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One-pot Stereoselective Syntheses of 2-Acylaziridines and 2-Acylpyrrolidines from *N*-(Propargylic)hydroxylamines

Yoshiaki Miyamoto, Norihiro Wada, Takahiro Soeta, Shuhei Fujinami, Katsuhiko Inomata, and Yutaka Ukaji*[a]

Abstract: A stereoselective direct transformation of *N*-(propargylic)hydroxylamines into *cis*-2-acylaziridines was realized by the combined use of $AgBF_4$ and CuCl. Copper salts were confirmed to promote the transformation of the intermediary 4-isoxazolines to 2-acylaziridines. Both 3-aryl and 3-alkyl substituted 2-acylaziridines could be prepared by this method. Furthermore, subsequent 1,3-dipolar cycloaddition of azomethine ylides generated in situ from the intermediary 2-acylaziridines with maleimides was achieved by one-pot procedure to afford the corresponding 2-acylpyrrolidines consisting of an octahydropyrrolo[3,4-*c*]pyrrole skeleton stereoselectively.

Keywords: 2-acylaziridine • 2-acylpyrrolidine • 4-isoxazoline • rearrangement • azomethine ylide

Introduction

2-Acylaziridines are versatile synthetic intermediates for a wide range of important nitrogen-containing chemicals, for example via ring-opening reactions,[1] and some of them have biological activities.[2] General procedure to prepare 2-acylaziridines includes metal catalyzed addition of nitrene to alkenes,[3] metal catalyzed carbene addition to imine functions,[4] Micheal addition-elimination of hydroxylamine and hydrazine derivatives to enones,[5] ring-closure of 2-azido-3-hydroxy ketones,[6] and nucleophilic reaction of amines to α,β-dibromoketones.[7] Although *trans*-2-acylaziridines could be readily prepared, stereoselective synthesis of *cis*-2-acylaziridines is rather difficult. Only a few methods for preparation of *cis*-3-alkyl substituted 2-acylaziridines were reported.[4a,b,d] Baldwin rearrangement of 4-isoxazolines was known to afford 2-acylaziridines, however, the reaction conditions were drastic and the diastereoselectivity was not always good.[8] Although cobalt-mediated rearrangement of 4-isoxazolines also gave the corresponding 2-acylaziridines, stereoselectivity was not so high.[8i] Recently, microwave-assisted rearrangement was reported, however, the methods was limited to 3-aryl substituted acylaziridines.[8m]

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Recently, we have reported a one-pot reaction consisting of an enantioselective nucleophilic addition of alkynylzinc reagents to nitrones and a subsequent cyclization to give the corresponding 4-isoxazolines with high enantioselectivity.[9] In order to prepare 4-isoxazolines more efficiently, the cyclization of *N*-(propargylic)hydroxylamines to 4-isoxazolines was investigated in the presence of a metal salt, and $AgBF_4$ was found to be a catalyst of choice for the cyclization.[10] During the investigation of the metal catalyzed ring closure of *N*-(propargylic)hydroxylamines, *cis*-2-acylaziridines were found to be produced diastereoselectively in the presence of a copper salt at rt. Herein, we wish to report the details about one-pot preparation of 2-acylaziridines from *N*-(propargylic)hydroxylamines via ring closure to 4-isoxazolines and the successive Baldwin rearrangement in the presence of $AgBF_4$ and a copper salt.[11] Furthermore, one-pot stereoselective synthesis of 2-acylpyrrolidines via 1,3-dipolar cylcloaddition of azomethine ylides generated from the 2-acylaziridines is also described.

Results and Discussion

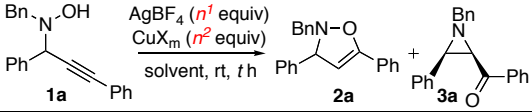
The cyclization of *N*-benzyl-*N*-(1,3-diphenylprop-2-ynyl)hydroxylamine (**1a**) was examined in the presence of various kinds of metal salts without an amine, and it was found that $AgBF_4$ was a good catalyst for cyclization to 4-isoxazolines.[10] During the survey of metal salts, it was found that not only 4-isoxazoline **2a** but also a *cis*-2-acylaziridine **3a**[8i,12] was produced with complete diastereoselectivity when CuCl was used in CH_2Cl_2 at rt (Table 1, Entry 1). Then, direct transformation of **1a** to 2-acylaziridine **3a** was intensively investigated and the results were summarized in Table 1.

The reaction by the use of 1.0 equiv of $CuCl_2$ or CuI was messy and the 2-acylaziridine **3a** was not obtained (Entries 2 and 3). The use of cationic copper salts afforded the *cis*-2-acylaziridine **3a** as a major product (Entries 4–7), however, the chemical yield was not high. By monitoring the reaction using TLC, it was observed that the 4-isoxazoline was once produced and gradually consumed. In order to promote the cyclization step to 4-isoxazoline, *N*-

(propargylic)hydroxylamine was firstly treated with 0.1 equiv $AgBF_4$ for 7 h and then CuCl was added to the reaction mixture: The chemical yield of **3a** was improved (Entry 8). The treatment with $AgBF_4$ together with CuCl further increased the yield of **3a** (Entry 9). By the use of 0.2 equiv of $AgBF_4$ and 1.0 equiv of CuCl, the reaction proceeded rather smoothly to afford **3a** in more than 80% yield (Entries 10 and 11). Solvent effect was examined in the reaction using 0.2 equiv of $AgBF_4$ and 1.0 equiv of CuCl, and CH_2Cl_2 was found to be best among the examined solvents (Entries 11–16). Although combination of 0.2 equiv of $AgBF_4$ and 1.0 equiv of several cationic copper salts were examined, the reactions were not so clean and resulted in decrease of the chemical yields of **3a** (Entries 17–20).

In order to explore the possibilities reducing the amount of copper salt, the reaction using 0.2 equiv of CuCl with 0.2 equiv of $AgBF_4$ was carried out: The transformation proceeded a little sluggishly to afford **3a**, but still in comparably good yield (Entries 21 and 22). In the present one-pot reaction, the active copper species was presumed to be $CuBF_4$ accompanied with generation of AgCl. Then the reaction in the presence of only 0.2 equiv of $CuBF_4(CH_3CN)_2$ was again examined to give the *cis*-2-acylaziridine **3a** in good yield (Entry 23), although the use of 1.0 equiv of $CuBF_4(CH_3CN)_4$ made the reaction rather complicated (Entry 6). Further addition of AgCl slightly decreased the yield (Entry 24). The use of 0.2 equiv of $CuOTf(C_6H_6)_{0.5}$ was also effective to give **3a** in good yield (Entry 25). Consequently, the combined use of 0.2 equiv of $AgBF_4$ and 1.0 equiv of CuCl was the best for the sequential cyclization and Baldwin rearrangement.

