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N-Bromosuccinimide as a Brominating Agent for the Transformation of *N*-H (or *N*-Benzyl) Ketoaziridines into Oxazoles

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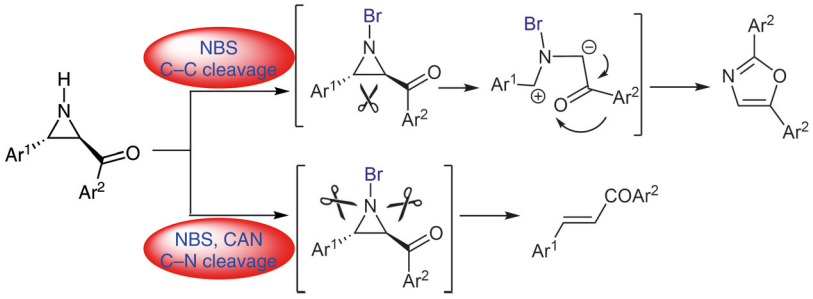

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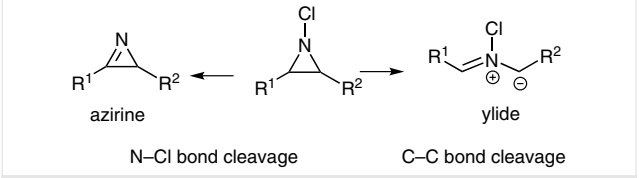
Abstract A novel procedure for the direct synthesis of 2,5-diaryloxazoles starting from *N*-H ketoaziridines is described. The method proceeds via the in situ formation of *N*-bromoketoaziridines in the presence of *N*-bromosuccinimide followed by the generation of intermediate azomethine ylides. A plausible mechanism for this transformation is proposed.

Key words aziridines, regiocontrol, ring expansion, oxazoles

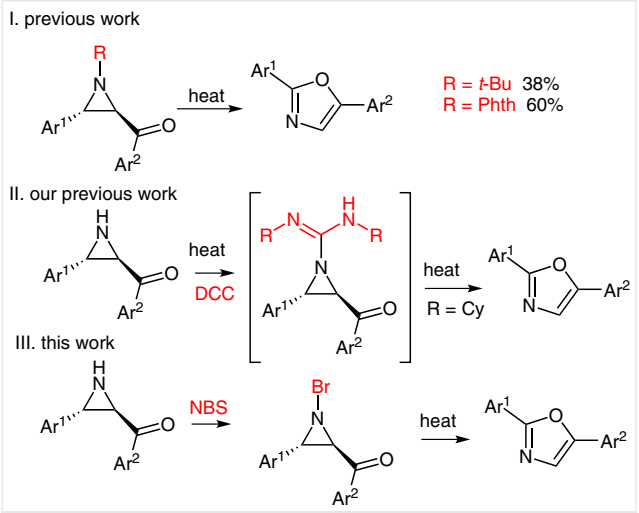
Owing to the electronegativity of the nitrogen atom and the strain present in the three-membered ring, aziridines exhibit intriguing and diverse reactivity, and thus have become interesting and versatile synthons in organic synthesis.[1] The aziridine ring can undergo C–N/C–C bond cleavage serving as a useful three-atom synthon with extensive applications in organic chemistry.[2] In particular, ketoaziridines are known to undergo ring opening via C–C bond cleavage to give azomethine ylides, which are useful reactive species for a wide range of synthetic applications.[3] Convincing support for the generation of azomethine ylide intermediates in the ring opening of ketoaziridines has been derived through trapping studies with dipolarophiles.[3h–n] It is also well known that an *N*-chloro-substituted aziridine ring undergoes concerted C–C bond cleavage (to give an azomethine ylide),[4a–f] or N–Cl bond cleavage (to form an azirine ring) (Scheme 1).[4g–h]

Recently, we have applied azomethine ylides generated from ketoaziridines for the synthesis of oxazoles (Scheme 2, reaction II).[5a] However, there are several other procedures available for the synthesis of oxazoles.[5b–h] Heating *N*-acyl-, *N*-phthalimido- or *N*-dicyclohexylcarbodiimido-ketoaziridines in the absence of dipolarophiles leads to oxazoles, via



Scheme 1 Examples of C–C and N–Cl bond cleavage in *N*-chloro-substituted aziridines

a process which may be attributed to a 1,5-electrocyclization of the azomethine ylide accompanied by loss of the N-substituent group (Scheme 2, reactions I–III).[5i–n]



