, 128.62, 126.55, 62.94, 47.69, 47.07, 14.43.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{16}H_{16}NO_3S^+$ 302.0845, found 302.0787.

trans-Benzyl (2S,3R)-2-benzoyl-3-phenylaziridine-1-carboxylate (6a)



Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: Colorless oil.

Mass and Yield: 47 mg, 65% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 7.99 (d, *J* = 7.4 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.42 – 7.31 (m, 10H), 4.09 (d, *J* = 2.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.42 – 7.31 (m, 10H), 4.09 (d, *J* = 2.4 Hz), 7.42 – 7.4 Hz, 10H), 4.09 (d, *J* = 2.4 Hz), 7.42 – 7.4 Hz, 10H), 4.09 (d, *J* = 2.4 Hz), 7.42 – 7.4 Hz), 7.50 (t, *J* = 7.7 Hz), 7.42 – 7.31 (m, 10H), 4.09 (d, *J* = 2.4 Hz), 7.42 – 7.4 Hz), 7.50 (t, *J* = 7.7 Hz), 7.42 – 7.4 Hz), 7.42 – 7.4 Hz), 7.50 (t, *J* = 7.7 Hz), 7.42 – 7.4 Hz), 7.44 – 7.44

1H), 3.97 (d, *J* = 2.4 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 192.17, 160.43, 136.38, 135.75, 135.65, 134.14, 128.97, 128.79, 128.65, 128.57, 128.53, 128.32, 126.53, 68.59, 47.58, 47.33.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{23}H_{20}NO_3^+$ 358.1438, found 358.1442.

trans-Tert-butyl (2S,3R)-2-benzoyl-3-phenylaziridine-1-carboxylate (6b)



Rf = 0.6 (PE/DCM/EA = 12:5:1).*Color and State*: Colorless oil.*Mass and Yield*: 36 mg, 55% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 8.02 (d, *J* = 7.9 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.37 (dd, *J* = 15.8, 7.8 Hz, 5H), 4.01 (d, *J* = 2.2 Hz, 1H), 3.94 (d, *J* = 2.0 Hz, 1H), 1.45 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 192.51, 159.01, 136.90, 136.20, 133.96, 128.97, 128.75, 128.58, 128.50, 126.66, 82.21, 47.22, 28.09.

HR-MS (ESI, $[M+H]^+$) calcd for C₂₀H₂₂NO₃⁺ 324.1594, found 324.1600.

trans-Isopropyl (2S,3R)-2-benzoyl-3-phenylaziridine-1-carboxylate (6c)



Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: Colorless oil.

Mass and Yield: 40 mg, 63% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 8.04 – 7.98 (m, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.42 – 7.33 (m, 5H), 5.09 – 4.99 (m, 1H), 4.04 (d, *J* = 2.5 Hz, 1H), 3.92 (d, *J* = 2.4 Hz, 1H), 1.31 (d, *J* = 6.2 Hz, 3H), 1.19 (d, *J* = 6.3 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 192.21, 160.02, 136.63, 136.01, 134.04,
128.97, 128.77, 128.57, 128.55, 126.58, 70.70, 47.38, 47.22, 22.03, 21.92.
HR-MS (ESI, [M+H]⁺) calcd for C₁₉H₂₀NO₃⁺ 310.1438, found 310.1427.

4. Experimental Procedures for the Preparation of Aziridines 7a-pl

	Ph Ph Ph	KI, K ₂ CO ₃ , TBHP MeOH, 40 °C	Ph Ph NH Ph (±) 7a	
Entry	KI (equiv.)	K ₂ CO ₃ (equiv.)	TBHP (equiv.)	Yield (%) ^[a]
1	0.8	3.0	4.5	68
2	0.8	4.0	4.5	64
3	0.8	5.0	4.5	78
4	0.8	6.0	4.5	69
5	0.4	5.0	4.5	69
6	1.0	5.0	4.5	69
7	1.2	5.0	4.5	72
8	0.8	5.0	1.1	42
9	0.8	5.0	2.3	53
10	0.8	5.0	6.0	73

4.1. Table 1. Reaction Condition Optimization of 7a

^{*a*} Reaction conditions: 1 (0.2 mmol), K₂CO₃, KI in MeOH (2 mL), TBHP, 40 °C, 3 h; isolated yields.

4.2. General procedure 4:



Scheme S4. General procedure for preparation of 7a-7p.