Table 1. Reaction conditions for direct transformation of **1a** into **3a**

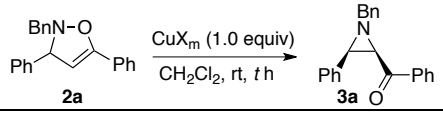


Entry	n^1 / equiv	CuX_m	n^2 / equiv	solvent	*t* / h	**2a** / %	**3a** / %
1	0	CuCl	1.0	CH_2Cl_2	41	16	2[a]
2	0	$CuCl_2$	1.0	CH_2Cl_2	44	--	--
3	0	CuI	1.0	CH_2Cl_2	44	--	--[b]
4	0	$CuOTf(C_6H_6)_{0.5}$	1.0	CH_2Cl_2	17	23	58
5	0	$Cu(OTf)_2$	1.0	CH_2Cl_2	48	--	45
6	0	$CuBF_4(CH_3CN)_4$	1.0	CH_2Cl_2	7	--	45
7	0	$Cu(BF_4)_2$	1.0	CH_2Cl_2	25	--	48
8[c]	0.1	CuCl	1.0	CH_2Cl_2	41	24	53
9	0.1	CuCl	1.0	CH_2Cl_2	8	32	61
10	0.2	CuCl	1.0	CH_2Cl_2	8	13	84
11	0.2	CuCl	1.0	CH_2Cl_2	20	4	88
12	0.2	CuCl	1.0	MeCN	20	24	--[a]
13	0.2	CuCl	1.0	MeOH	20	12	21
14	0.2	CuCl	1.0	THF	20	23	47
15	0.2	CuCl	1.0	Et_2O	20	22	6[a]
16	0.2	CuCl	1.0	toluene	20	28	13[a]
17	0.2	$CuOTf(C_6H_6)_{0.5}$	1.0	CH_2Cl_2	7	--	35
18	0.2	$Cu(OTf)_2$	1.0	CH_2Cl_2	8	--	13
19	0.2	$CuBF_4(CH_3CN)_4$	1.0	CH_2Cl_2	8	--	42
20	0.2	$Cu(BF_4)_2$	1.0	CH_2Cl_2	8	10	42
21	0.2	CuCl	0.2	CH_2Cl_2	8	10	58
22	0.2	CuCl	0.2	CH_2Cl_2	23	--	82
23	0	$CuBF_4(CH_3CN)_4$	0.2	CH_2Cl_2	23	--	74
24	0.2[d]	$CuBF_4(CH_3CN)_4$	0.2	CH_2Cl_2	23	--	65
25	0	$CuOTf(C_6H_6)_{0.5}$	0.2	CH_2Cl_2	41	--	78

[a] The hydroxylamine **1a** was recovered in 69% (Entry 1), 32% (Entry 12), 65% (Entry 15), and 7% (Entry 16) yields, respectively. [b] Most of the hydroxylamine **1a** was recovered. [c] The hydroxylamine **1a** was firstly treated with $AgBF_4$ for 7 h, and then CuCl was added to the resulting reaction mixture. [d] 0.2 Equiv of AgCl was used instead of $AgBF_4$.

Toward the rearrangement from 4-isoxazoline to 2-acylaziridine, evaluation of copper salts was separately performed, that is, the 4-isoxazoline **2a** was treated with copper salts as shown in the Table 2. Although the reaction was rather sluggish when only CuCl was used, addition of $AgBF_4$ again promoted the rearrangement (Entries 1 and 2). Cationic Cu(I) salts, especially $CuOTf(C_6H_6)_{0.5}$, were found to be effective as a promoter for this rearrangement (Entries 3 and 5), whereas Cu(II) salts were not effective (Entries 4 and 6).

Table 2. Evaluation of copper salts for Baldwin rearrangement

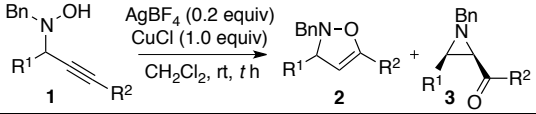


Entry	CuX_m	*t* / h	Yield / %
1	CuCl	41	23[a]
2[b]	CuCl	18	89
3	$CuOTf(C_6H_6)_{0.5}$	4	81
4	$Cu(OTf)_2$	41	3
5	$CuBF_4(CH_3CN)_4$	22	71
6	$Cu(BF_4)_2$	41	45

[a] The 4-isoxazoline **2a** was recovered in 68% yield. [b] In addition to CuCl, 0.2 equiv of $AgBF_4$ was also added to the reaction.

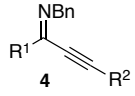
The one-pot cyclization-rearrangement was applied to several *N*-(propargylic)hydroxylamines **1** bearing aromatic and/or aliphatic substituents by the treatment with $AgBF_4$ (0.2 equiv) and CuCl (1.0 equiv). As listed in Table 3, the corresponding *cis*-acylaziridines **3** were produced stereoselectively.[12] A *cis*-2-heptanoyl-3-phenylaziridine **3b** was obtained in reasonable chemical yield (Entry 2). In the case of 2-pivaloylaziridine **3c**, a small amount of *trans*-isomer was furnished (Entry 3). Although transformation of propyl-substituted hydroxylamine **1d** was not so clean and a small amount of the corresponding *trans*-isomer and a dehydrated imine **4d** were formed, *cis*-2-benzoyl-3-propylaziridine **3d** was predominantly produced (Entry 4). In the case of cyclohexyl-substituted *N*-(propargylic)hydroxylamine **1e**, increase of the amount of $AgBF_4$ could improve the chemical yield (Entries 5 and 6). The reaction of a hydroxylamine **1f**, in which both R^1 and R^2 were alkyl groups, afforded *cis*-2-acylaziridine **3f** stereoselectively (Entry 7).

Table 3. Direct transformation of *N*-(propargylic)hydroxylamines into 2-acylaziridines



Entry	R^1	R^2		*t* / h	**2a** / %	**3a** / %
1	Ph	Ph	**a**	20	4	88
2	Ph	*n*Hex	**b**	27	--	63
3	Ph	*t*Bu	**c**	24	--	72[a]
4	*n*Pr	Ph	**d**	41	--	49[a,b]
5	*c*Hex	Ph	**e**	25	14	64
6[c]				24	7	76
7	Me	*n*Hex	**f**	23	--	58

[a] The corresponding *trans*-isomer of **3** was obtained in 6% (Entry 3) and 10% (Entry 4) yields, respectively. [b] An imine, 1-phenyl-*N*-(1-phenylhex-1-yn-3-ylidene)methanamine (**4d**), was obtained in 28 % yield. [c] The amount of $AgBF_4$ was 0.3 equiv.



In the case of $Co_2(CO)_8$ (0.5 equiv) mediated rearrangement of 4-isoxazoline, a radical pathway was proposed to give 2.8/1 mixture of *cis*/*trans*-2-acylaziridines starting from **1a**.[8i] When **1a** was treated with 1.0 equiv of $CuOTf(C_6H_6)_{0.5}$ under a similar conditions (in $ClCH_2CH_2Cl$ at 80 °C for 0.5 h), **3a** was obtained in 80% yield and the diastereoselectivity was still high (**3a**/*trans*-isomer = 20/1, determined by ^1H NMR spectrum of the crude products), different from the result of the reaction catalyzed by $Co_2(CO)_8$. Furthermore, addition of galvinoxyl free radical did not affect the reaction from

2a to **3a** (according to Entry 3 in Table 2) as a radical inhibitor. These facts might suggest that a radical pathway might be ruled out. Although the precise reaction mechanism of the present rearrangement is not yet clear, [1,3]-sigmatropic rearrangement proposed for original Baldwin rearrangement without metal salts is a probable pathway to afford the *cis*-2-acylaziridine (Figure 1).[8c,d,f] The reaction might be activated by coordination of nitrogen to copper resulting in weakening the N–O bond (Figure 1).

