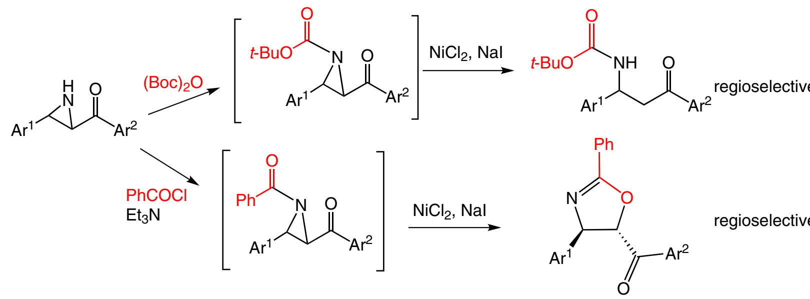
Synthesis of *tert*-Butyl 1,3-Diaryl-3-oxopropylcarbamates by a Regiocontrolled Reduction of Ketoaziridines

Heshmat A. Samimi[*a]
Bohari M. Yamin[b]
Fatemeh Saberi[a]

[a] Faculty of Science, Department of Chemistry, Shahrekord University, PO Box 115, Shahrekord, Iran
samimi-h@sci.sku.ac.ir
[b] School of Chemical Sciences and Food Technology, University Kebangsaan Malaysia, UKM 43500 Bangi Selangor, Malaysia



Received: 03.07.2014
Accepted after revision: 06.08.2014
Published online: 17.09.2014
DOI: 10.1055/s-0034-1379029; Art ID: ss-2014-z0402-op

Abstract A new, convenient approach for the reductive ring opening of *N*-H ketoaziridines is described. Treatment of *N*-H ketoaziridines with di-*tert*-butyl dicarbonate [(Boc)$_2$O] in the presence of sodium iodide and nickel(II) chloride results in the corresponding *tert*-butyl 1,3-diaryl-3-oxopropylcarbamates by a regiocontrolled reaction. The structure of the regioisomeric product was confirmed by X-ray crystal structure analysis.

Key words aziridines, regioselectivity, ring opening, reduction, nickel(II) chloride

The reductive ring opening of aziridines is a synthetically useful transformation for the preparation of amino compounds, especially in the synthesis of β-amino ketones,[1,2] which are important for the synthesis of biologically active compounds.[3–7]

Several methods are known for the synthesis of β-amino ketones from the ring opening of aziridines. A literature survey shows the few reducing agents, including Raney nickel in ethanol,[8] Pearlman's catalyst [Pd(OH)$_2$/C],[9] Adam's catalyst (PtO$_2$/HCO$_2$H),[10] sodium borohydride,[11] tributyltin hydride,[12] poly(methylhydrosiloxane) (PMHS),[13] silyllithium reagents,[14] magnesium[15] and lithium[16] metal reagents, titanium tetraiodide,[17] samarium(II) iodide[18] and visible-light photoredox ruthenium catalysts,[19] for the reductive ring opening of aziridines. None of these methods, however, result in a direct reduction reaction of *N*-H aziridines to give derivatives of β-carbamato ketones.

Our recent interest in the ring opening and ring expansion of ketoaziridines motivated us to synthesize *tert*-butyl 1,3-diaryl-3-oxopropylcarbamates.[20–27]

Previous reports have shown that replacement of the hydrogen of the N–H moiety with an electron-withdrawing substituent increases the susceptibility of *N*-H aziridines to ring-opening or ring-enlargement reactions.[28–30] So, our first aim was to synthesize *N*-Boc-substituted ketoaziridines as a precursor for preparation of the corresponding nitrogen-containing compounds via ring opening or ring enlargement. At first, we investigated the reaction of di-*tert*-butyl dicarbonate [(Boc)$_2$O] and 2-(4-chlorobenzoyl)-3-(4-chlorophenyl)aziridine (**1a**) in chloroform, acetonitrile, ethanol or acetone in the presence of triethylamine. The mixture was stirred for 10 hours under refluxing conditions, but **1a** was recovered unchanged (Table 1, entries 1–4); none of the desired product was detected.