Scheme 2 Synthesis of oxazoles from N–H or N–R ketoaziridines

Despite there being a few examples of the application of N-substituted aziridines for the synthesis of oxazoles in low yields,[5] no method for the direct synthesis of oxazoles from

N-H aziridines has been reported so far, apart from the case in which we described the activation of ketoaziridines in the presence of *N*,*N*′-dicyclohexylcarbodiimide (DCC) and iodine to give the corresponding 2,5-diaryloxazoles via C–C bond cleavage of the aziridine ring.[5a] In continuation of our recent interest in the ring expansion and ring opening of ketoaziridines via C–N or C–C bond cleavage,[5a,6] and inspired by research describing the conversion of *N*-chloroaziridines into azomethine ylides, herein we report the synthesis of oxazoles via C–C bond cleavage of aziridine rings using *N*-bromosuccinimide (NBS). A literature survey indicated that this would represent the first example of using a halogenating reagent for the direct formation of oxazoles from ketoaziridines.

We initially assumed that ketoaziridines in the presence of a brominating or chlorinating reagent, in analogy to previous work,[4g–h] would give *N*-chloro- or *N*-bromo-ketoaziridines, which would then form a 2*H*-azirine ring. However, our results showed that chlorination or bromination of the aziridine under thermal conditions afforded the corresponding oxazole via regioselective C–C bond cleavage.

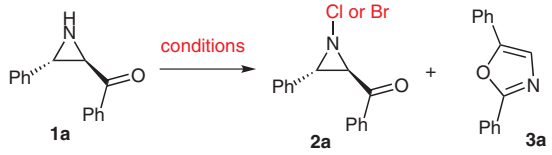
In our initial experiment, *trans*-2-aroyl-3-arylaziridines (**1**) were prepared via bromination of the corresponding α,β-unsaturated carbonyl compounds, followed by reaction with methanolic ammonia solution at room temperature.[7a,b] Of course, there are several other methods available for the preparation of ketoaziridines.[7c–g]

Next, the reaction of a mixture of ketoaziridine **1a** and calcium hypochlorite [$Ca(OCl)_2$], as a chlorination reagent, in chloroform at reflux temperature was monitored by TLC analysis (Table 1, entry 1). The crude product was purified by column chromatography (silica gel, EtOAc–hexane, 1:4) to provide 2,5-diphenyloxazole (**3a**) in 26% yield. Surprisingly, none of the corresponding *N*-chloro-substituted aziridine was obtained.

The effects of different solvents, including tetrahydrofuran, acetonitrile, acetone, ethylene glycol, *tert*-butanol and 1,4-dioxane, on the reaction of 2-benzoyl-3-phenylaziridine (**1a**) with calcium hypochlorite under refluxing conditions were unsatisfactory with yields of 8–29% being obtained (Table 1, entries 2–7). The effect of the amount of the catalyst was also investigated: changing the ratio of aziridine to calcium hypochlorite from 1:1 to 1:3 gave low to moderate yields (29–57%) of the desired oxazole **3a** (Table 1, entries 7–9).

In the presence of triethylamine (Et_3N), the reaction gave a low 25% yield of product **3a** and chalcone (38%) as a by-product (Table 1, entry 10). The use of a mixture of calcium hypochlorite and *N*-bromosuccinimide (**1a**/$Ca(OCl)_2$/NBS = 1:3:3) proved successful giving a significantly increased 86% yield of oxazole **3a** (Table 1, entry 11). The best result (93% yield) was obtained in the presence of *N*-bromosuccinimide at reflux temperature in 1,4-dioxane (Table 1, entry 12).

Table 1 Optimization of the Reaction of Aziridine **1a** with Chlorinating and Brominating Reagents



Entry	Conditions[a]	Time (h)	Yield (%)[g]	
			3a	**2a**
1	$CHCl_3$, $Ca(OCl)_2$	5	26	0
2	THF, $Ca(OCl)_2$	5	22	0
3	MeCN, $Ca(OCl)_2$	5	24	0
4	acetone, $Ca(OCl)_2$	5	19	0
5	$HOCH_2CH_2OH$, $Ca(OCl)_2$	5	8	0
6	*t*-BuOH, $Ca(OCl)_2$	3	26	0
7	1,4-dioxane, $Ca(OCl)_2$	4	29	0
8	1,4-dioxane, $Ca(OCl)_2$[b]	4	35	0
9	1,4-dioxane, $Ca(OCl)_2$[c]	4	57	14
10	1,4-dioxane, $Ca(OCl)_2$/Et_3N[d]	4	25	0
11	1,4-dioxane, $Ca(OCl)_2$/NBS[e]	4	86	0
12	**1,4-dioxane, NBS**	**1**	**93**	**0**
13	1,4-dioxane, NBS[f]	1	0	81
14	1,4-dioxane, NBS, Et_3N[f]	3	0	0
15	1,4-dioxane, $Ca(OCl)_2$[f]	3	0	0
16	1,4-dioxane	7	0	0