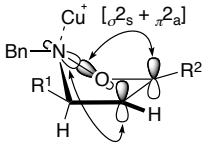


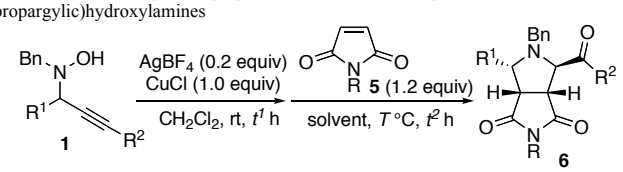
Figure 1. [1,3]-Sigmatropic rearrangement proposed for the present transformation

2-Acylaziridines are well-known to generate azomethine ylides via thermal ring-opening, which proceeds through a conrotatory C–C bond-breaking process according to the Woodward–Hoffmann rules. Following 1,3-dioplar cycloaddition of the generated azomethine ylides with electron-deficient olefins afforded 2-acylpyrrolidine skeletons,[13,14] some of which were bioactive.[15] For example, the cycloaddition of azomethine ylides generated from *cis*- and/or *trans*-2-benzoylaziridines with *N*-phenylmaleinimde gave a diastereomeric mixture of pyrrolidines depends on the reaction conditions.[14d,e] However, *cis*-2-acylaziridines were not so easy to be prepared and related cycloaddition of azomethine ylides derived from 2-acylaziridines with various substituents including aliphatic groups at C3 position was scarcely reported. Now, we could prepare 2-acylaziridines possessing aromatic and/or aliphatic substitutents in a *cis*-selective manner. Therefore, we investigated 1,3-dipolar cycloaddition of azomethine ylides generated in situ from the 2-acylaziridines via one-pot procedure starting from *N*-(propargylic)hydroxylamines **1**.

After treatment of *N*-(propargylic)hydroxylamines **1a** with 0.2 equiv of $AgBF_4$ and 1.0 equiv of CuCl for 24 h at rt in CH_2Cl_2, *N*-methylmaleimide (**5A**) was added to the reaction mixture. When the reaction was carried out at rt, the desired product was not obtained. However, the expected 1,3-dipolar cycloaddition proceeded at 75 °C in $ClCH_2CH_2Cl$, after exchanging the solvent from CH_2Cl_2, to give a 2-acylpyrrolidine **6aA** consisting of an octahydropyrrolo[3,4-*c*]pyrrole skeleton diastereoselectively in 33% yield (Table 4, Entry 1). Cycloaddition to *N*-benzylmaleimide (**5B**) afforded the corresponding cycloadduct **6aB** in a similar chemical yield (Entry 2). Due to easy handling of *N*-benzylmaleimide (**5B**) and its product **6aB** especially for their relatively high solubility, 1,3-dipolar cycloaddition was further examined using **5B**. When the reaction temperature was increased, the chemical yield was improved (Entry 3). The cycloadduct **6aB** was obtained in 60% yield when cycloaddition was carried out at 145 °C in xylene (Entry 4). When the reaction was performed under more condensed conditions, the chemical yield was further improved up to 85% yield (Entry 5).

One-pot synthesis of substituted pyrrolidines was then investigated starting from *N*-(propargylic)hydroxylamines **1** possessing not only aromatic but also aliphatic substituents. Phenyl-substituted pyrrolidines **6bB** and **6cB** (R^1 = Ph) were obtained in ca 60% yields with complete diastereoselectivity (Entries 6 and 7). It was revealed that 1,3-dipolar cycloaddition of azomethine ylides via 2-acylaziridines **3d–f** bearing an aliphatic substituent at C3 position (R^1 = alkyl) afforded the corresponding pyrrolidines stereoselectively although total chemical yields were not good enough (Entries 8–11). In the case of 5-cylohexyl-substituted pyrrolidines **6eA** and **6eB**, chemical yields were still over 50% yields after 3 step-reaction consisting of ring-closure, Baldwin rearrangement, and 1,3-dipolar cycloaddition (Entries 9 and 10).

Table 4. One-pot preparation of 2-acylpyrrolidines from *N*-(propargylic)hydroxylamines



Entry	R^1	R^2	R	t^1 / h	solvent	T / °C	t^2 / h	**6**	Yield / %
1	Ph	Ph	Me	24	$ClCH_2CH_2Cl$[a]	75	24	**6aA**	33
2	Ph	Ph	Bn	24	$ClCH_2CH_2Cl$[a]	75	24	**6aB**	32
3				24	toluene[a]	110	6		53
4				27	xylene[a]	145	1		60
5				24	xylene[b]	145	2		85
6	Ph	*n*Hex	Bn	31	xylene[b]	145	3	**6bB**	56
7	Ph	*t*Bu	Bn	31	xylene[b]	145	1	**6cB**	66
8	*n*Pr	Ph	Bn	48	xylene[b]	145	2	**6dB**	39
9[c]	*c*Hex	Ph	Me	27	xylene[b]	145	3	**6eA**	52
10[c]	*c*Hex	Ph	Bn	27	xylene[b]	145	3	**6eB**	53
11	Me	*n*Hex	Bn	24	xylene[b]	145	1.5	**6fB**	27

[a] Concentration was 0.06 mmol mL^{-1}. [b] Concentration was 0.25 mmol mL^{-1}. [c] Amount of $AgBF_4$ was 0.3 equiv.

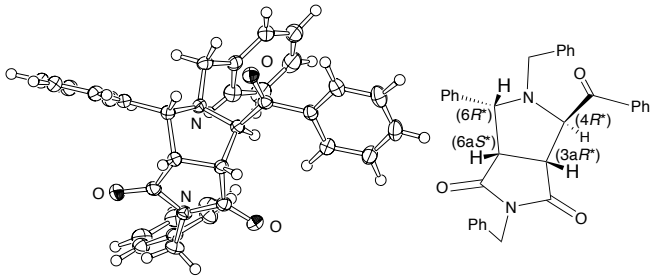


Figure 2. X-ray structure of **6aB**

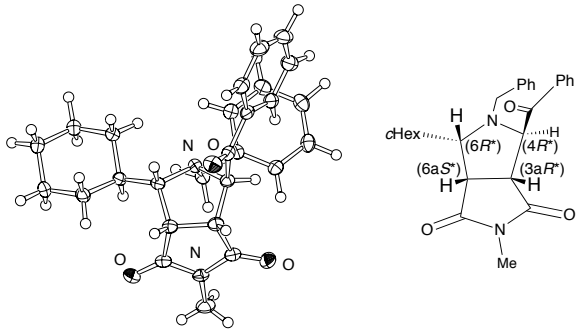
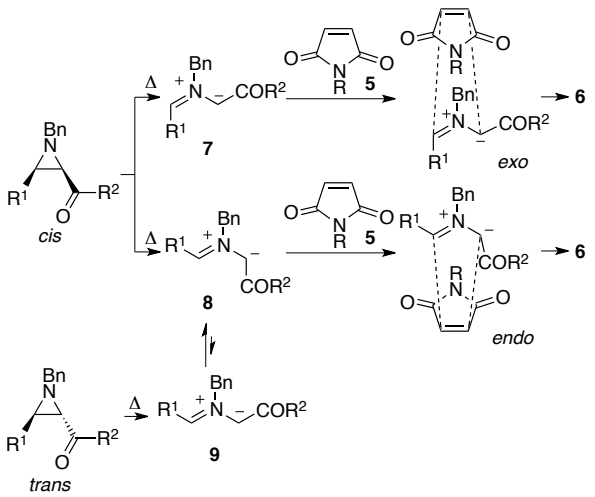