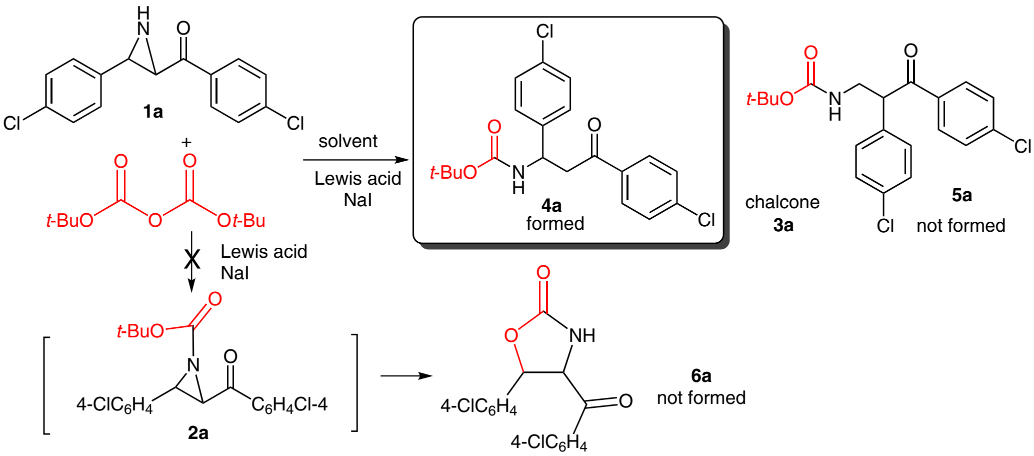
Based on the well-documented transformation of *N*-acyl- or *N*-Boc-substituted aziridines into oxazolines in the literature[31–34] and our success[20,21] with the ring-expansion reaction of *N*-acyl-substituted aziridines with sodium iodide, we envisioned that ring expansion of **1a** with (Boc)$_2$O in the presence of sodium iodide might be similarly achieved to give oxazolidin-2-one **6a** in a one-pot reaction. Thus, we examined the reaction of aziridine **1a** with (Boc)$_2$O in the presence of sodium iodide in acetone for achieving this aim; however, no reaction occurred, even under refluxing conditions (Table 1, entry 5).

In order to evaluate the effect of a Lewis acid in this reaction, we tried the reaction of 2-(4-chlorobenzoyl)-3-(4-chlorophenyl)aziridine (**1a**) with (Boc)$_2$O in the presence of sodium iodide and some Lewis acids (ZnCl$_2$, CuCl$_2$) in refluxing acetone; with zinc chloride and copper(II) chloride, a new product **4a** was obtained in low yields (Table 1, entries 6 and 7).

In another attempt, we examined the reaction of **1a** with (Boc)$_2$O in the presence of nickel(II) chloride and sodium iodide (1 mmol) (Table 1, entry 8). At this stage, thin-layer chromatography confirmed the formation of a new

This document was downloaded for personal use only. Unauthorized distribution is strictly prohibited.

Table 1 Optimization of the Conditions for the Reaction of Aziridine **1a** with $(Boc)_2O$[a]



Entry	Reagent	Solvent	Time (h)	Yield[b] (%)	
				3a	**4a**
1[c]	Et_3N	$CHCl_3$	10	0	0
2[c]	Et_3N	MeCN	10	0	0
3[c]	Et_3N	EtOH	10	0	0
4[c]	Et_3N	acetone	10	0	0
5[c]	NaI	acetone	6	0	0
6	NaI, $ZnCl_2$	acetone	8	0	16
7	NaI, $CuCl_2$	acetone	8	0	23
8	NaI, $NiCl_2$	acetone	8	19	71
9[c]	$ZnCl_2$	acetone	10	0	0
10[c]	$CuCl_2$	acetone	10	0	0
11	$NiCl_2$	acetone	10	44	0

[a] **1a**/$(Boc)_2O$/reagent = 1:1:1.
[b] Isolated yields.
[c] The starting material was recovered.

compound, along with the corresponding chalcone **3a**. The crude product was purified by column chromatography, surprisingly to provide *tert*-butyl 1,3-bis(4-chlorophenyl)-3-oxopropylcarbamate (**4a**) or *tert*-butyl 2,3-bis(4-chlorophenyl)-3-oxopropylcarbamate (**5a**). Since the spectroscopic data were not conclusive for **4a** or **5a**, X-ray crystallographic analysis was conducted to verify the product structure as **4a** (Figure 1).

It is striking to note that X-ray crystal structure analysis of the representative product **4a** (Figure 1) confirms the regiocontrolling nature of this reaction. The reaction proceeded with selective ring opening at the C–N bond α to the benzoyl moiety, whereas the C–N bond of the benzyl group was not cleaved. The same stereochemistry has been generalized for all other products formed from this reaction.