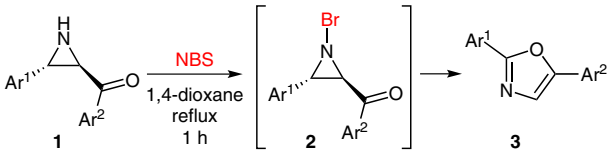
[a] Reactions were typically performed at the solvent reflux temperature using a 1:1 ratio of aziridine/halogenating reagent.
[b] A 1:2 ratio of aziridine/$Ca(OCl)_2$ was employed.
[c] A 1:3 ratio of aziridine/$Ca(OCl)_2$ was employed.
[d] A 1:3:3 ratio of aziridine/$Ca(OCl)_2$/Et_3N was employed; chalcone (38%) was obtained as a by-product.
[e] A 1:3:3 ratio of aziridine/$Ca(OCl)_2$/NBS was employed.
[f] The reaction was performed at 15 °C.
[g] Yield of isolated product(s).

Our investigations also showed that the use of thermal conditions were critical for the reaction to proceed via C–C bond cleavage of the aziridine ring (Table 1, entries 13 and 14). A mixture of **1a** and *N*-bromosuccinimide in 1,4-dioxane at 15 °C gave only *N*-bromoketoaziridine **2a** in a good 81% yield (Table 1, entry 13), while the reactions of aziridine **1a** with *N*-bromosuccinimide/triethylamine (Table 1, entry 14) or calcium hypochlorite at 15 °C (Table 1, entry 15) gave neither of the possible products. In the absence of *N*-bromosuccinimide, substrate **1a** did no undergo the desired transformation even after heating at reflux temperature for seven hours (Table 1, entry 16).

Having optimized the reaction conditions, we next investigated the scope of this novel methodology. Several 2-aroyl-3-arylaziridines (**1a**–**g**) were transformed into the corresponding 2,5-diaryloxazoles (**3a**–**k**) using *N*-bromo-

succinimide in 1,4-dioxane at reflux temperature (Table 2). All the products were characterized by ^{1}H, ^{13}C NMR and IR spectroscopy.

Table 2 Synthesis of 2,5-Diaryloxazoles from 2-Aroyl-3-arylaziridines in the Presence of *N*-Bromosuccinimide[a,b]

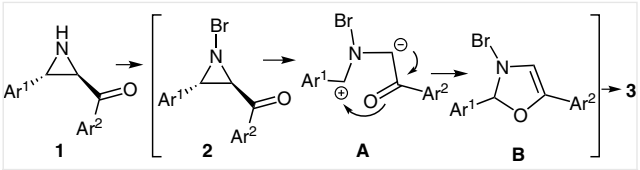


Product	Ar^1	Ar^2	Yield (%)[c]	Mp (°C)
3a	Ph	Ph	93	71–72[5a,b]
3b	2-ClC_6H_4	Ph	88	78–80
3c	Ph	3-$O_2NC_6H_4$	86	145–147
3d	2,4-$Cl_2C_6H_3$	Ph	94	91–92[5a]
3e	4-ClC_6H_4	Ph	86	100–102
3f	Ph	4-BrC_6H_4	84	93–95[5a,b]
3g	4-ClC_6H_4	4-ClC_6H_4	92	205–207
3h	3-$MeOC_6H_4$	Ph	75	81–83
3i	Ph	4-$MeOC_6H_4$	78	117–119[5a,b]
3j	3-ClC_6H_4	Ph	89	98–100
3k	Ph	4-ClC_6H_4	81	78–80
3l	4-$O_2NC_6H_4$	4-ClC_6H_4	0	–
3m	3-$O_2NC_6H_4$	Ph	0	–

[a] Reactions were performed at reflux temperature in 1,4-dioxane for 1 h.
[b] A 1:1 ratio of aziridine/NBS was employed.
[c] Yield of isolated product.