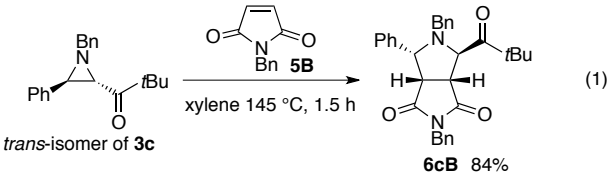
Figure 3. X-ray structure of **6eA**

Relative stereochemistry of the product **6aB** and **6eA** was determined to be 3a*R**,4*R**,6*R**,6a*S** by X-ray crystallographic analyses of their single crystals (Figures 2 and 3). The stereochemistry of other cycloadducts was tentatively assigned to be also 3a*R**,4*R**,6*R**,6a*S**, since the coupling constants J_{3a-4} and J_{6-6a} between the methine protons in their ^1H NMR spectra were in accordance with those of **6aB** and **6eA**, the stereochemistry of which was determined by X-ray crystallography. Based on this assignment, 1,3-dipolar cycloaddition was considered to proceed via *exo*-mode with *S*-shaped azomethine ylide **7** and/or *endo*-mode with *S*-shaped azomethine ylide **8** regardless of R^1, whether it is an aromatic or aliphatic substituent (Scheme 1).[16] In the case of pyrrolidines **6cB** and **6dB**, the products were isolated as single diastereomers although the intermediary *cis*-2-acylaziridines might be contaminated with their *trans*-isomers as observed in Table 3 (Entries 3 and 4). We confirmed that 1,3-dipolar cycloaddition of

the isolated *trans*-isomer of **3c** with **5B** gave **6cB** stereoselectively at 145 °C in xylene in 84% yield (eq. 1).[17] These results suggested existence of the equilibrium between *W*-dipole **9**, which might be favorable than *U*-dipole,[18] and *S*-dipole **7** and/or **8** under high temperature even in the case of 3-alkyl substituted 2-acylaziridine **3d**.[19] Therefore, the *trans*-2-acylaziridine also afforded **6** via 1,3-dipolar cycloaddition through *S*-dipole **7** and/or **8**.



Scheme 1. Proposed pathway of 1,3-dipolar cycloaddition



(1)

Conclusion

As described above, a direct transformation of *N*-(propargylic)hydroxylamines into *cis*-2-acylaziridines has been developed. Furthermore, one-pot stereoselective preparation of 2-acylpyrrolidine consisting of an octahydropyrrolo[3,4-*c*]pyrrole skeleton was achieved via 1,3-dipolar cycloaddition of azomethine ylides, generated in situ by thermal ring-opening of the intermediary 2-acylaziridines, in the presence of maleimides. The present methods would be quite useful for the synthesis of a wide range of nitrogen containing biologically active compounds because *cis*-2-acylaziridines and 2-acylpyrrolidines are versatile synthons for such chemicals.

Experimental Section

General Remarks: The ^{1}H NMR spectra were recorded on a JEOL ECS 400 NMR (400 MHz) spectrometer in $CDCl_3$ and the chemical shifts were determined in the δ-scale relative to TMS (δ = 0 ppm) as an internal standard. The ^{13}C NMR spectra were measured on a JEOL ECS 400 NMR (100 MHz) spectrometer in $CDCl_3$ and the chemical shifts were determined in the δ-scale relative to $CDCl_3$ (δ = 77.0 ppm) as an internal standard. The IR spectra were performed on a JASCO FT/IR-230 spectrometer. All measurements for X-ray crystallographic analyses were made on a Rigaku/MSC Mercury diffractometer with graphite monochromated Mo-Kα radiation. Elemental analyses were carried out on a Yanaco CHN Corder MT-5 elemental analyzer. The MS spectra were recorded with JEOL JMS-SX102A and JMS-700 mass spectrometers. All solvents were distilled and stored over drying agents. Merck silica gel 60 PF254 (Art. 7749) and Cica silica gel 60N spherical neutral (37563-84) were used for thin-layer chromatography (TLC) and flash column chromatography, respectively. All of the melting points were determined with a micro melting apparatus (Yanagimoto-Seisakusho) and are uncorrected.

Representative procedure of direct transformation of *N*-(propargylic)hydroxylamine 1a to 2-acylaziridine 3a (Table 3, Entry 1): A mixture of *N*-(propargylic)hydroxylamine **1a** (219 mg, 0.7 mmol), $AgBF_4$ (27 mg, 0.14 mmol) and CuCl (69 mg, 0.7 mmol) in CH_2Cl_2 (20 mL) was stirred at rt under an argon atmosphere. After 20 h, the mixture was filtered through a pad of Celite and the solvent was removed under reduced pressure. The residue was purified by preparative TLC (hexane/AcOEt = 5/1) to give *cis*-2-acylaziridine **3a** (193 mg, 88% yield) and 4-isoxazoline **2a**[20] (9 mg, 4% yield).

In a similar manner, 2-acylaziridines **3b**–**3f** were prepared from the corresponding *N*-(propargylic)hydroxylamines **1b**–**1f**, respectively.

[(2*R**,3*R**)-1-Benzyl-3-phenylaziridin-2-yl](phenyl)methanone (**3a**):[8i] R_f = 0.35 (hexane/AcOEt = 5/1); a solid; m.p. 94–96 °C (from EtOH/hexane); ^{1}H NMR δ 3.22 (d, 1H, *J* = 6.9 Hz), 3.30 (d, 1H, *J* = 6.9 Hz), 3.71 (d, 1H, *J* = 14.0 Hz), 3.93 (d, 1H, *J* = 14.0 Hz), 7.01–7.40 (m, 13 H), 7.77 (d, 2H, *J* = 6.4 Hz); ^{13}C NMR δ 49.6, 51.0, 63.5, 127.0, 127.2, 127.4, 127.7, 127.8, 127.9, 128.2, 132.8, 134.8, 136.7, 137.7, 192.9; IR (KBr) 3027, 1681, 1495, 1449, 1355, 1223, 1056, 935, 747, 737, 707, 696 cm^{-1}.