A further examination of the reaction of **1a** and $(Boc)_2O$ with zinc chloride, copper(II) chloride or nickel(II) chloride in the absence of sodium iodide failed to give any product **4a** (Table 1, entries 9–11).

To expand the scope of this novel method, several substituted ketoaziridines **1** were reacted with $(Boc)_2O$ in the presence of nickel(II) chloride and sodium iodide, resulting in production of the *tert*-butyl 1,3-diaryl-3-oxopropylcarbamates **4** in moderate to good yields (Table 2). All the products were characterized by ^1H NMR, ^{13}C NMR and IR spectroscopy.

We have previously reported the mechanism of the iodide ion catalyzed isomerization of *N*-acyl-substituted aziridines by attack of the nucleophile at C-2 of the aziridine and subsequent cyclization to the corresponding oxazolines.[20] We have now found that the action of nickel(II) chloride with sodium iodide on 2-aroyl-3-arylaziridines is

This document was downloaded for personal use only. Unauthorized distribution is strictly prohibited.

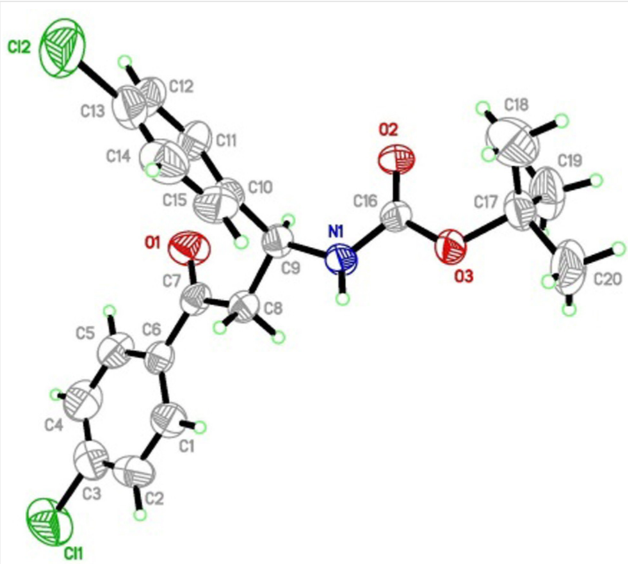
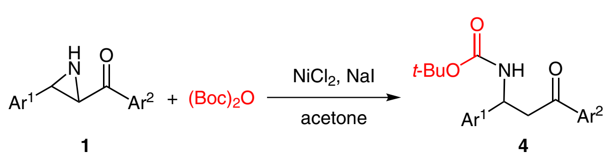


Figure 1 ORTEP view of the crystal structure of **4a**

Table 2 Substrate Scope for the Reductive Ring Opening of *N*-H Ketoaziridines **1** to the Corresponding *tert*-Butyl 1,3-Diaryl-3-oxopropylcarbamates **4**[a]



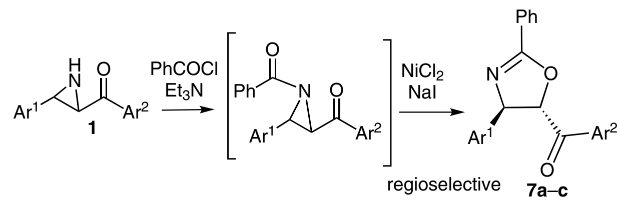
Product	Ar¹	Ar²	Time (h)	Yield[b] (%)
4a	4-ClC$_6$H$_4$	4-ClC$_6$H$_4$	8	71
4b	3-O$_2$NC$_6$H$_3$	Ph	10	68
4c	4-ClC$_6$H$_4$	Ph	8	73
4d	Ph	Ph	12	78
4e	2,4-Cl$_2$C$_6$H$_3$	4-ClC$_6$H$_4$	10	76
4f	3-O$_2$NC$_6$H$_3$	4-ClC$_6$H$_4$	12	62
4g	2,4-Cl$_2$C$_6$H$_3$	Ph	8	73
4h	4-BrC$_6$H$_4$	Ph	10	56

[a] Refluxing conditions with **1**/(Boc)$_2$O/NiCl$_2$/NaI = 1:1:1:1.
[b] Isolated yields.

the same as that of iodide, also involving a regio- and stereocontrolled ring-expansion process. To test the scope of this novel method, substituted ketoaziridines **1** were reacted with benzoyl chloride in the presence of nickel(II) chloride and sodium iodide, which resulted in the production of oxazolines **7** in moderate to good yields (Table 3); no trace of another regioisomer was detected. All the products were characterized by ^{1}H NMR, ^{13}C NMR and IR spectroscopy.