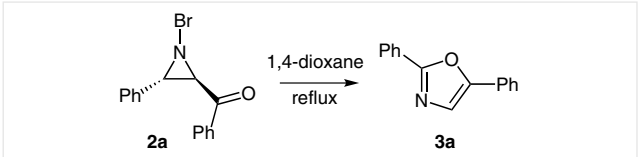
A plausible mechanism for the transformation of *N*-H ketoaziridines into the corresponding oxazoles is proposed (Scheme 3). In the presence of *N*-bromosuccinimide, the *N*-H ketoaziridine affords the corresponding *N*-bromo-substituted ketoaziridine, which gives an azomethine ylide via C–C bond cleavage under thermal conditions. The bromide is assumed to act as an activating group similar to acyl, alkyl, phthalimido or dicyclohexylcarbodiimido (Scheme 2, reactions I–III) leading to ring-cleavage of the aziridine to give the ylide. In addition, aziridines bearing an electron-withdrawing carbonyl group, which stabilizes the carbanionic center, and an electron-donating aryl group, which stabilizes the benzylic cationic center in azomethine ylide **A**, seemed to favor formation of the ylide. The reaction proceeds via ring closure of the ylide to give cyclized intermediate **B**, followed by thermal elimination of hydrogen bromide to complete the formation of the oxazole (Scheme 3).

It is evident that the reaction of *N*-bromosuccinimide with aziridines bearing a nitro group at the Ar^1 position for synthesis of oxazoles **3l** and **3m** (Table 2) was unsatisfactory, owing to the formation of an unstable intermediate **A**.



Scheme 3 A plausible reaction mechanism

Additional convincing support for the proposed mechanism is that at low temperature, the reaction with *N*-bromosuccinimide produced the *N*-bromoketoaziridine from the starting *N*-H ketoaziridine (Table 1, entry 13). In a separate experiment, *N*-bromo-2-benzoyl-3-phenylaziridine (**2a**), under thermal conditions in 1,4-dioxane, gave 2,5-diphenyloxazole (**3a**) in a high 95% yield (Scheme 4), while the thermal reaction of **1a** without *N*-bromosuccinimide did not give any trace of oxazole **3a** (Table 1, entry 16).

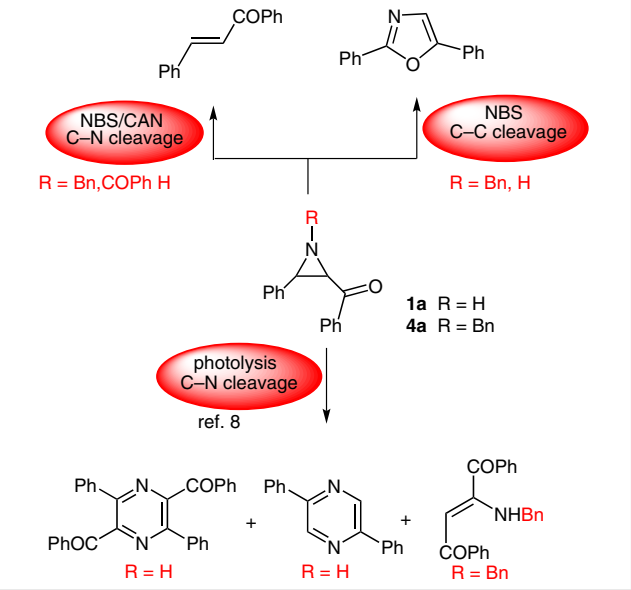


Scheme 4 Conversion of *N*-bromoketoaziridine **2a** into 2,5-diphenyloxazole (**3a**)

This result shows that the presence of the bromine group on the nitrogen of the aziridine ring is crucial for the thermal C–C bond cleavage of the ketoaziridine ring. It is assumed that the bromine on the nitrogen atom has a stabilizing effect on the formation of azomethine ylide **A** (Scheme 3).

Encouraged by the results obtained via this transformation, it was felt necessary to investigate the effect of *N*-bromosuccinimide on the thermal transformation of N-substituted 2-phenyl-3-benzoylaziridine **4a**, which was prepared via the Gabriel procedure.[7a,b] Our results showed that the reaction of compound **4a** in 1,4-dioxane at reflux temperature in the presence of *N*-bromosuccinimide for 30 minutes gave 2,5-diphenyloxazole (**3a**) in high yield (87%), while the same reaction in the absence of *N*-bromosuccinimide for 10 hours afforded only a 17% yield of 2,5-diphenyloxazole (**3a**). This suggests that *N*-bromosuccinimide functions as an activating group enabling exclusive C–C bond scission to give the desired product in good yield. A striking feature of this reaction is the difference in the behavior of ketoaziridines with respect to C–N or C–C bond cleavage under the thermal or photolysis conditions. Scheme 5 shows a comparison of the photolysis and thermolysis of 2-benzoyl-3-phenylaziridines. George and co-workers reported that the phototransformations of N-substituted 2-phenyl-3-benzoylaziridine **4a** and **1a** occurred via C–N bond cleavage of the aziridine ring, while herein we report a thermal C–C bond cleavage of *N*-benzyl-2-phenyl-3-benzoylaziridine and *N*-H ketoaziridines in the presence of *N*-bromosuccinimide. The

