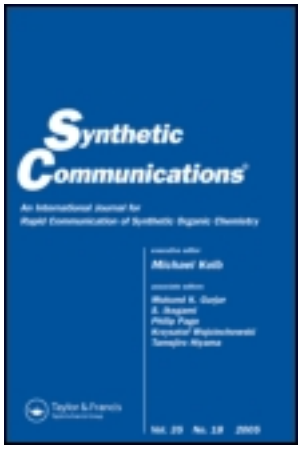

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EFFICIENT AZIRIDINATION OF α,β-UNSATURATED KETONES WITH *O*-(2,4-DINITROPHENYL)-HYDROXYLAMINE

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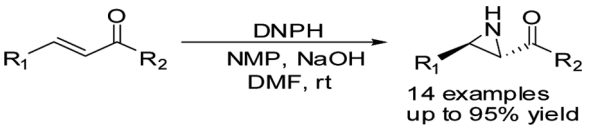
GRAPHICAL ABSTRACT



Abstract *The aziridination of* α,β*-unsaturated ketones with* O-*(2,4-dinitrophenyl)-hydroxylamine and tertiary amine was developed.* trans-*Aziridines were obtained exclusively in good yields. The reaction is proposed to occur via an aminimide intermediate.*

Keywords Aziridination; *O*-(2,4-dinitrophenyl)-hydroxylamine; α,β-unsaturated ketone

INTRODUCTION

Aziridines are important structural units in many drugs and natural products.[1] They are also valuable intermediates for the synthesis of a wide range of nitrogen-containing products.[2] A number of synthetic methods for aziridines have been developed.[3] Among them, the synthesis of *N*-unsubstituted aziridines is extremely important, considering the flexibility for further functionalization at the nitrogen atom. In 1980, Ikeda and coworkers reported the first direct aziridination of chalcones via hydrazinium salts.[4] Then Xu, Armstrong, and their coworkers improved this method with different hydrazinium salts and bases.[5,6] These reactions were assumed to proceed via the conjugate addition of the aminimide intermediates and consequent ring-closure steps.[4,5] Shi,[7] Armstrong,[8] and coworkers further developed the method by in situ combination of tertiary amines, amino transfer reagents, and bases. The hydrazinium salts generated in situ were deprotonated to provide aminimide intermediates. *O*-Mesitylenesulfonylhydroxylamine (MSH) and *O*-(diphenylphosphinyl)hydroxylamine (DPPH) were used as the amino transfer reagents (Scheme 1). However, MSH is highly unstable and requires special

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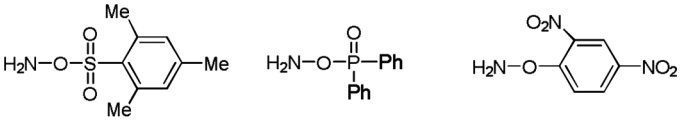
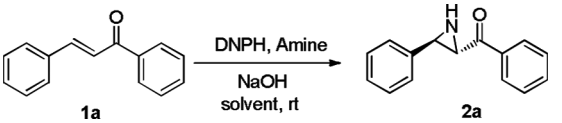


Scheme 1. Amino transfer reagents MSH, DPPH, and DNPH.

cautions.[9] DPPH is a better amino transfer reagent, but it is more expensive.[10] We speculate that *O*-(2,4-dinitrophenyl)-hydroxylamine (DNPH),[11] readily available from *N*-hydroxyphthalimide and 1-chloro-2,4-dinitrobenzene, is a cheap and stable amino transfer reagent. The application of DNPH can provide a more practical method for the aziridination of α,β-unsaturated ketones. The experiment results are reported in this article.

Initially, the aziridination of chalcone with DNPH was studied. *N*-Methylmorpholine (NMM) and NaOH were used as the tertiary amine and base respectively. A series of solvents were screened, and the results are summarized in Table 1. The reactions in less polar solvents, such as toluene, CH_2Cl_2, and tetrahydrofuran (THF), afforded **2a** in poor yields (Table 1, entries 1–3). However, the reaction in acetonitrile gave **2a** in 81% yield after 24 h (Table 1, entry 4). Further study indicated that dimethylformamide (DMF) is a better solvent. The product **2a** was obtained in 85% yield after 2.5 h (Table 1, entry 5). The importance of the tertiary amine was

Table 1. Effect of reaction solvents and tertiary amines[a]



Entry	Solvent	Amine	Time (h)	Yield[b] (%)
1	Toluene	NMM	24	16
2	CH_2Cl_2	NMM	24	38
3	THF	NMM	24	18
4	CH_3CN	NMM	24	81
5	DMF	NMM	2.5	85
6	DMF	—	24	—
7	DMF	Morpholine	24	—
8	DMF	NMP	4	72
9	DMF	Triethylamine	4	75
10	DMF	DABCO	2.5	79
11[c]	CH_3CN	NMM	4	85
12[d]	CH_3CN	NMM	9	88

[a]The reactions were carried out with chalcone (0.25 mmol), amine (0.26 mmol), DNPH (0.37 mmol), and NaOH (0.5 mmol) in solvent (4 mL) at room temperature.