A striking feature of this process is that *N*-acyl-substituted ketoaziridines, in the presence of nickel(II) chloride and sodium iodide, result in oxazolines **7** via a regio- and

Table 3 Substrate Scope for the Ring Expansion of *N*-H Ketoaziridines **1** to the Corresponding Oxazolines **7**



Product	Ar¹	Ar²	Time (h)	Yield[a] (%)
7a	2,4-Cl$_2$C$_6$H$_3$	Ph	6	77
7b	4-ClC$_6$H$_4$	4-ClC$_6$H$_4$	8	74
7c	Ph	Ph	8	73[20]

[a] Isolated yields.

stereocontrolled ring-expansion reaction, while *N*-Boc-substituted ketoaziridines produce ***tert***-butyl 1,3-diaryl-3-oxopropylcarbamates **4** through a reductive ring-opening reaction. This shows the influence of the N-substituent on the ring expansion or reductive ring opening of ketoaziridines.

The exact mechanism of the novel reductive ring-opening reaction is not clear. Research in this respect is under way.

In conclusion, we have disclosed the highly efficient, reductive ring opening of *N*-H ketoaziridines under refluxing conditions via a regioselective reaction promoted with (Boc)$_2$O in the presence of nickel(II) chloride and sodium iodide as an inexpensive reagent system.

All yields refer to isolated products after purification by column chromatography or by distillation under reduced pressure. Products were characterized by comparison with authentic samples (IR and ^{1}H NMR spectra, TLC, melting and boiling points). NMR spectra were recorded in CDCl$_3$ on a Bruker AMX-400 spectrometer (^{1}H NMR at 400 MHz and ^{13}C NMR at 100 MHz) with chemical shift values (δ) in ppm downfield from TMS. IR spectra were recorded on a JASCO FT/IR-6300 spectrometer. All solvents used were dried and distilled according to standard procedures.

tert-Butyl 1,3-Diaryl-3-oxopropylcarbamates 4a–h (Table 2); General Procedure

NiCl$_2$ (1.0 mmol) and NaI (1.0 mmol) were added to a solution of the ketoaziridine **1** (1.0 mmol) and (Boc)$_2$O (1.0 mmol) in acetone (15 mL). The mixture was refluxed for 8–12 h. The crude product was purified by column chromatography (silica gel; EtOAc–hexane, 2:5) to provide the desired corresponding *tert*-butyl 3-oxopropylcarbamate **4**; yield: 56–78%.

tert-Butyl 1,3-Bis(4-chlorophenyl)-3-oxopropylcarbamate (4a)

Yield: 279 mg (71%); white solid; mp 140–142 °C.

IR (KBr): 3280, 1685, 1596, 1452, 1321, 1228 cm^{-1}.

This document was downloaded for personal use only. Unauthorized distribution is strictly prohibited.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (s, 9 H), 3.31 (dd, *J* = 16.8, 6.1 Hz, 1 H), 3.55 (br d, 1 H), 5.12 (br d, 1 H), 5.48 (br, 1 H), 7.20 (m, 4 H), 7.35 (d, *J* = 8.6 Hz, 2 H), 7.76 (d, *J* = 8.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.3, 44.0, 50.8, 79.9, 127.7, 128.7, 129.0, 129.1, 129.5, 133.1, 134.8, 140.0, 155.1, 196.6.

Anal. Calcd for $C_{20}H_{21}Cl_2NO_3$: C, 60.92; H, 5.37; N, 3.55. Found: C, 60.89; H, 5.39; N, 3.59.

tert-Butyl 1-(3-Nitrophenyl)-3-oxo-3-phenylpropylcarbamate (4b)

Yield: 251 mg (68%); white solid; mp 138–140 °C.