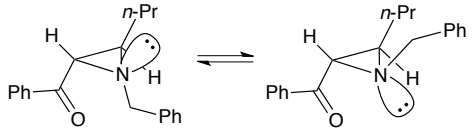
1-[(2*R**,3*R**)-1-Benzyl-3-phenylaziridin-2-yl]heptan-1-one (**3b**): R_f = 0.45 (hexane/AcOEt = 5/1); an oil; ^{1}H NMR δ 0.80 (t, 3H, *J* = 7.4 Hz), 0.88–1.30 (m, 8H), 1.88 (ddd, 1H, *J* = 17.4, 8.2, 6.4 Hz), 2.20 (ddd, 1H, *J* = 17.4, 8.2, 6.4 Hz), 2.64 (d, 1H, *J* = 7.0 Hz), 3.14 (d, 1H, *J* = 7.0 Hz), 3.69 (d, 1H, *J* = 13.8 Hz), 3.78 (d, 1H, *J* = 13.8 Hz), 7.18–7.43 (m, 10H); ^{13}C NMR δ 14.0, 22.3, 22.8, 28.5, 31.4, 40.7, 48.6, 52.4, 64.0, 127.36, 127.43, 127.8, 128.10, 128.14, 128.4, 135.3 138.0, 207.4; IR (neat) 3062, 3031, 2928, 2857, 1699, 1604, 1496, 1454, 1376, 1204, 1067, 1029, 738, 699 cm^{-1}; HRMS (EI$^+$) (M$^+$), Found: *m/z* 321.2087; Calcd for $C_{22}H_{27}NO$: 321.2093.

1-[(2*R**,3*R**)-1-Benzyl-3-phenylaziridin-2-yl]-2,2-dimethylpropan-1-one (**3c**): R_f = 0.45 (hexane/AcOEt = 5/1); a solid; m.p. 85–88 °C (from EtOH/hexane); ^{1}H NMR δ 0.96 (s, 9H), 3.05 (d, 1H, *J* = 6.8 Hz), 3.12 (d, 1H, *J* = 6.8 Hz), 3.67 (d, 1H, *J* = 14.0 Hz), 3.94 (d, 1H, *J* = 14.0 Hz), 7.19–7.41 (m, 10H); ^{13}C NMR δ 25.7, 43.2, 49.4, 50.0, 63.4, 126.8, 127.1, 127.4, 127.5, 128.1, 134,9, 137.7, 206.6; IR (KBr) 3027, 2973, 1703, 1604, 1495, 1455, 1378, 1312, 1265, 1091, 1027, 840, 758, 732 cm^{-1}; Found: C, 81.81; H, 7.79; N, 4.79%; Calcd for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.77%.

1-[(2*S**,3*R**)-1-Benzyl-3-phenylaziridin-2-yl]-2,2-dimethylpropan-1-one (*trans*-isomer of **3c**): R_f = 0.50 (hexane/AcOEt = 5/1); an oil; ^{1}H NMR δ 1.04 (s, 9H), 3.15 (d, 1H, *J* = 2.5 Hz), 3.37 (d, 1H, *J* = 2.5 Hz), 3.93 (d, 1H, *J* = 13.8 Hz), 4.20 (d, 1H, *J* = 13.8 Hz), 7.19–7.41 (m, 10H); ^{13}C NMR δ 25.7, 44.6, 45.9, 49.7, 54.0, 126.3, 126.9, 128.2, 128.4, 128.5, 138.9, 139.3, 210.2; IR (neat) 3038, 2966, 1683, 1541, 1507, 1457, 1395, 1362, 1073, 752, 698 cm^{-1}; HRMS (EI$^+$) (M$^+$), Found: *m/z* 293.1774; Calcd for $C_{20}H_{23}NO$: 293.1780.

[(2*R**,3*R**)-1-Benzyl-3-propylaziridin-2-yl](phenyl)methanone (**3d**): R_f = 0.40 (hexane/AcOEt = 4/1); an oil; ^{1}H NMR δ 0.80 (t, 3H, *J* = 7.3 Hz), 1.18–1.52 (m, 4H), 2.21 (q, 1H, *J* = 6.4 Hz), 3.08 (d, 1H, *J* = 6.9 Hz), 3.61 (d, 1H, *J* = 13.7 Hz), 3.77 (d, 1H, *J* = 13.7 Hz), 7.22–7.56 (m, 8H), 8.00 (d, 2H, *J* = 8.2 Hz); ^{13}C NMR δ 13.7, 20.6, 29.6, 47.4, 48.9, 64.1, 127.1, 128.0, 128.1, 128.3, 128.5, 133.1, 137.3, 137.9, 195.2; IR (neat) 3059, 2954, 2869, 1673, 1596, 1578, 1496, 1449, 1389, 1361, 1228, 1067, 1020, 930, 737, 700, 661 cm^{-1}; HRMS (EI$^+$) (M$^+$), Found: *m/z* 279.1621; Calcd for $C_{19}H_{21}NO$: 279.1623.

[(2*S**,3*R**)-1-Benzyl-3-propylaziridin-2-yl](phenyl)methanone (*trans*-isomer of **3d**): R_f = 0.45 (hexane/AcOEt = 4/1); an oil; NMR showed the presence of two isomers (ratio = 3.5/1), which might be a sort of diastereomers in equilibrium as depicted below.[21] Major isomer: ^{1}H NMR δ 0.86 (t, 3H, *J* = 7.3 Hz), 1.30–1.37 (m, 2H), 1.48–1.56 (m, 2H), 2.59 (dt, 1H, *J* = 2.7, 6.0 Hz), 3.40 (d, 1H, *J* = 2.7 Hz), 3.78 (d, 1H, *J* = 13.3 Hz), 3.86 (d, 1H, *J* = 13.3 Hz), 7.18–7.59 (m, 8H), 7.92–7.95 (m, 2H); ^{13}C NMR δ 13.8, 20.4, 34.9, 44.2, 48.1, 55.3, 126.9, 128.2, 128.3, 128.5, 128.6, 133.1, 138.4, 139.1, 196.1; Minor isomer: ^{1}H NMR δ 0.99 (t, 3H, *J* = 7.3 Hz), 1.47–1.91 (m, 4H), 2.66 (dt, 1H, *J* = 2.7, 7.4 Hz), 2.87 (d, 1H, *J* = 2.7 Hz), 3.72 (d, 1H, *J* = 14.2 Hz), 4.10 (d, 1H, *J* = 14.2 Hz), 7.18–7.59 (m, 8H), 7.92–7.95 (m, 2H); ^{13}C NMR δ 14.0, 21.5, 28.0, 47.6, 48.3, 127.6. 128.1, 128.4, 128.5, 133.0, 138.9, 196.6 (Three signals might be overlaped with those of major isomer); IR (neat) 3061, 2959, 2929, 2871, 1667, 1538, 1449, 1379, 1265, 1070, 1026, 695 cm^{-1}; HRMS (EI$^+$) (M$^+$), Found: *m/z* 279.1627; Calcd for $C_{19}H_{21}NO$: 279.1623.