[b]Isolated yield after column chromatography.

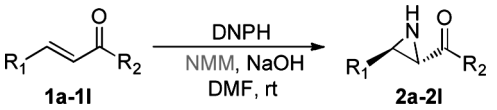
[c]MSH (2.0 equiv) was used, and the yield was reported in Ref. 7.

[d]DPPH (1.05 equiv) was used, and the yield was reported in Ref. 8a.

confirmed by the fact that no product **2a** was obtained in the absence of NMM (Table 1, entry 6). In addition, morpholine is completely ineffective (Table 1, entry 7). The results support the reaction mechanism via aminimide intermediates. Other tertiary amines are also efficient. *N*-Methylpyrrolidine (NMP), triethylamine, and 1,4-diazabicyclo[2.2.2]octane (DABCO) provided **2a** in 72–79% yields (Table 1, entries 8–10). For a comparison, the yields obtained with MSH and DPPH are also listed (Table 1, entries 11 and 12).[7,8a] Comparable yields were achieved with these three amino transfer reagents; however, less reaction time was required by DNPH.

A variety of α,β-unsaturated ketones were examined in the reaction, and the results are summarized in Table 2. In general, 4-substitutions at β-phenyl group of chalcone were tolerated very well. Good yields were achieved for 4-methyl, 4-methoxy, 4-chloro, and 4-bromo substituted chalcones (Table 2, entries 1–5); however, 4-nitro substitution significantly decreased the yield (Table 2, entry 6). 2-Chloro-substituted chalcone gave satisfactory yield (Table 2, entry 7). β-(2-Thiophenyl)- and β-1-naphthyl-α,β-unsaturated ketones afforded the corresponding aziridines in good yields (Table 2, entries 8 and 9). β-*tert*-Butyl-α,β-unsaturated ketone is applicable, but in lower yield (Table 2, entry 10). On the other hand, the substitutions at 1-phenyl group of chalcone are also tolerable (Table 2, entries 11 and 12). Actually, 4-methoxy substituted substrate **1k** provided the product in better yield. The reaction of benzylidene acetone provided complex products, from which no aziridine product was obtained (Table 2, entry 13). Methyl cinnamate was found to be unreactive in this reaction (Table 2, entry 14).

Table 2. Aziridination of α,β-unsaturated ketones[a]

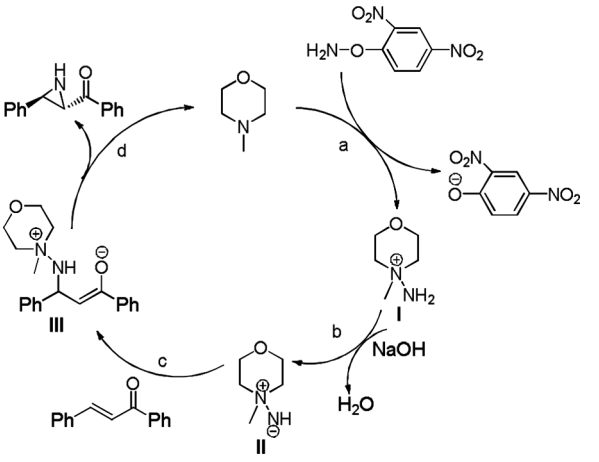


1a-1l **2a-2l**

Entry	R^1	R^2	Time (h)	Yield[b] (%)
1	**1a**, Ph	Ph	2.5	**2a**, 85
2	**1b**, 4-MePh	Ph	2.5	**2b**, 85
3	**1c**, 4-MeOPh	Ph	8	**2c**, 81
4	**1d**, 4-ClPh	Ph	2	**2d**, 83
5	**1e**, 4-BrPh	Ph	2	**2e**, 81
6	**1f**, 4-NO_2Ph	Ph	1.5	**2f**, 39
7	**1g**, 2-ClPh	Ph	2	**2g**, 80
8	**1h**, 2-Thiophenyl	Ph	3	**2h**, 78
9	**1i**, 1-Naphthyl	Ph	2	**2i**, 81
10	**1j**, *t*-Bu	Ph	7	**2j**, 65
11	**1k**, Ph	4-MeOPh	5	**2k**, 95
12	**1l**, Ph	4-ClPh	1.5	**2l**, 82
13	Ph	Me	8	—
14	Ph	OMe	8	—

[a]The reactions were carried out with chalcone (0.25 mmol), NMM (0.26 mmol), DNPH (0.37 mmol), and NaOH (0.5 mmol) in DMF (4 mL) at room temperature.