IR (KBr): 3310, 1688, 1594, 1535, 1458, 1324, 1350 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.35 (s, 9 H), 3.43 (dd, *J* = 17.3, 5.4 Hz, 1 H), 3.63 (br d, 1 H), 5.26 (br d, 1 H), 5.78 (br, 1 H), 7.43 (m, 3 H), 7.50 (td, *J* = 7.4, 1.3 Hz, 1 H), 7.64 (d, *J* = 7.1 Hz, 1 H), 7.78 (m, 2 H), 8.11 (dd, *J* = 8.2, 1.3 Hz, 1 H), 8.14 (t, *J* = 1.9 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.3, 43.6, 50.5, 80.2, 121.3, 122.3, 128.0, 128.8, 129.5, 129.6, 132.8, 133.8, 136.2, 148.3, 155.2, 189.8.

Anal. Calcd for $C_{20}H_{22}N_2O_5$: C, 64.85; H, 5.99; N, 7.56. Found: C, 64.70; H, 6.19; N, 7.69.

tert-Butyl 1-(4-Chlorophenyl)-3-oxo-3-phenylpropylcarbamate (4c)

Yield: 262 mg (73%); white solid; mp 142–144 °C.

IR (KBr): 3310, 1688, 1594, 1459, 1331, 1221 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (s, 9 H), 3.34 (dd, *J* = 16.8, 5.8 Hz, 1 H), 3.56 (br d, 1 H), 5.14 (br d, 1 H), 5.59 (br, 1 H), 7.22 (m, 4 H), 7.35 (t, *J* = 7.1 Hz, 2 H), 7.47 (t, *J* = 7.1 Hz, 1 H), 7.78 (t, *J* = 7.5 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.3, 43.9, 50.7, 79.8, 127.7, 128.0, 128.7, 128.8, 132.9, 133.5, 136.5, 140.3, 155.1, 197.8.

Anal. Calcd for $C_{20}H_{22}ClNO_3$: C, 66.75; H, 6.16; N, 3.89. Found: C, 66.64; H, 6.24; N, 3.94.

tert-Butyl 3-Oxo-1,3-diphenylpropylcarbamate (4d)

Yield: 253 mg (78%); white solid; mp 135–137 °C.

IR (KBr): 3289, 1681, 1591, 1449, 1318, 1221 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (s, 9 H), 3.36 (dd, *J* = 16.6, 6.1 Hz, 1 H), 3.57 (br d, 1 H), 5.17 (br d, 1 H), 5.52 (br, 1 H), 7.16 (t, *J* = 6.9 Hz, 1 H), 7.22 (m, 4 H), 7.34 (t, *J* = 7.8 Hz, 2 H), 7.46 (t, *J* = 7.4 Hz, 1 H), 7.80 (t, *J* = 7.1 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.3, 44.2, 51.4, 79.6, 126.3, 127.3, 128.1, 128.6, 128.7, 133.3, 136.7, 141.6, 155.2, 190.2.

Anal. Calcd for $C_{20}H_{23}NO_3$: C, 73.82; H, 7.12; N, 4.30. Found: C, 73.70; H, 7.15; N, 4.41.

tert-Butyl 3-(4-Chlorophenyl)-1-(2,4-dichlorophenyl)-3-oxopropylcarbamate (4e)

Yield: 324 mg (76%); white solid; mp 142–144 °C.

IR (KBr): 3288, 1685, 1599, 1452, 1325, 1220 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.49 (s, 9 H), 3.33 (dd, *J* = 16.7, 5.4 Hz, 1 H), 3.55 (br d, 1 H), 5.40 (br d, 1 H), 5.87 (br, 1 H), 7.14 (d, *J* = 8.6 Hz, 1 H), 7.27 (m, 3 H), 7.33 (t, *J* = 8.8 Hz, 2 H), 7.74 (d, *J* = 8.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.3, 43.9, 50.7, 79.8, 127.8, 128.0, 128.3, 128.7, 128.8, 128.9, 132.9, 133.5, 136.5, 140.3, 155.1, 197.8.

Anal. Calcd for $C_{20}H_{20}Cl_3NO_3$: C, 56.03; H, 4.70; N, 3.27. Found: C, 56.20; H, 4.85; N, 3.39.

tert-Butyl 3-(4-Chlorophenyl)-1-(3-nitrophenyl)-3-oxopropylcarbamate (4f)

Yield: 250 mg (62%); red oil.