1-Phenyl-*N*-(1-phenylhex-1-yn-3-ylidene)methanamine (**4d**): R_f = 0.20 (hexane/AcOEt = 5/1); a solid; m.p. 77–78 °C (from AcOEt/hexane); ^{1}H NMR δ 0.93 (t, 3H, *J* = 7.3 Hz), 1.57–1.68 (m, 2H), 2.55 (t, 2H, *J* = 7.8 Hz), 5.31 (s, 2H), 7.23–7.31 (m, 6 H), 7.37–7.40 (m, 2H), 7.44 (d, 2H, *J* = 7.8 Hz); ^{13}C NMR δ 13.7, 18.8, 32.4, 66.6, 82.9, 104.2, 121.5, 128.3, 128.5, 128.6, 129.3, 131.0, 133.9, 134.0; IR (KBr) 3058, 2955, 2870, 1517, 1485, 1438, 1303, 1250, 1176, 1164, 935, 759 cm^{-1}; HRMS (FAB$^+$) (M$^+$ + H), Found: *m/z* 262.1592; Calcd for $C_{19}H_{20}N$: 262.1596.

[(2*R**,3*R**)-1-Benzyl-3-cyclohexylaziridin-2-yl](phenyl)methanone (**3e**): R_f = 0.40 (hexane/AcOEt = 5/1); a solid; m.p. 113–115 °C (from hexane/EtOH); ^{1}H NMR δ 0.92–1.26 (m, 6H), 1.40–1.76 (m, 5H), 1.96 (dd, 1H, *J* = 8.7, 6.9 Hz), 3.10 (d, 1H, *J* = 6.9 Hz), 3.60 (d, 1H, *J* = 13.7 Hz), 3.73 (d, 1H, *J* = 13.7 Hz), 7.23–7.58 (m, 8H), 8.01 (d, 2H, *J* = 7.3 Hz); ^{13}C NMR δ 25.27, 25.29, 26.0, 30.2, 31.2, 35.5, 47.3, 55.1, 64.5, 127.1, 128.0, 128.17, 128.19, 128.4, 132.9, 137.3, 137.8, 195.0; IR (KBr) 3031, 2924, 2849, 1683, 1598, 1448, 1225, 1049, 1023, 915, 738, 688 cm^{-1}; Found: C, 82.72; H, 7.89; N, 4.38%; Calcd for $C_{22}H_{25}NO$: C, 82.41; H, 7.94; N, 4.42%.

1-[(2*R**,3*R**)-1-Benzyl-3-methylaziridin-2-yl]heptan-1-one (**3f**): R_f = 0.45 (hexane/AcOEt = 4/1); an oil; ^{1}H NMR δ 0.86 (t, 3H, *J* = 5.5 Hz), 1.19 (d, 3H, *J* = 5.5 Hz), 1.19–1.30 (m, 6H), 1.46–1.56 (m, 2H), 2.05 (dq, 1H, *J* = 6.9, 5.5 Hz), 2.32 (d, 1H, *J* = 6.9 Hz), 2.38–2.53 (m, 2H), 3.43 (d, 1H, *J* = 13.7 Hz), 3.69 (d, 1H, *J* = 13.7 Hz), 7.21–7.36 (m, 5H); ^{13}C NMR δ 13.3, 14.0, 22.4, 23.5, 28.9, 31.5, 42.3, 43.4, 49.1, 63.9, 127.1, 127.8, 128.3, 138.2, 207.8; IR (neat) 3030, 2956, 2928, 2858, 1699, 1496, 1454, 1413, 1354, 1142, 1121, 1073, 1030, 733, 698 cm^{-1}; HRMS (EI$^+$) (M$^+$), Found: *m/z* 259.1937; Calcd for $C_{17}H_{25}NO$: 259.1936.

Representative procedure of one-pot synthesis of 2-acylpyrrolidine 6aB starting from *N*-(propargylic)hydroxylamine 1a (Table 4, Entry 5): A mixture of *N*-(propargylic)hydroxylamine **1a** (157 mg, 0.5 mmol), $AgBF_4$ (19 mg, 0.1 mmol) and CuCl (50 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) was stirred at rt under an argon atmosphere. After 24 h, *N*-benzylmaleimide (**5B**) (112 mg, 0.6 mmol) in xylene (2 mL) was added to the reaction mixture and CH_2Cl_2 was evaporated under the reduced pressure. The resulting mixture in xylene was heated at 145 °C for 2 h and cooled to rt. The insoluble substance was filtered off through a pad of Celite and the solvent was removed under reduced pressure. The residue was purified by preparative TLC (hexane/Et_2O = 1/1) to give **6aB** (215 mg, 85% yield).

In a similar manner, other 2-acylpyrrolidines **6aA**, **6eA**, and **6bB**–**6fB** were prepared from the corresponding *N*-(propargylic)hydroxylamines **1a**–**1f**, respectively.

(3a*R**,4*R**,6*R**,6a*S**)-4-Benzoyl-5-benzyl-2-methyl-6-phenyltetrahydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (**6aA**): R_f = 0.30 (hexane/Et_2O = 1/1); a solid; m.p. 164–165 °C (from AcOEt/hexane); ^{1}H NMR δ 2.94 (s, 3H), 3.24 (d, 1H, *J* = 7.8 Hz), 3.63 (d, 1H, *J* = 13.7 Hz), 3.70 (dd, 1H, *J* = 9.6, 7.8 Hz), 3.77 (d, 1H, *J* = 13.7 Hz), 5.15 (d, 1H, *J* = 9.6 Hz), 5.24 (s, 1H), 7.04–7.12 (m, 2H), 7.19–7.22 (m, 3H), 7.29–7.41 (m, 7H), 7.56 (t, 1H, *J* = 7.3 Hz), 7.80 (dd, 2H, *J* = 8.3, 0.9 Hz); ^{13}C NMR δ 25.0, 48.5, 50.2, 51.1, 62.4, 68.2, 127.2, 128.1, 128.30, 128.31, 128.4, 128.6, 128.7, 133.8, 135.0, 137.8, 137.9, 175.7, 177.3, 200.7; IR (KBr) 3031, 2876, 1773, 1697, 1668, 1591, 1494, 1434, 1381, 1323, 1284, 1230, 1115, 1069, 1001, 870, 755, 731, 697 cm^{-1}; Found: C, 76.25; H, 5.82; N, 6.57%; Calcd for $C_{27}H_{24}N_2O_3$: C, 76.39; H, 5.70; N, 6.60%.