[b]Isolated yield after column chromatography.



Scheme 2. Proposed catalytic mechanism.

A catalytic mechanism is proposed (Scheme 2).[7] First, NMM reacts with DNPH to form the hydrazinium salt (**I**), which is deprotonated by NaOH to provide the aminimide (**II**). The conjugate addition of **II** to chalcone provides intermediate **III**, which undergoes an intramolecular cyclization to give the aziridine product and regenerate NMM. Although only a catalytic amount of NMM is theoretically necessary, significantly lower yields were obtained, while substoichiometric amount of NMM (such as 30 mol% or 50 mol%) was used in our study. Other side reactions of the aminimide (**II**) are supposed to account for the loss of NMM in substantial amounts during the reaction.

In conclusion, we have found that DNPH is an efficient amino transfer reagent for the aziridination of α,β-unsaturated ketones. Good yields of aziridine products were obtained for a variety of α,β-unsaturated ketones under mild reaction conditions. The present method provides a practical synthetic route for a number of *N*-unsubstituted aziridines.

EXPERIMENTAL

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance 400 spectrometer. Chemical shifts of protons are reported in parts per million downfield from TMS ($\delta = 0$). Chemical shifts of carbon are referenced to the carbon resonances of the solvent ($CHCl_3$: $\delta = 77.0$). Peaks are labeled as singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). Melting points were measured on a WRS-2A melting-point apparatus and are uncorrected. The high-resolution mass spectroscopic (HRMS) data were obtained on a Shimadazu LCMS-IT-TOF spectrometer. Infrared (IR) spectra were recorded on a Bruker Tensor 37 spectrophotometer. Data are represented as follows: frequency of absorption (cm^{-1}) and intensity of absorption (s = strong, m = medium, w = weak). Flash chromatography was performed over silica gel (230–400 mesh), purchased from Qingdao Haiyang Chemical Co., Ltd.

Commercial reagents were used as received. Analytical-grade solvents and commerically available reagents were used without further purification. DNPH was prepared according to the literature procedures.[12]

General Procedure for the Aziridination of α,β-Unsaturated Ketones with DNPH

NMM (0.26 mmol) was added to a solution of DNPH (0.38 mmol) in DMF (4 mL) at room temperature. The mixture was allowed to stir for 15 min, and then NaOH (0.5 mmol) and chalcone (0.25 mmol) were added. The mixture was stirred until the thin-layer chromatographic (TLC) analysis indicated the complete consumption of chalcone. The reaction mixture was diluted with EtOAc (30 mL) and washed with saturated brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuum. The crude mixture was purified by flash chromatography over silica gel (AcOEt/petroleum ether = 1/8) to give the aziridine product.

Phenyl(3-phenylaziridin-2-yl)methanone (2a)

White solid; mp 98–99 °C (lit. 100–101 °C[5]). IR (KBr): 3222 (m), 1660 (s), 1449 (m), 1413 (m), 1264 (s). NMR data are in agreement with reported values.[8a] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00–7.99 (m, 2H), 7.63–7.59 (m, 1H), 7.51–7.47 (m, 2H), 7.37–7.31 (m, 5H), 3.51 (dd, $J = 8.0$, 2.0 Hz, 1H), 3.18 (dd, $J = 9.2$, 2.0 Hz, 1H), 2.69–2.65 (br m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.7, 138.3, 135.9, 133.8, 128.8, 128.5, 128.3, 127.9, 126.2, 44.1, 43.5. HRMS (ESI) calcd. for $C_{15}H_{12}NO$ $(M-H)^-$: 222.0919; found: 222.0916.