IR (KBr): 3294, 1681, 1591, 1355, 1452, 1345, 1228 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.35 (s, 9 H), 3.41 (dd, *J* = 17.1, 5.7 Hz, 1 H), 3.61 (br d, 1 H), 5.27 (br d, 1 H), 5.67 (br, 1 H), 7.35 (d, *J* = 8.7 Hz, 2 H), 7.41–7.45 (d, *J* = 8.0 Hz, 1 H), 7.63 (d, *J* = 7.2 Hz, 1 H), 7.78 (d, *J* = 8.7 Hz, 2 H), 8.02 (dd, *J* = 8.0, 1.2 Hz, 1 H), 8.40 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.3, 43.4, 50.5, 80.3, 121.2, 122.4, 122.9, 129.1, 129.4, 129.5, 132.8, 134.5, 140.3, 148.4, 155.1, 193.8.

Anal. Calcd for $C_{20}H_{21}ClN_2O_5$: C, 59.53; H, 5.23; N, 6.92. Found: C, 59.53; H, 5.41; N, 6.84.

tert-Butyl 1-(2,4-Dichlorophenyl)-3-oxo-3-phenylpropylcarbamate (4g)

Yield: 287 mg (73%); white solid; mp 131–133 °C.

IR (KBr): 3299, 1683, 1584, 1451, 1329, 1220 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (s, 9 H), 3.32 (dd, *J* = 16.82, 6.13 Hz, 1 H), 3.65 (br d, 1 H), 5.13 (br d, 1 H), 5.54 (br, 1 H), 7.19 (m, 3 H), 7.34 (t, *J* = 7.67 Hz, 2 H), 7.49 (t, *J* = 7.2 Hz, 1 H), 7.71 (d, *J* = 7.48 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.3, 43.6, 50.5, 80.3, 121.2, 122.4, 129.1, 129.3, 129.5, 129.7, 132.8, 140.3, 148.4, 155.1, 193.8.

Anal. Calcd for $C_{20}H_{21}Cl_2NO_3$: C, 60.92; H, 5.37; N, 3.55. Found: C, 60.84; H, 5.46; N, 3.61.

tert-Butyl 1-(4-Bromophenyl)-3-oxo-3-phenylpropylcarbamate (4h)

Yield: 226 mg (56%); white solid; mp 137–139 °C.

IR (KBr): 3288, 1684, 1593, 1458, 1325, 1222 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (s, 9 H), 3.32 (dd, *J* = 16.7, 5.8 Hz, 1 H), 3.55 (br d, 1 H), 5.13 (br d, 1 H), 5.59 (br, 1 H), 7.30–7.55 (m, 4 H), 7.37 (t, *J* = 7.2 Hz, 2 H), 7.75 (t, *J* = 7.2 Hz, 1 H), 7.8 (d, *J* = 7.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.3, 43.9, 50.7, 79.8, 127.7, 128.1, 128.7, 128.8, 132.9, 133.5, 136.5, 140.3, 155.1, 197.8.

Anal. Calcd for $C_{20}H_{22}BrNO_3$: C, 59.42; H, 5.48; N, 3.46. Found: C, 59.38; H, 5.61; N, 3.51.

X-ray Crystal Structure Analysis for 4a

Formula: $C_{20}H_{21}Cl_2NO_3$, *M* = 394.28, yellow crystal 0.50 × 0.15 × 0.01 mm, *a* = 11.6327(13) Å, *b* = 19.181(2) Å, *c* = 9.9585(11) Å, *V* = 2039.6(4) Å^3, ρ_{calcd} = 1.284 mg·cm^{-3}, μ = 0.337 mm^{-1}, *Z* = 4, monoclinic, λ = 0.71073 Å, *T* = 296 K, ω and ϕ scans, 3580 reflections collected (±*h*, ±*k*, ±*l*) [$I \geq 2\sigma(I)$], 1959 independent (R_{int} = 0.1319) and 1852 observed reflections [$I \geq 2\sigma(I)$], 242 refined parameters, *R* = 0.0544, wR^2 = 0.1260, max residual electron density 0.24 (–0.29) e·Å^{-3}, Flack parameter 0.0040(6). The data set was collected with a Bruker SMART APEX CCD area detector diffractometer, absorption correction: multi-scan (SADABS[35]), at the School of Chemical Sciences and Food Technology, University Kebangsaan Malaysia.

Oxazolines 7a,b (Table 3); General Procedure

Benzoyl chloride (1.0 mmol) was added dropwise to a solution of an aziridine **1** (1.0 mmol) and Et_3N (2.0 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The mixture was stirred for 1.5 h at this temperature and for 4 h at r.t., and then rinsed with H_2O (2 × 10 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure.