A 10 mL pressure tube was charged with Chalcone (0.2 mmol, 1.0 equiv.), KI (0.16 mmol, 26.6 mg, 0.8 equiv.), K₂CO₃ (1.0 mmol, 144 mg, 5.0 equiv.), and methanol (2.0 mL), then TBHP (4.5 mol/L in *n*-Hexane, 1.0 mmol, 200 μ L, 4.5 equiv.) was added to the reaction mixture slowly, The reaction mixture was stirred at 40 °C for 1 hour. The resultant solution was quenched with aqueous saturated sodium thiosulfate solution (4 mL),

 H_2O (10 mL) and extracted with ethyl acetate (3×30 mL), dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The crude product was further purified by column chromatography on silica gel (PE/DCM/EA = 25:5:1) to afford the title compound as a white solid.

trans-Phenyltrans-3-phenylaziridin-2-yl)methanone (7a)^{S3, S4}



Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: white solid.

Mass and Yield: 36 mg, 81% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, J = 7.3 Hz, 2H),
7.61 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H), 7.42 – 7.27 (m, 5H), 3.55 – 3.48 (m, 1H), 3.18 (dd, J = 8.9, 1.7 Hz, 1H), 2.68 (t, J = 8.0 Hz, 1H).
¹³C NMR (100 MHz, CDCl₃) δ 195.84, 138.48, 136.06, 133.95, 128.95,
128.69, 128.46, 128.02, 126.34, 44.25, 43.67.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{15}H_{14}NO^+$ 224.1070, found 224.1076.

trans-Phenyltrans-3-(2-(trifluoromethyl)phenyl)aziridin-2-

yl)methanone (7b)



Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: white solid.

Mass and Yield: 43 mg, 73% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.95 – 7.87 (m, 2H), 7.71

(d, *J* = 7.8 Hz, 1H), 7.60 – 7.45 (m, 3H), 7.44 – 7.36 (m, 2H), 7.36 – 7.28 (m, 1H), 3.42 (d, *J* = 8.9 Hz, 1H), 3.34 (dd, *J* = 7.9, 2.3 Hz, 1H), 2.56 (t, *J* = 8.3 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 195.47, 136.85, 135.84, 134.01, 132.39,
129.46, 129.16, 128.88, 128.56, 127.74, 127.31, 125.78, 125.74, 125.69,
125.63, 123.06, 43.58, 40.24.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{16}H_{13}F_3NO^+$ 292.0944, found 292.0950.

trans-Phenyl*trans*-3-(o-tolyl)aziridin-2-yl)methanone (7c)

Ph NH Me (±) Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: white solid.

Mass and Yield: 29 mg, 61% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.07 – 8.02 (m, 2H), 7.63 (ddd, *J* = 7.0, 2.4, 1.2 Hz, 1H), 7.54 – 7.46 (m, 3H), 7.25 – 7.14 (m, 3H), 3.45 (m, 1H), 3.27 (m, 1H), 2.65 – 2.53 (m, 1H), 2.31 (s, 3H).
¹³C NMR (100 MHz, CDCl₃) δ 196.24, 136.76, 136.50, 135.97, 134.04, 129.97, 129.02, 128.43, 127.74, 126.38, 125.57, 42.96, 42.20, 19.22.
HR-MS (ESI, [M+H]⁺) calcd for C₁₆H₁₆NO⁺ 238.1226, found 238.1224.

trans-3-(3-Bromophenyl)aziridin-2-yl)(phenyl)methanone (7d)



Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: white solid.

Mass and Yield: 30 mg, 49% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 8.03 – 7.96 (m, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (dd, *J* = 13.1, 4.9 Hz, 3H), 7.47 – 7.41 (m, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 3.48 (dd, *J* = 8.1, 2.3 Hz, 1H), 3.13 (dd, *J* = 9.3, 2.2 Hz, 1H), 2.67 (t, *J* = 8.6 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 195.44, 140.89, 135.88, 134.11, 131.12, 130.21, 129.25, 129.01, 128.48, 125.21, 122.94, 44.11, 42.73.

HR-MS (ESI, $[M+H]^+$) calcd for C₁₅H₁₃BrNO⁺ 302.0175, found 302.0173.

trans-3-(3-Methoxyphenyl)aziridin-2-yl)(phenyl)methanone (7e)



Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: white solid.