photoactivated intermolecular dimerization of the aziridinyl ketone leads to 2,5-dibenzoyl-3,6-diphenylpyrazine (11%) and 2,5-diphenylpyrazine (8%).[8]



Scheme 5 A comparison of the photolysis and thermolysis of 2-benzoyl-3-phenylaziridines

Another striking feature of this reaction was that *trans*-1-alkyl (H or benzoyl)-2-benzoyl-3-phenylaziridine, in the presence of *N*-bromosuccinimide/cerium(IV) ammonium nitrate (CAN), underwent a completely stereocontrolled deamination to afford the corresponding alkenes (Scheme 5).[6j]

In conclusion, we have reported the direct synthesis of 2,5-diaryloxazoles from *N*-H ketoaziridine derivatives by using *N*-bromosuccinimide as a brominating reagent. The intermediate *N*-bromoketoaziridines underwent established thermal C–C bond cleavage to afford a range of 2,5-diaryloxazoles in good to high yields. Further research on this topic is ongoing.

All solvents were dried and distilled according to standard procedures. The yields refer to those of isolated products obtained after purification by column chromatography on Kieselgel 60 GF 254 silica gel or by distillation under vacuum. The products were characterized by comparison with authentic samples (IR and ^{1}H NMR spectra, TLC, melting and boiling points). Melting points were obtained using an Electrothermal 9100 apparatus. IR spectra were recorded on a JASCO FT/IR-6300 FT Infrared spectrometer. NMR spectra were recorded on a Bruker AMX-400 spectrometer (^{1}H at 400 MHz and ^{13}C at 100 MHz) in $CDCl_3$ or DMSO-d_6, with chemical shift values (δ) reported in ppm downfield from TMS. Elemental analyses were obtained using a LECO CHNS 932 Elemental Analyzer.

2,5-Diaryloxazoles 3; General Procedure

NBS (1 mmol) was added to a solution of aziridine (**1**) (1 mmol) in 1,4-dioxane (5 mL) and the mixture was heated at reflux temperature. The progress of the reaction was monitored by TLC (EtOAc–hexane, 1:4). After completion, the mixture was allowed to cool to r.t. Purification of the residue by column chromatography (silica gel, EtOAc–hexane, 1:4) gave the corresponding 2,5-diaryloxazole (Table 2).

2,5-Diphenyloxazole (3a)

Yield: 205 mg (93%); white solid; mp 71–72 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.4 Hz, 2 H), 7.72 (d, *J* = 7.6 Hz, 2 H), 7.49–7.42 (m, 6 H), 7.32 (t, *J* = 7.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.1, 151.3, 130.5, 128.9, 128.8, 128.5, 127.8, 127.1, 126.4, 124.2, 123.0.

Anal. Calcd for $C_{15}H_{11}NO$: C, 81.45; H, 4.98; N, 6.33. Found: C, 81.28; H, 4.54; N, 6.20.

2-(2-Chlorophenyl)-5-phenyloxazole (3b)

Yield: 198 mg (88%); white solid; mp 78–80 °C.

IR (KBr): 3063, 2991, 1654, 1582, 825, 758, 691 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10–8.07 (m, 1 H), 7.74–7.73 (m, 2 H), 7.56–7.51 (m, 2 H), 7.49–7.34 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1, 151.9, 132.5, 131.6, 131.2, 130.7, 129.0, 128.8, 127.9, 127.0, 126.4, 124.5, 123.3.

Anal. Calcd for $C_{15}H_{10}ClNO$: C, 70.46; H, 3.94; N, 5.48. Found: C, 70.22; H, 3.87; N, 5.32.

5-(3-Nitrophenyl)-2-phenyloxazole (3c)

Yield: 229 mg (86%); white solid; mp 145–147 °C.

IR (KBr): 3060, 2993, 1657, 1554, 1530, 824, 751, 691 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.53 (t, *J* = 1.9 Hz, 1 H), 8.19–8.10 (m, 3 H), 8.00 (m, 1 H), 7.63 (m, 1 H), 7.59 (s, 1 H), 7.52–7.49 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.1, 148.9, 148.7, 130.9, 130.0, 129.6, 129.5, 128.9, 126.8, 126.5, 125.5, 122.7, 118.8.