This document was downloaded for personal use only. Unauthorized distribution is strictly prohibited.

Acetone (15 mL), NaI (1 mmol) and $NiCl_2$ (1 mmol) were added to the crude product and the mixture was stirred at 50 °C for 6 h. Then, the mixture was rinsed with H_2O (2 × 10 mL), and the organic layer was separated and dried with anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure and subsequent purification of the residue by column chromatography (silica gel; EtOAc–hexane, 1:4) provided the corresponding oxazoline **7**.

trans-5-Benzoyl-4-(2,4-dichlorophenyl)-2-phenyl-2-oxazoline (7a)

Yield: 304 mg (77%); white solid; mp 128–130 °C.

IR (KBr): 3066, 2907, 1680, 1652, 1591, 1481, 1261, 760, 707, 695 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.58 (d, *J* = 6.7 Hz, 1 H), 5.75 (d, *J* = 6.7 Hz, 1 H), 7.36–7.67 (m, 9 H), 7.99 (d, *J* = 7.3 Hz, 2 H), 8.14 (d, *J* = 7.3 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 74.3, 87.4, 127.4, 127.5, 128.3, 128.6, 128.8, 129.2, 129.3, 129.4, 129.5, 132.3, 134.4, 134.6, 141.1, 164.3, 194.9.

Anal. Calcd for $C_{22}H_{15}Cl_2NO_2$: C, 66.68; H, 3.82; N, 3.53. Found: C, 66.57; H, 3.84; N, 3.47.

trans-5-(4-Chlorobenzoyl)-4-(4-chlorophenyl)-2-phenyl-2-oxazoline (7b)

Yield: 292 mg (74%); white solid; mp 135–137 °C.

IR (KBr): 3058, 2921, 1684, 1650, 1594, 1483, 1266, 761, 709, 696 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.50 (d, *J* = 6.5 Hz, 1 H), 5.70 (d, *J* = 6.5 Hz, 1 H), 7.30–7.70 (m, 9 H), 7.90 (d, *J* = 7.3 Hz, 2 H), 8.10 (d, *J* = 7.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 74.3, 87.4, 125.6, 127.5, 128.8, 129.2, 129.3, 129.4, 129.5, 130.7, 134.4, 134.6, 138.7, 141.1, 163.3, 194.6.

Anal. Calcd for $C_{22}H_{15}Cl_2NO_2$: C, 66.68; H, 3.82; N, 3.53. Found: C, 66.61; H, 3.79; N, 3.74.

(*E*)-1,3-Bis(4-chlorophenyl)prop-2-en-1-one (3a)

Yellow crystals; mp 156–158 °C.

IR (KBr): 3041, 1655, 1597, 883, 774, 699, 682 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (m, 2 H), 7.53 (dd, *J* = 7.6, 1.8 Hz, 1 H), 7.60 (m, 2 H), 7.73 (m, 2 H), 7.76 (d, *J* = 15.5 Hz, 1 H), 8.20 (dd, *J* = 7.5, 2.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.2, 128.4, 128.5, 129.3, 129.4, 132.3, 133.9, 136.8, 139.1, 144.1, 189.8.

Anal. Calcd for $C_{15}H_{10}Cl_2O$: C, 65.01; H, 3.64. Found: C, 65.08; H, 3.69.

Acknowledgment

We are thankful to the Research Council of Shahrekord University for supporting this work, and to the Universiti Kebangsaan Malaysia Instrumentation Center (UKM-DIP 2012-11) for the X-ray analysis.

Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1379029.