(3a*R**,4*R**,6*R**,6a*S**)-4-Benzoyl-2,5-dibenzyl-6-phenyltetrahydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (**6aB**): R_f = 0.35 (hexane/Et_2O = 1/1); a solid; m.p. 165–166 °C (from AcOEt/hexane); ^{1}H NMR δ 3.28 (d, 1H, *J* = 7.8 Hz), 3.56 (d, 1H, *J* = 13.7 Hz), 3.62 (dd, 1H, *J* = 9.6, 7.8 Hz), 3.67 (d, 1H, *J* = 13.7 Hz), 4.56 (d, 1H, *J* = 13.8 Hz), 4.65 (d, 1H, *J* = 13.8 Hz), 5.11 (d, 1H, *J* = 9.6 Hz), 5.19 (s, 1H), 6.93–6.97 (m, 2H), 7.02–7.12 (m, 2H), 7.13–7.27 (m, 6H), 7.37–7.46 (m, 7H), 7.55 (t, 1H, *J* = 7.3 Hz), 7.83 (d, 2H, *J* = 7.8 Hz); ^{13}C NMR δ 42.6, 48.0, 49.9, 50.5, 62.6, 68.0, 127.1, 127.8, 128.0, 128.1, 128.3, 128.35, 128.40, 128.5, 128.7, 129.4, 133.7, 135.0, 135.8, 136.9, 138.0, 175.0, 177.3, 200.3. IR (KBr) 3030, 2878, 1772, 1702, 1579, 1494, 1453, 1422, 1396, 1339, 1235, 1175, 1136, 1027, 989, 727, 699 cm^{-1}; Found: C, 79.25; H, 5.65; N, 5.63%; Calcd for $C_{33}H_{28}N_2O_3$: C, 79.18; H, 5.64; N, 5.60%. Crystal data: $C_{33}H_{28}N_2O_3$, M_r = 500.60, monoclinic, $P2_1/n$, *a* = 11.7284(8), *b* = 9.1475(5), *c* = 24.016(2) Å, *V* = 2528.7(3) Å^3, β = 101.057(2)°, *Z* = 4, D_{calcd} = 1.315 g cm^{-3}, *R* = 0.065 (R_w = 0.070) for 5599 reflections with I > 3.00σ(I) and 343 variable parameters. Crystallographic data for **6aB** have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 913503.

(3a*R**,4*R**,6*R**,6a*S**)-2,5-Dibenzyl-4-heptanoyl-6-phenyltetrahydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (**6bB**): R_f = 0.30 (hexane/AcOEt = 3/1); an oil; ^{1}H NMR δ 1.00–1.31 (m, 5H), 1.52–1.71 (m, 6H), 1.95–2.05 (m, 2H), 3.16 (d, 1H, *J* = 13.3 Hz), 3.40–3.43 (m, 2H), 3.54 (d, 1H, *J* = 6.8 Hz), 3.70 (d, 1H, *J* = 13.3 Hz), 4.68 (d, 1H, *J* = 13.7 Hz), 4.75 (d, 1H, *J* = 13.7 Hz), 4.85 (s, 1H), 6.86 (d, 2H, *J* = 6.8 Hz), 7.16–7.30 (m, 6H), 7.35 (t, 2H, *J* = 7.3 Hz), 7.42–7.47 (m, 3H), 7.51 (d, 2H, *J* = 7.4 Hz); ^{13}C NMR δ 14,0, 22.4, 23.0, 28.7, 31.5, 42.1, 42.7, 47.2, 49.8, 51.0, 66.5, 68.1, 127.4, 127.9, 128.11, 128.13, 128.50, 128.54, 128.6, 129.5, 135.8, 136.7, 138.0, 175.0, 177.1, 212.7; IR (neat) 3063, 3032, 2929, 2857, 1775, 1713, 1604, 1585, 1495, 1454, 1433, 1398, 1347, 1290, 1215, 1173, 1144, 1074, 1029, 921, 882, 832, 754, 699 cm^{-1}; HRMS (FAB$^+$) (M$^+$ + H), Found: *m/z* 509.2808; Calcd for $C_{33}H_{37}N_2O_3$: 509.2804.

(3a*R**,4*R**,6*R**,6a*S**)-2,5-Dibenzyl-4-phenyl-6-pivaloyltetrahydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (**6cB**): R_f = 0.35 (hexane/Et_2O = 1/1); a solid; m.p. 133–134 °C (from AcOEt/hexane); ^{1}H NMR δ 0.99 (s, 9H), 3.11 (d, 1H, *J* = 8.2 Hz), 3.37 (d, 1H, *J* = 15.1 Hz), 3.55 (dd, 1H, *J* = 9.6, 8.2 Hz), 3.68 (d, 1H, *J* = 15.1 Hz), 4.55 (d, 1H, *J* = 13.7 Hz), 4.62 (d, 1H, *J* = 13.7 Hz), 4.83 (s, 1H), 5.27 (d, 1H, *J* = 9.6 Hz), 6.96–7.29 (m, 10H), 7.35–7.41 (m, 3H), 7.43–7.46 (m, 2H); ^{13}C NMR δ 26.0, 42.6, 44.9, 48.3, 49.3, 50.4, 61.7, 68.4, 126.9, 127.2, 128.0, 128.1, 128.4, 128.5, 129.5, 135.8, 137.3, 138.2, 175.0, 177.0, 217.8; IR (KBr) 3037, 2977, 1774, 1702, 1493, 1477, 1436, 1394, 1343, 1215, 1172, 1136, 1062, 988, 878, 778, 753, 730, 701 cm^{-1}; Found: C, 77.35; H, 6.80; N, 5.79%; Calcd for $C_{31}H_{32}N_2O_3$: C, 77.47; H, 6.71; N, 5.83%.

(3a*R**,4*R**,6*S**,6a*S**)-4-Benzoyl-2,5-dibenzyl-6-propyltetrahydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (**6dB**): R_f = 0.30 (hexane/AcOEt = 4/1); a solid; m.p. 146–147 °C (from AcOEt/hexane); ^{1}H NMR δ 0.93 (t, 3H, *J* = 6.9 Hz), 1.33–1.42 (m, 2H), 1.67–1.81 (m, 2H), 3.25 (d, 1H, *J* = 7.8 Hz), 3.38 (t, 1H, *J* = 7.8 Hz), 3.71 (d, 1H, *J* = 14.2 Hz), 3.87–3.96 (m, 1H), 3.94 (d, 1H, *J* = 14.2 Hz), 4.69 (d, 1H, *J* = 14.2 Hz), 4.76 (d, 1H, *J* = 14.2 Hz), 4.88 (s, 1H), 6.92 (d, 2H, *J* = 6.0 Hz), 7.09–7.18 (m, 3H), 7.29–7.44 (m, 7H), 7.52 (t, 1H, *J* = 7.3 Hz), 7.84 (d, 2H, *J* = 8.2 Hz); ^{13}C NMR δ 14.4, 19.7, 31.8, 42.6, 47.1, 47.4, 50.8, 63.6, 65.0, 127.0, 127.9, 128.0, 128.4, 128.5, 128.56, 128.64, 128.7, 133.6, 134.9, 135.6, 138.8, 176.2, 177.8, 199.7; IR (KBr) 2960, 2869, 1772, 1702, 1541, 1506, 1490, 1428, 1398, 1340, 1238, 1185, 1135, 1000, 724, 702 cm^{-1}; Found: C, 77.15; H, 6.62; N, 5.96%; Calcd for $C_{30}H_{30}N_2O_3$: C, 77.23; H, 6.48; N, 6.00%.