Mass and Yield: 37 mg, 72% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 7.91 (dd, J = 5.1, 3.4 Hz, 2H), 7.57 – 7.49 (m, 1H), 7.40 (dd, J = 10.6, 4.7 Hz, 2H), 7.18 (dd, J = 9.5, 6.3 Hz, 1H), 6.89 (d, J = 7.6 Hz, 1H), 6.87 – 6.83 (m, 1H), 6.77 (ddd, J =8.2, 2.6, 0.8 Hz, 1H), 3.74 (s, 3H), 3.42 (d, J = 5.4 Hz, 1H), 3.08 (d, J = 7.0Hz, 1H), 2.58 (t, J = 7.5 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 195.79, 160.06, 140.13, 136.02, 133.96, 129.71, 128.94, 128.46, 118.90, 113.85, 111.29, 55.39, 44.19, 43.62.
HR-MS (ESI, [M+H]⁺) calcd for C₁₆H₁₆NO₂⁺ 254.1176, found 254.1185.

trans-3-(4-Chlorophenyl)aziridin-2-



yl)(phenyl)methanone (7f) S5

Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: white solid.

Mass and Yield: 38 mg, 74% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.02 – 7.95 (m, 2H), 7.66 – 7.58 (m, 1H),
7.49 (dd, *J* = 10.7, 4.7 Hz, 2H), 7.36 – 7.28 (m, 4H), 3.45 (dd, *J* = 7.9, 2.2 Hz, 1H), 3.14 (dd, *J* = 9.2, 2.1 Hz, 1H), 2.67 (t, *J* = 8.4 Hz, 1H).
¹³C NMR (100 MHz, CDCl₃) δ 195.51, 137.05, 135.93, 134.07, 133.79,
129.00, 128.86, 128.44, 127.68, 44.21, 42.89.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{15}H_{13}CINO^+$ 258.0680, found 258.0680.

trans-3-(Naphthalen-1-yl)aziridin-2-yl)(phenyl)methanone (7g)



Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: white solid.

Mass and Yield: 35 mg, 64% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.11 – 8.04 (m, 2H), 8.01
(d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.78
(d, J = 7.1 Hz, 1H), 7.63 (t, J = 7.4 Hz, 1H), 7.55 – 7.41 (m, 5H), 3.78 (d, J = 7.0 Hz, 1H), 3.60 – 3.51 (m, 1H), 2.74 (t, J = 7.7 Hz, 1H).
¹³C NMR (100 MHz, CDCl₃) δ 196.28, 135.98, 134.15, 134.05, 133.51, 131.99, 128.98, 128.94, 128.56, 128.30, 126.51, 125.99, 125.79, 124.05,

122.83, 43.16, 41.96.

HR-MS (ESI, $[M+H]^+$) calcd for C₁₉H₁₆NO⁺ 274.1226, found 274.1226.

trans-((2-Chlorophenyl)-3-phenylaziridin-2-yl)methanone (7h)



Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: white solid.

Mass and Yield: 33 mg, 64% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 7.64 – 7.59 (m, 1H), 7.48 – 7.41 (m, 2H), 7.39 – 7.27 (m, 6H), 3.37 (s, 1H), 3.30 (s, 1H), 2.70 (s, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 198.50, 138.18, 137.31, 133.07, 132.53,

130.89, 130.25, 128.62, 128.03, 127.24, 126.36, 47.72, 45.18.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{15}H_{13}CINO^+$ 258.0680, found 258.0865.





Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: white solid.

Mass and Yield: 32 mg, 68% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 7.80 (d, *J* = 8.6 Hz, 2H), 7.46 – 7.28 (m, 7H), 3.51 (d, *J* = 5.7 Hz, 1H), 3.18 (d, *J* = 7.1 Hz, 1H), 2.67 (br, 1H), 2.41 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 196.04, 138.88, 138.57, 136.12, 134.78, 128.89, 128.84, 128.69, 128.00, 126.39, 125.76, 44.21, 43.69, 21.47.

HR-MS (ESI, $[M+H]^+$) calcd for C₁₆H₁₆NO⁺ 238.1226, found 238.1218.

trans-3-Phenylaziridin-2-yl)(p-tolyl)methanone (7j)^{S5}



Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: white solid.

Mass and Yield: 33 mg, 69% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, J = 8.2 Hz, 2H), 7.40 – 7.30 (m, 5H), 7.28 (d, J = 8.0 Hz, 2H), 3.49 (dd, J = 8.0, 2.3 Hz, 1H), 3.16 (dd, J = 9.3, 2.3 Hz, 1H), 2.66 (t, J = 8.6 Hz, 1H), 2.43 (s, 3H).
¹³C NMR (100 MHz, CDCl₃) δ 195.33, 144.99, 138.60, 133.58, 129.63, 128.66, 128.58, 127.94, 126.35, 44.08, 43.47, 21.88.