Anal. Calcd for $C_{15}H_{10}N_2O_3$: C, 67.68; H, 3.80; N, 10.52. Found: C, 67.59; H, 3.72; N, 10.18.

2-(4-Chlorophenyl)-5-phenyloxazole (3e)

Yield: 219 mg (86%); yellow solid; mp 100–102 °C.

IR (KBr): 3060, 2993, 1657, 1580, 751, 691 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, *J* = 7.5 Hz, 2 H), 7.85–7.63 (m, 3 H), 7.50–7.31 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.3, 151.5, 136.4, 130.2, 129.1, 128.6, 127.8, 127.5, 125.8, 124.4, 123.4.

Anal. Calcd for $C_{15}H_{10}ClNO$: C, 70.46; H, 3.94; N, 5.48. Found: C, 70.04; H, 3.90; N, 5.18.

2,5-Bis(4-chlorophenyl)oxazole (3g)

Yield: 267 mg (92%); yellow solid; mp 205–207 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.09 (d, *J* = 8.0 Hz, 2 H), 7.87 (m, 3 H), 7.63 (d, *J* = 8.0 Hz, 2 H), 7.57 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 159.5, 150.0, 135.4, 133.1, 129.3, 129.2, 127.7, 126.1, 125.8, 125.4, 124.9.

Anal. Calcd for $C_{15}H_9Cl_2NO$: C, 62.09; H, 3.13; N, 4.83. Found: C, 62.01; H, 3.03; N, 4.74.

2-(3-Methoxyphenyl)-5-phenyloxazole (3h)

Yield: 188 mg (75%); white solid; mp 81–83 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.70 (m, 3 H), 7.65–7.64 (m, 1 H), 7.47–7.43 (m, 3 H), 7.40 (t, *J* = 8.0 Hz, 1 H), 7.38–7.33 (m, 1 H), 7.02 (ddd, *J* = 8.3, 2.6, 0.8 Hz, 1 H), 3.90 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2, 160.0, 151.4, 130.1, 129.1, 128.8, 128.6, 128.1, 124.4, 123.6, 118.9, 117.0, 111.1, 55.6.

Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.77. Found: C, 76.32; H, 5.12; N, 5.63.

2-(3-Chlorophenyl)-5-phenyloxazole (3j)

Yield: 227 mg (89%); white solid; mp 98–100 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11–8.10 (m, 1 H), 8.01–7.98 (m, 1 H), 7.74–7.71 (m, 2 H), 7.47–7.42 (m, 5 H), 7.37–7.33 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 151.9, 135.1, 130.4, 130.3, 129.2, 129.1, 128.8, 127.9, 126.4, 124.5, 124.4, 123.7.

Anal. Calcd for $C_{15}H_{10}ClNO$: C, 70.46; H, 3.94; N, 5.48. Found: C, 70.24; H, 3.86; N, 5.38.

5-(4-Chlorophenyl)-2-phenyloxazole (3k)

Yield: 206 mg (81%); white solid; mp 78–80 °C.

IR (KBr): 3063, 2991, 1654, 1582, 825, 758, 691 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 7.5 Hz, 2 H), 7.75 (d, *J* = 7.5 Hz, 2 H), 7.59–7.55 (m, 2 H), 7.50–7.37 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.3, 150.3, 130.7, 128.8, 128.7, 128.4, 127.8, 127.2, 126.4, 124.3, 123.2.

Anal. Calcd for $C_{15}H_{10}ClNO$: C, 70.46; H, 3.94; N, 5.48. Found: C, 70.26; H, 3.81; N, 5.37.

1-Benzyl-2-benzoyl-3-phenylaziridine (4a)

Yield: 225 mg (72%); white solid; mp 110–112 °C.

IR (KBr): 3100, 2994, 1668, 1595, 1495, 1000, 760, 690 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 7.2 Hz, 2 H), 7.51 (m, 3 H), 7.42 (m, 6 H), 7.30 (t, *J* = 7.5 Hz, 1 H), 7.23 (t, *J* = 7.6 Hz, 2 H), 7.16 (t, *J* = 7.8 Hz, 1 H), 4.09 (d, *J* = 13.9 Hz, 1 H), 3.86 (d, *J* = 13.9 Hz, 1 H), 3.43 (d, *J* = 7.2 Hz, 1 H), 3.35 (d, *J* = 7.2 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 193.6, 138.2, 135.4, 133.3, 128.8, 128.6, 128.4, 128.3, 127.9, 127.8, 127.6, 64.3, 51.2, 50.2.