(3a*R**,4*R**,6*S**,6a*S**)-4-Benzoyl-5-benzyl-6-cyclohexyl-2-methyltetrahydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (**6eA**): R_f = 0.40 (hexane/Et_2O = 1/1); a solid. m.p. 142–143 °C (from AcOEt/hexane); ^{1}H NMR δ 1.11–1.37 (m, 5H), 1.66–1.78 (m, 4H), 1.94–2.04 (m, 1H), 2.08–2.15 (m, 1H), 3.04 (s, 3H), 3.41–3.53 (m, 4H), 3.85 (d, 1H, *J* = 13.3 Hz), 4.97 (s, 1H), 7.10–7.14 (m, 2H), 7.21–7.27 (m, 5H), 7.43–7.49 (m, 3H); ^{13}C NMR δ 25.3, 26.2, 26.4, 26.5, 29.5, 30.0, 36.1, 47.2, 47.3, 52.2, 65.4, 69.2, 127.5, 128.3, 128.56, 128.65, 129.2, 133.1, 134.8, 137.8, 178.0, 179.0, 198.2. IR (KBr) 2922, 2851, 1769, 1697, 1593, 1432, 1381, 1337, 1277, 1230, 1189, 1131, 1094, 1048, 752, 730, 694 cm^{-1}; Found: C, 75.26; H, 7.11; N, 6.53%; Calcd for $C_{27}H_{30}N_2O_3$: C, 75.32; H, 7.02; N, 6.51%. Crystal data: $C_{27}H_{30}N_2O_3$, M_r = 430.55, monoclinic, $P2_1/c$, *a* = 8.4348(7), *b* = 21.818(2), *c* = 12.635(1) Å, *V* = 2231.4(3) Å^3, β = 106.338(2)°, *Z* = 4, D_{calcd} = 1.281 g cm^{-3}, *R* = 0.051 (R_w = 0.066) for 3690 reflections with I > 3.00σ(I) and 289 variable parameters. Crystallographic data for **6eA** have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 913504.

(3a*R**,4*R**,6*S**,6a*S**)-4-Benzoyl-2,5-benzyl-6-cyclohexyltetrahydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (**6eB**): R_f = 0.40 (hexane/Et_2O = 1/1); a solid; m.p. 161–162 °C (from AcOEt/hexane); ^{1}H NMR δ 1.01–1.31 (m, 5H), 1.62–1.71 (m, 4H), 1.88–1.96 (m, 1H), 1.98–2.15 (m, 1H), 3.16 (d, 1H, *J* = 12.8 Hz), 3.39–3.43 (m, 2H), 3.52–3.55 (m, 1H), 3.70 (d, 1H, *J* = 12.8 Hz), 4.68 (d, 1H, *J* = 13.8 Hz), 4.74 (d, 1H, *J* = 13.8 Hz), 4.85 (s, 1H), 6.87 (d, 2H, *J* = 6.4 Hz), 7.16–7.31 (m, 6H), 7.33 (t, 2H, *J* = 7.8 Hz), 7.41–7.48 (m, 1H), 7.46 (d, 2H, *J* = 7.3 Hz), 7.51 (d, 2H, *J* = 7.4 Hz); ^{13}C NMR δ 26.2, 26.3, 26.4, 29.6, 30.0, 36.0, 43.0, 47.2, 47.3, 51.8, 65.8, 69.2, 127.3, 128.2, 128.35, 128.41, 128.6, 128.7, 129.0, 129.5, 133.1, 134.75, 134.83, 138.0, 177.4, 178.6, 197.9; IR (KBr) 3038, 2933, 2853, 1774, 1705, 1673, 1577, 1494, 1396, 1343, 1227, 1172, 1142, 1073, 732, 704 cm^{-1}; Found: C, 78.25; H, 6.78; N, 5.55%; Calcd for $C_{33}H_{34}N_2O_3$: C, 78.23; H, 6.76; N, 5.53%.

(3a*R**,4*R**,6*S**,6a*S**)-2,5-Dibenzyl-4-heptanoyl-6-methyltetrahydropyrrolo[3,4-c]pyrrole-1,3(2*H*,3a*H*)-dione (**6fB**): R_f = 0.35 (hexane/Et_2O = 1/1); an oil; ^{1}H NMR δ 0.87 (t, 3H, *J* = 6.9 Hz), 1.14 (d, 3H, *J* = 6.4 Hz), 1.13–1.27 (m, 6H), 1.40–1.45 (m, 2H), 2.15 (td, 1H, *J* = 7.4, 17.4 Hz), 2.30 (td, 1H, *J* = 7.8, 17.4 Hz), 3.04 (d, 1H, *J* = 7.8 Hz), 3.24 (t, 1H, *J* = 7.8 Hz), 3.58 (d, 1H, *J* = 13.8 Hz), 3.82–3.89 (m, 1H), 3.84 (d, 1H, *J* = 13.8 Hz), 3.98 (s, 1H), 4.67 (d, 1H, *J* = 14.2 Hz), 4.72 (d, 1H, *J* = 14.2 Hz), 7.00–7.02 (m, 2H), 7.18–7.42 (m, 8H); ^{13}C NMR δ 14.0, 15.7, 22.3, 23.1, 28.7, 31.4, 41.4, 42.5, 46.5, 48.1, 50.8, 57.9, 68.2, 127.2, 127.9, 128.0, 128.39, 128.41, 128.5, 135.6, 138.4, 176.2, 177.5, 211.9; IR (neat) 3038, 2929, 2857, 1774, 1708, 1496, 1455, 1432, 1397, 1345, 1178, 1078, 732, 700 cm^{-1}; HRMS (FAB$^+$) (M$^+$ + H), Found: *m/z* 447.2640; Calcd for $C_{28}H_{35}N_2O_3$. 447.2648.

1,3-Dipolar cycloaddition of azomethine ylide generated from *trans*-isomer of 3c: A mixture of *trans*-isomer of **3c** (26 mg, 0.09 mmol) and *N*-benzylmaleimide (**5B**) (20 mg, 0.11 mmol) in xylene (0.9 mL) was heated at 145 °C for 1.5 h and cooled to rt. The solvent was removed under reduced pressure. The residue was purified by preparative TLC (hexane/AcOEt = 5/1) to give **6cB** (36 mg, 84% yield).

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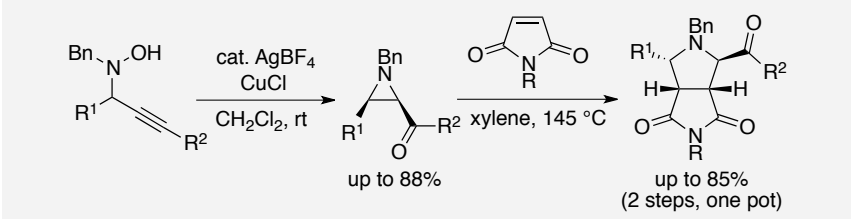
One-pot Stereoselective Syntheses of 2-Acylaziridines and 2-Acylpyrrolidines from *N*-(Propargylic)hydroxylamines



A stereoselective direct transformation of *N*-(propargylic)hydroxylamines into *cis*-2-acylaziridines was realized by the combined use of $AgBF_4$ and CuCl. The subsequent 1,3-dipolar cycloaddition of azomethine ylides generated in situ from the intermediary 2-acylaziridines with maleimides was achieved by one-pot procedure to afford the corresponding 2-acylpyrrolidines consisting of an octahydropyrrolo[3,4-*c*]pyrrole skeleton stereoselectively.