HR-MS (ESI, $[M+H]^+$) calcd for C₁₆H₁₆NO⁺ 238.1226, found 238.1216.

trans-3-Phenylaziridin-2-yl)(thiophen-2-yl)methanone (7k)



Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: white solid.

Mass and Yield: 24 mg, 52% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, J = 3.7 Hz, 1H), 7.73 (d, J = 4.8 Hz, 1H), 7.40 – 7.28 (m, 5H), 7.20 – 7.13 (m, 1H), 3.39 (d, J = 6.0 Hz, 1H), 3.27 (d, J = 7.5 Hz, 1H), 2.58 (t, J = 7.4 Hz, 1H).
¹³C NMR (100 MHz, CDCl₃) δ 188.39, 142.96, 138.40, 134.94, 133.03, 128.67, 128.64, 128.03, 126.38, 44.50, 43.42.

HR-MS (ESI, $[M+H]^+$) calcd for C₁₃H₁₂NOS⁺ 230.0634, found 230.0628.

trans-3-(tert-butyl)aziridin-2-yl)(phenyl)methanone (7l) S5



Rf = 0.4 (PE/DCM/EA = 12:5:1).

Color and State: white solid.

Mass and Yield: 32 mg, 77% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 8.01 (d, *J* = 7.9 Hz, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 3.36 (s, 1H), 2.10 – 1.99 (m, 2H), 0.98 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 197.79, 136.23, 133.70, 128.91, 128.21,
52.78, 36.88, 31.41, 26.90.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{13}H_{18}NO^+$ 204.1383, found 204.1388.





Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: white solid.

Mass and Yield: 37 mg, 62% yield.

¹H NMR (400 MHz, CDCl₃) δ δ 8.06 – 7.99 (m, 2H),

7.65 – 7.58 (m, 1H), 7.51 (dd, *J* = 10.6, 4.6 Hz, 2H), 3.31 (d, *J* = 2.4 Hz, 1H), 2.05 (s, 1H), 2.00 – 1.90 (m, 2H), 1.75 (ddd, *J* = 41.8, 24.5, 11.8 Hz, 4H), 1.30 – 1.10 (m, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 197.50, 136.30, 133.72, 128.92, 128.28,

48.80, 41.83, 38.96, 31.10, 30.66, 26.40, 25.97, 25.84.

HR-MS (ESI, $[M+H]^+$) calcd for C₁₅H₂₀NO⁺ 230.1539, found 230.1539.

trans-3-Isopropylaziridin-2-yl)(phenyl)methanone (7n)



Rf = 0.6 (PE/DCM/EA = 12:5:1).

Color and State: Colorless oil.

Mass and Yield: 24 mg, 65% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.03 (dd, J = 5.2, 3.3 Hz, 2H), 7.64 – 7.59 (m, 1H), 7.51 (dd, J = 10.5, 4.7 Hz, 2H), 3.30 (d, J = 2.4 Hz, 1H), 2.07 (s, 1H), 1.97 (dd, J = 7.7, 2.4 Hz, 1H), 1.51 (dq, J = 13.9, 6.9 Hz, 1H), 1.08 (d, J = 6.7 Hz, 3H), 1.04 (d, J = 6.8 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 197.42, 136.28, 133.75, 128.94, 128.27, 49.95, 39.18, 32.27, 20.39, 19.82.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{12}H_{16}NO^+$ 190.1226, found 190.1226.

trans-3-Pentylaziridin-2-yl)(phenyl)methanone (70)



Rf = 0.3 (PE/DCM/EA = 12:5:1).

Color and State: white solid.

Mass and Yield: 14 mg, 68% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 8.05 – 8.00 (m, 2H), 7.62 (dd, *J* = 10.5, 4.3 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 3.31 – 3.24 (m, 1H), 2.22 – 2.06 (m, 2H), 1.64 – 1.54 (m, 2H), 1.53 – 1.45 (m, 2H), 1.37 – 1.30 (m, 4H), 0.89 (t, *J* =

7.0 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 197.45, 136.33, 133.77, 128.93, 128.31,
43.52, 40.00, 33.50, 31.74, 27.07, 22.73, 14.16.

HR-MS (ESI, $[M+H]^+$) calcd for C₁₄H₂₀NO⁺ 218.1539, found 218.1538.

trans-3-Methylaziridin-2-yl)(phenyl)methanone (7p)



Rf = 0.4 (PE/DCM/EA = 12:5:1).