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References

(1) (a) Osborn, H. M. I.; Sweeney, J. *Tetrahedron: Asymmetry* **1997**, *8*, 1693. (b) Hu, X. E. *Tetrahedron* **2004**, *60*, 2701. (c) Sweeney, J. B. *Chem. Soc. Rev.* **2002**, *31*, 247. (d) Stanković, S.; D'Hooghe, M.; Catak, S.; Eum, H.; Waroquier, M.; Van Speybroeck, V.; De Kimpe, N.; Ha, H.-J. *Chem. Soc. Rev.* **2012**, *41*, 643.

(2) (a) Watson, I. D. G.; Yu, L.; Yudin, A. K. *Acc. Chem. Res.* **2006**, *39*, 194. (b) Baeg, J. O.; Bensimo, C.; Alper, H. *J. Am. Chem. Soc.* **1995**, *117*, 4700. (c) Ungureanu, I.; Klotz, P.; Mann, A. *Angew. Chem. Int. Ed.* **2000**, *39*, 4615. (d) Munegumi, T.; Azumaya, I.; Kato, T.; Masu, H.; Saito, S. *Org. Lett.* **2006**, *8*, 379. (e) Wender, P. A.; Strand, D. *J. Am. Chem. Soc.* **2009**, *131*, 7528.

(3) (a) Heine, H. W.; Peavy, R. *Tetrahedron Lett.* **1965**, *6*, 3123. (b) Padwa, A.; Hamilton, L. *Tetrahedron Lett.* **1965**, *6*, 4363. (c) Huisgen, R.; Scheer, W.; Szeimies, G.; Huber, H. *Tetrahedron Lett.* **1966**, *7*, 397. (d) Huisgen, R.; Scheer, W.; Huber, H. *J. Am. Chem. Soc.* **1967**, *89*, 1753. (e) Texier, F.; Carrie, R.; Jaz, J. *J. Chem. Soc., Chem. Commun.* **1972**, 199. (f) Attanasi, O. A.; Davoli, P.; Favi, G.; Filippone, P.; Forni, A.; Moscatelli, G.; Prati, F. *Org. Lett.* **2007**, *9*, 3461. (g) Pankova, A. S.; Voronin, V. V.; Kuznetsov, M. A. *Tetrahedron Lett.* **2009**, *50*, 5990. (h) Zhao, W.; Lu, Z.; Wulff, W. D. *J. Org. Chem.* **2014**, *79*, 1008. (i) Wang, S.; Zhu, X.; Chai, Z.; Wang, S. *Org. Biomol. Chem.* **2014**, *12*, 1351. (j) Vaultier, M.; Carrié, R. *Tetrahedron Lett.* **1978**, *19*, 1195. (k) Pohlhaus, P. D.; Bowman, R. K.; Johnson, J. S. *J. Am. Chem. Soc.* **2004**, *126*, 2294. (l) Wu, X.; Lei, L.; Zhang, J. *Chem. Commun.* **2011**, *47*, 7824. (m) Wang, S.; Zhu, Y.; Wang, Y.; Lu, P. *Org. Lett.* **2009**, *11*, 2615. (n) Schirmeister, T. *Liebigs Ann.* **1997**, 1895. (o) Gomes, P. J. S.; Nunes, C. M.; Pais, A. A. C. C.; Pinho e Melo, T. M. V. D.; Arnaut, L. G. *Tetrahedron Lett.* **2006**, *47*, 5475.

(4) (a) Felix, D.; Eschenmoser, A. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 224. (b) Zhong, Y.-L.; Bulger, P. G. *Org. Synth.* **2010**, *87*, 8. (c) Claxton, G. P.; Allen, L.; Grisar, J. M. *Org. Synth.* **1977**, *56*, 118. (d) Padwa, A.; Battisti, A. *J. Am. Chem. Soc.* **1971**, *36*, 230. (e) Gassman, D. P. G.; Dygos, D. K. *J. Am. Chem. Soc.* **1969**, *91*, 1543. (f) Gassman, P. G.; Dygos, D. K.; Trent, J. E. *J. Am. Chem. Soc.* **1970**, *92*, 2084. (g) Gentiluc, L.; Grijzen, Y.; Thijs, L.; Zwanenburg, B. *Tetrahedron Lett.* **1995**, *36*, 4665. (h) Legters, J.; Thijs, L.; Zwanenburg, B. *Recl. Trav. Chim. Pays-Bas* **1992**, *111*, 75.