Phenyl(3-*p*-tolylaziridin-2-yl)methanone (2b)

White solid; mp 106–107 °C (lit. 106–107 °C[5]). IR (KBr): 3222 (m), 1660 (s), 1449 (m), 1264 (m), 1231 (m). NMR data are in agreement with reported values.[8a] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00–7.98 (m, 2H), 7.63–7.59 (m, 1H), 7.50–7.46 (m, 2H), 7.26 (d, $J = 8.0$ Hz, 2H), 7.17 (d, $J = 8.0$ Hz, 2H), 3.49 (d, $J = 2.0$ Hz, 1H), 3.15 (d, $J = 2.4$ Hz, 1H), 2.65 (br s, 1H), 2.36 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.8, 137.7, 136.0, 135.4, 133.8, 129.2, 128.8, 128.3, 126.1, 44.2, 43.5, 21.2. HRMS (ESI) calcd. for $C_{16}H_{14}NO$ $(M-H)^-$: 236.1075; found: 236.1071.

(3-(4-Methoxyphenyl)aziridin-2-yl)(phenyl)methanone (2c)

Orange oil. IR (KBr): 3228 (m), 1660 (s), 1517 (s), 1252 (s). NMR data are in agreement with reported values.[8a] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00–7.94 (m, 2H), 7.62–7.58 (m, 1H), 7.49–7.45 (m, 1H), 7.30–7.25 (m, 2H), 6.90–6.88 (m, 2H), 3.80 (s, 3H), 3.47 (d, $J = 2.0$ Hz, 1H), 3.13 (d, $J = 1.6$ Hz, 1H), 2.67 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.7, 159.4, 135.9, 133.7, 130.4, 128.8, 128.3, 127.3, 114.0, 55.3, 44.1, 43.3. HRMS (ESI) calcd. for $C_{16}H_{14}NO_2$ $(M-H)^-$: 252.1025; found: 252.1019.

(3-(4-Chlorophenyl)aziridin-2-yl)(phenyl)methanone (2d)

Pale yellow solid; mp 88–89 °C (lit. 88–89 °C[5]). IR (KBr): 3221 (m), 1658 (s), 1492 (m), 1267 (s). NMR data are in agreement with reported values.[7] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00–7.97 (m, 2H), 7.65–7.60 (m, 1H), 7.52–7.48 (m, 2H), 7.35–7.29 (m, 4H), 3.46 (d, $J = 2.4$ Hz, 1H), 3 (d, $J = 2.0$ Hz, 1H), 2.67 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.4, 136.9, 135.8, 133.9, 133.7, 128.9, 128.7, 128.3, 128.0, 44.1, 42.8. HRMS (ESI) calcd. for $C_{15}H_{11}NOCl$ $(M\ H)^-$: 256.0529; found: 256.0520.

(3-(4-Bromophenyl)aziridin-2-yl)(phenyl)methanone (2e)

White solid; mp 109–111 °C (lit. 110–111 °C[5]). IR (KBr): 3219 (m), 1660 (s), 1596 (w), 1388 (m), 1268 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99–7.97 (m, 2H), 7.65–7.60 (m, 1H), 7.52–7.47 (m, 4H), 7.26–7.24 (m, 2H), 3.46–3.45 (m, 1H), 3.14–3.13 (m, 1H), 2.67 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.4, 137.4, 135.8, 133.9, 131.7, 128.9, 128.3, 127.9, 121.8, 44.1, 42.8. HRMS (ESI) calcd. for $C_{15}H_{11}NOBr$ $(M - H)^-$: 300.0024; found: 300.0014.

(3-(4-Nitrophenyl)aziridin-2-yl)(phenyl)methanone (2f)

Yellow solid; mp 131–132 °C (lit. 142–143 °C[5]). IR (KBr): 3264 (m), 1662 (s), 1599 (m), 1515 (s), 1344 (m). NMR data are in agreement with reported values.[7] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23–8.21 (m, 2H), 8.00–7.98 (m, 2H), 7.67–7.63 (m, 1H), 7.56–7.50 (m, 4H), 3.52 (dd, $J = 8.0$, 2.0 Hz, 1H), 3.27 (dd, $J = 9.2$, 2.0 Hz, 1H), 2.80–2.76 (br m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.8, 147.6, 145..8, 135.6, 134.2, 129.0, 128.3, 127.1, 123.8, 44.2, 42.3. HRMS (ESI) calcd. for $C_{15}H_{11}N_2O_3$ $(M - H)^-$: 267.0770; found: 267.0767.