Color and State: Colorless oil.

Mass and Yield: 20 mg, 65% yield.

¹**H NMR** (400 MHz, CDCl₃) δ 8.04 (d, J = 7.5 Hz, 2H), 7.65 (t, J = 7.4 Hz,

1H), 7.55 (t, *J* = 7.6 Hz, 2H), 3.24 (s, 1H), 2.90 – 2.90 (m, 1H), 2.30 – 2.10

(m, 2H), 1.39 (d, J = 5.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 197.31, 136.27, 133.83, 128.93, 128.35, 40.78, 38.43, 18.68.

HR-MS (ESI, $[M+H]^+$) calcd for $C_{10}H_{12}NO^+$ 162.0913, found 162.0913.
5. Scale-up Synthesis



a): A 10 mL pressure tube was charged with Chalcone (3 mmol, 1.0 equiv.), KI (0.16 mmol, 26.6 mg, 0.8 equiv.), K₂CO₃ (3.6 mmol, 1.2 equiv.), THF (24 mL) and methanol (6 mL), TBHP (5.0 mol/L in *n*-Hexane, 13.5 mmol, 4.5 equiv.) was then added to the reaction mixture slowly, The reaction mixture was stirred at room temperate for 1 hour. The resultant solution was quenched with aqueous saturated sodium thiosulfate solution (10 mL), H₂O (10 mL) and extracted with ethyl acetate (3×30 mL), dried over anhydrous sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by column chromatography on silica gel (PE/DCM/EA = 30:5:1 to 25:5:1) to afford **2c** as a colorless oil.

b): A 10 mL pressure tube was charged with Chalcone (3 mmol, 1.0 equiv.), KI (0.16 mmol, 26.6 mg, 0.8 equiv.), K₂CO₃ (15 mmol, 5.0 equiv.), THF (3 mL) and methanol (30 mL), TBHP (5.0 mol/L in *n*-Hexane, 13.5 mmol, 4.5 equiv.) was then added to the reaction mixture slowly, The reaction mixture was stirred at room temperate for 1 hour. The

resultant solution was quenched with aqueous saturated sodium thiosulfate solution (10 mL), H₂O (10 mL) and extracted with ethyl acetate (3×30 mL), dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The crude product was further purified by column chromatography on silica gel (25:5:1) to afford **7a** as a colorless oil.

6. Control Experiments.



6.1 Control Experiments

Scheme S3. Control experiments.

A 10 mL pressure tube was charged with Chalcone (0.4 mmol, 1.0 equiv.), KI (0.32 mmol, 0.8 equiv.), K₂CO₃ (0.48 mmol, 1.2 equiv.), and TEMPO (1.2 mmol, 3.0 equiv.) (b: BHT), THF (3.2 mL) and methanol (0.8 mL), TBHP (4.5 mol/L in *n*-Hexane, 0.8 mmol, 0.4 mL, 4.5 equiv.) then was added to the reaction mixture slowly, The reaction mixture was stirred at room temperate for 1 hour. The resultant solution was quenched with aqueous saturated sodium thiosulfate solution (4 mL), H₂O (10 mL) and extracted with ethyl acetate (3×30 mL), dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The crude product was further purified by column chromatography on silica gel (PE/DCM/EA = 30:5:1 to 25:5:1) to afford the title compound.

7. References

S1 L.-W. Xu, C.-G. Xia and X.-X. Hu, Chem. Commun., 2003, 2570-2571.

S2 T. Kano, T. Yurino, D. Asakawa and K. Maruoka, *Angew. Chem., Int. Ed.*, 2013, **52**, 5532.

S3 Y.-M. Shen, M.-X. Zhao, J. Xu and Y. Shi, *Angew. Chem. Int. Ed.*, 2006, **45**, 8005-8008

S4 S. Sabir, C. B. Pandey, A. K. Yadav, B. Tiwari and J. L. Jat, *J. Org. Chem.*, 2018, **83**, 12255–12260.

S5 A. Armstrong, C. A. Baxter, S. G. Lamont, A. R. Pape and R. Wincewicz, *Org. Lett.*, 2007, **9**, 351-353

8. ¹H NMR and ¹³C NMR Spectra of the Products

2a







2c



2d



2e



2f



2g



2h



2i





2k



21



2m



2n



20



2p



2q



S58



2s



2t



S61

2u



4a





S63

4b



4c



4d



4e



4f



4g



4h



4i



S71



S72


6b



6c











7e



7f



7g



7h



7i



7j



7k



7**1**



7m









7p