(5) (a) Samimi, H. A.; Mohammadi, S. *Synlett* **2013**, *24*, 223. (b) Keni, M.; Tepe, J. J. *J. Org. Chem.* **2005**, *70*, 4211. (c) Beletskii, E. V.; Kuznetsov, M. A. *Russ. J. Org. Chem.* **2009**, *45*, 1229. (d) Beccalli, E. M.; Borsini, E.; Broggini, G.; Palmisano, G.; Sottocornola, S. *J. Org. Chem.* **2008**, *73*, 4746. (e) Wang, S.-X.; Wang, M.-X.; Wang, D.-X.; Zhu, J. *Eur. J. Org. Chem.* **2007**, 4076. (f) Kelly, T. R.; Lang, F. *J. Org. Chem.* **1996**, *61*, 4623. (g) Phillips, A. J.; Uto, Y.; Wipf, P.; Reno, M. J.; Williams, D. R. *Org. Lett.* **2000**, *2*, 1165. (h) Pusch, S.; Opatz, T. *Org. Lett.* **2014**, *16*, 5430. (i) Padwa, A.; Eisenhardt, W. *Chem. Commun.* **1968**, 380. (j) Padwa, A.; Eisenhardt, W. *J. Am. Chem. Soc.* **1968**, *90*, 2442. (k) Padwa, A.; Eisenhardt, W. *J. Am. Chem. Soc.* **1971**, *93*, 1400. (l) Lown, J. W.; Moser, J. P. *J. Chem. Soc., Chem. Commun.* **1970**, 247. (m) Kuznetsov, M. A.; Voronin, V. V. *Chem. Heterocycl. Compd.* **2011**, *47*, 173. (n) Padwa, A.; Eastman, D.; Hamilton, L. *J. Org. Chem.* **1968**, *33*, 1317.

(6) (a) Samimi, H. A.; Mamaghani, M.; Tabatabeian, K. *J. Heterocycl. Chem.* **2008**, *45*, 1765. (b) Mamaghani, M.; Tabatabeian, K.; Samimi, H. A. *Z. Kristallogr. - New Cryst. Struct.* **2008**, *223*, 390. (c) Samimi, H. A.; Mohammadi, S. *J. Iran Chem. Soc.* **2013**, *11*, 69. (d) Samimi, H. A.; Kiyani, H.; Shams, Z. *J. Chem. Res.* **2013**, 282. (e) Samimi H. A., Bohari M. Y., Hiedari Z., Narimani L.; *J. Iran Chem. Soc.*, in press. (f) Samimi, H. A.; Bohari, M. Y. *J. Chem. Res.* **2014**, *38*, 358. (g) Samimi, H. A.; Mohammadi, S. *J. Iran Chem. Soc.* **2014**, *11*, 69. (h) Samimi, H. A.; Shams, Z. *J. Iran Chem. Soc.* **2014**, *11*, 979. (i) Samimi, H. A.; Bohari, M. Y.; Soltani, M. *J. Iran Chem. Soc.* **2014**, *11*, 1467. (j) Samimi, H. A.; Salehi, E.; Dadvar, F. *J. Chem. Res.* **2014**, *38*, 731. (k) Samimi, H. A.; Bohari, M. Y.; Saberi, F. *Synthesis* **2015**, *47*, 129.

(7) (a) Gabriel, S. *Chem. Ber.* **1888**, *21*, 1049. (b) Cromwell, N. H.; Hoeksema, H. *J. Am. Chem. Soc.* **1949**, *71*, 708. (c) Armstrong, A.; Baxter, C. A.; Lamont, S. G.; Pape, A. R.; Wincewicz, R. *Org. Lett.* **2007**, *9*, 351. (d) Armstrong, A.; Carbery, D. R.; Lamont, S. G.; Pape, A. R.; Wincewicz, R. *Synlett* **2006**, 2504. (e) Ikeda, I.;

Machii, Y.; Okahara, M. *Synthesis* **1980**, 650. (f) Xu, J.; Jiao, P. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1491. (g) Shen, Y.-M.; Zhao, M.-X.; Xu, J.; Shi, Y. *Angew. Chem. Int. Ed.* **2006**, *45*, 8005.

(8) Ramaiah, D.; Muneer, M.; Gopidas, K. R.; Das, P. K.; Rath, N. P.; George, M. V. *J. Org. Chem.* **1996**, *61*, 4240.