References

(1) Hu, X. E. *Tetrahedron* **2004**, *60*, 2701.
(2) Casimir, J. R.; Turetta, C.; Ettouati, L.; Paris, J. *Tetrahedron Lett.* **1995**, *36*, 4797.
(3) David, F. A.; Reddy, G. V.; Liang, C.-H. *Tetrahedron Lett.* **1997**, *38*, 5139.
(4) Fiedler, E.; Fiedler, H.-P.; Gerhard, A.; Keller-Schierlein, W.; König, W. A.; Zähner, H. *Arch. Microbiol.* **1976**, *107*, 249.
(5) Tiwari, A. K.; Kumbhare, R. M.; Agawane, S. B.; Ali, A. Z.; Kumar, K. V. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 4130.
(6) For general reviews, see: *Enantioselective Synthesis of β-Amino Acids*; Juaristi, E., Ed.; Wiley-VCH: Weinheim, **1997**.
(7) Cardillo, G.; Tolomelli, A.; Tomasini, C. *J. Org. Chem.* **1996**, *61*, 8651.
(8) Davis, F. A.; Zhang, Y.; Rao, A.; Zhang, Z. *Tetrahedron* **2001**, *57*, 6345.
(9) Hwang, G.-I.; Chung, J.-H.; Lee, W. K. *J. Org. Chem.* **1996**, *61*, 6183.
(10) Higashiyama, K.; Matsumura, M.; Shiogama, A.; Yamauchi, T.; Ohmiya, S. *Heterocycles* **2002**, *58*, 85.
(11) Dauban, P.; Dodd, R. H. *Tetrahedron Lett.* **1998**, *39*, 5739.
(12) Kim, S.; Jung, M. S.; Cho, C. H.; Schiesser, C. H. *Tetrahedron Lett.* **2001**, *42*, 943.
(13) Chandrasekhar, S.; Ahmed, M. *Tetrahedron Lett.* **1999**, *40*, 9325.
(14) Davis, A. L.; Korous, A. A.; Hartel, A. M. *Tetrahedron Lett.* **2013**, *54*, 3673.
(15) Pak, C. S.; Kim, T. H.; Ha, S. J. *J. Org. Chem.* **1998**, *63*, 10006.
(16) Almena, J.; Foubelo, F.; Yus, M. *J. Org. Chem.* **1994**, *59*, 3210.
(17) Shimizu, M.; Kurokawa, H.; Nishiura, S.; Hachiya, I. *Heterocycles* **2006**, *70*, 57.
(18) Reynolds, S. C.; Wengryniuk, S. E.; Hartel, A. M. *Tetrahedron Lett.* **2007**, *48*, 6751.
(19) Larraufie, M.-H.; Pellet, R.; Fensterbank, L.; Goddard, J.-P.; Lacote, E.; Malacria, M.; Ollivier, C. *Angew. Chem. Int. Ed.* **2011**, *50*, 4463.
(20) Samimi, H. A.; Mamaghani, M.; Tabatabaeian, K. *J. Heterocycl. Chem.* **2008**, *45*, 1765.
(21) Mamaghani, M.; Tabatabaeian, K.; Samimi, H. A. *Z. Kristallogr. - New Cryst. Struct.* **2008**, *223*, 390.
(22) Samimi, H. A.; Shams, Z. *J. Iran. Chem. Soc.* **2014**, *11*, 979.
(23) Samimi, H. A.; Mohammadi, S. *Synlett* **2013**, *24*, 223.
(24) Samimi, H. A.; Mohammadi, S. *J. Iran. Chem. Soc.* **2014**, *11*, 69.
(25) Samimi, H. A.; Kiyani, H.; Shams, Z. *J. Chem. Res.* **2013**, *37*, 282.
(26) Samimi, H. A.; Yamin, B. M.; Hiedari, Z.; Narimani, L. *J. Heterocycl. Chem.* accepted for publication.
(27) Samimi, H. A.; Yamin, B. M. *J. Chem. Res.* **2014**, *38*, 358.
(28) Tomasini, C.; Vecchione, A. *Org. Lett.* **1999**, *1*, 2153.
(29) Kump, J. E. G. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Eds.; Pergamon Press: Oxford, **1991**, 469.
(30) Sabitha, G.; Babu, R. S.; Rajkumar, M.; Reddy, C. S.; Yadav, J. S. *Tetrahedron Lett.* **2001**, *42*, 3955.
(31) Saha, B.; Nandy, J. P.; Shukla, S.; Siddiqui, I.; Iqbal, J. *J. Org. Chem.* **2002**, *67*, 7858.
(32) Lucarini, S.; Tomasini, C. *J. Org. Chem.* **2001**, *66*, 727.
(33) Cardillo, G.; Gentilucci, L.; Gianotti, M.; Tolomelli, A. *Synlett* **2000**, 1309.
(34) Quinze, K.; Laurent, A.; Mison, P. *J. Fluorine Chem.* **1989**, *44*, 233.
(35) Sheldrick, G. M. *SADABS A Program for Structure Determination*; University of Göttingen: Germany, **1996**.

This article differs from the e-first online version only in its layout; no content has been changed.

This document was downloaded for personal use only. Unauthorized distribution is strictly prohibited.