(3-(2-Chlorophenyl)aziridin-2-yl)(phenyl)methanone (2g)

Pale yellow solid; mp 91–92 °C (lit. 92–94[5]). IR (KBr): 3197 (m), 1666 (s), 1598 (w), 1417 (m), 1385 (m), 1228 (m). NMR data are in agreement with reported values.[7] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07–8.06 (m, 2H), 7.65–7.61 (m, 1H), 7.56–7.49 (m, 3H), 7.37 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.32–7.24 (m, 2H), 3.46 (d, $J = 1.6$ Hz, 1H), 3.40 (d, $J = 2.0$ Hz, 1H), 2.62 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.9, 136.0, 135.8, 134.2, 133.9, 129.1, 128.9, 128.8, 128.5, 127.6, 127.0, 42.8, 41.5. HRMS (ESI) calcd. for $C_{15}H_{11}NOCl$ $(M - H)^-$: 256.0529; found: 256.0522.

Phenyl(3-(thiophen-2-yl)aziridin-2-yl)methanone (2h)

White solid; mp 108–110 °C. IR (KBr): 3207 (m), 1661 (s), 1449 (m), 1399 (m), 1261 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03–8.01 (m, 2H), 7.65–7.61 (m, 1H), 7.53–7.49 (m, 2H), 7.23 (dd, $J = 5.2$, 0.8 Hz, 1H), 7.10 (dd, $J = 3.2$, 0.4 Hz, 1H), 6.99 (dd, $J = 5.2$, 3.6 Hz, 1H), 3.62 (dd, $J = 8.0$, 2.4 Hz, 1H), 3.41 (dd, $J = 9.2$, 2.0 Hz, 1H), 2.81–2.76 (br m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.1, 143.1,

135.8, 133.9, 128.9, 128.4, 127.2, 125.3, 124.5, 44.9, 40.0. HRMS (ESI) calcd. for $C_{13}H_{10}NOS$ $(M-H)^-$: 228.0483; found: 228.0487.

(3-(Naphthalen-1-yl)aziridin-2-yl)(phenyl)methanone (2i)

Pale yellow solid; mp 146–147 °C (lit. 148–150 °C[8a]). IR (KBr): 3253 (m), 1663 (s), 1595 (m), 1450 (s), 1261 (s). NMR data are in agreement with reported values.[8a] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07–8.05 (m, 2H), 8.01 (d, $J = 8.4$ Hz, 1H), 7.91 (d, $J = 8.0$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.76 (d, $J = 7.2$ Hz, 1H), 7.63 (t, $J = 6.8$ Hz, 1H), 7.61–7.42 (m, 5H), 3.78–3.76 (m, 1H), 3.54–3.53 (m, 1H), 2.72 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.2, 135.9, 134.0, 133.9, 133.4, 131.9, 128.9, 128.8, 128.5, 128.2, 126.4, 125.9, 125.7, 123.9, 122.7, 43.1, 41.9. HRMS (ESI) calcd. for $C_{19}H_{16}NO$ $(M+H)^+$: 274.1232; found: 274.1228.

(3-*tert*-Butylaziridin-2yl)(phenyl)methanone (2j)

Yellow solid; mp 59–61 °C. IR (KBr): 3264 (m), 2956 (s), 1660 (s), 1596 (w), 1450 (m), 1229 (m). NMR data are in agreement with reported values.[13] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04–8.00 (m, 2H), 7.64–7.60 (m, 1H), 7.53–7.27 (m, 2H), 3.37 (s, 1H), 2.04–1.92(m, 2H), 0.99 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 136.1, 133.5, 128.8, 128.1, 52.6, 36.7, 31.3, 26.7. HRMS (ESI) calcd. for $C_{13}H_{16}NO$ $(M-H)^-$: 202.1232; found: 202.1239.

(4-Methoxyphenyl)(3-phenylaziridin-2-yl)methanone (2k)

White solid; mp 50–51 °C (lit. 50–51 °C[8a]). IR (KBr): 3236 (m), 1650 (s), 1608 (s), 1454 (m), 1260 (s). NMR data are in agreement with reported values.[8a] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, $J = 8.8$ Hz, 2H), 7.37–7.29 (m, 5H), 6.94 (d, $J = 9.2$ Hz, 2H), 3.86 (s, 3H), 3.46 (d, $J = 2.0$ Hz, 1H), 3.14 (d, $J = 2.0$ Hz, 1H), 2.68 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.8, 164.1, 138.5, 130.6, 128.9, 128.5, 127.7, 126.1, 114.0, 55.5, 43.6, 43.0. HRMS (ESI) calcd. for $C_{16}H_{14}NO_2$ $(M-H;)^-$: 252.1025; found: 252.1027.

(4-Chlorophenyl)(3-phenylaziridin-2-yl)methanone (2l)

Pale yellow solid; mp 75–76 °C (lit. 76–78 °C[5]). IR (KBr): 3245 (m), 1660 (s), 1590 (s), 1354 (s), 1229 (s). NMR data are in agreement with reported values.[8a] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, $J = 8.4$ Hz, 2H), 7.45 (d, $J = 8.4$ Hz, 2H), 7.37–7.31 (m, 5H), 3.45 (s, 1H), 3.18 (s, 1H), 2.67 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.5, 140.3, 138.1, 134.2, 129.7, 129.1, 128.6, 127.9, 126.1, 44.0, 43.7. HRMS (ESI) calcd. for $C_{15}H_{11}NOCl$ $(M-H;)^-$: 256.0529; found: 256.0533.

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REFERENCES

1. Sweeney, J. B. Aziridines: Epoxides' ugly cousins? *Chem. Soc. Rev.* **2002**, *31*, 247–258.
2. (a) Hu, X. E. Nucleophilic ring opening of aziridines. *Tetrahedron* **2004**, *60*, 2701–2743; (b) McCoull, M.; Davis, F. A. Recent synthetic applications of chiral aziridines. *Synthesis* **2000**, 1347–1365; (c) Zwanenburg, B.; Holte, P. T. The synthetic potential of three-membered ring aza-heterocycles. *Top. Curr. Chem.* **2001**, *216*, 93–124; (d) Lu, P. F. Recent developments in regioselective ring opening of aziridines. *Tetrahedron* **2010**, *66*, 2549–2560.
3. (a) Halfen, J. A. Recent advances in metal-mediated carbon–nitrogen bond-formation reactions: Aziridination and amidation. *Curr. Org. Chem.* **2005**, *9*, 657–659; (b) Muller, P.; Fruit, C. Enantioselective catalytic aziridinations and asymmetric nitrene insertions into C-H bonds. *Chem. Rev.* **2003**, *103*, 2905–2920; (c) Osborn, H. M. I.; Sweeney, J. B. The asymmetric synthesis of aziridines. *Tetrahedron: Asymmetry* **1997**, *8*, 1693–1715.
4. Ikeda, I.; Machii, Y.; Okahara, M. Direct imination of chalcones with aminimide: Formation of aziridines. *Synthesis* **1980**, 650–651.
5. Xu, J. X.; Jiao, P. Direct NH-aziridination of α,β-unsaturated ketones. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1491–1493.
6. Armstrong, A.; Carbery, D. R.; Lamont, S. G.; Pape, A. R.; Wincewicz, R. N-Amino-N-methylmorpholinium salts: Highly active aziridination reagents for chalcones. *Synlett* **2006**, 2504–2506.
7. Shen, Y. M.; Zhao, M. X.; Xu, J. X.; Shi, Y. An amine-promoted aziridination of chalcones. *Angew. Chem. Int. Ed.* **2006**, *45*, 8005–8008.
8. (a) Armstrong, A.; Baxter, C. A.; Lamont, S. G.; Pape, A. R.; Wincewicz, R. Amine-promoted, organocatalytic aziridination of enones. *Org. Lett.* **2007**, *9*, 351–353; (b) Armstrong, A.; Pullin, R. D. C.; Jenner, C. R.; Scutt, J. N. Amine-promoted synthesis of vinyl aziridines. *J. Org. Chem.* **2010**, *75*, 3499–3502.
9. (a) Johnson, C. R.; Kirchhoff, R. A.; Corkins, H. G. Chemistry of sulfoxides and related compounds, XLIX: Synthesis of optically active sulfoximines from optically active sulfoxides. *J. Org. Chem.* **1974**, *39*, 2458–2459 (b) Tamura, Y.; Minamikawa, J.; Sumoto, K.; Fujii, S.; Ikeda, M. Synthesis and some properties of O-acyl-and O-nitrophenylhydroxylamines. *J. Org. Chem.* **1973**, *38*, 1239–1241.
10. (a) Harger, M. J. P. O-(Diphenylphosphinyl)hydroxylamine: Preparation and some characteristic chemical reactions. *J. Chem. Soc., Perkin. Trans. 1* **1981**, 3284–3288; (b) Colvin, E. W.; Kirby, G. W.; Wilson, A. C. (Diphenylphosphinyl)hydroxylamine: A new reagent for electrophilic amination. *Tetrahedron Lett.* **1982**, *23*, 3835–3836; (c) Kloetzer, W.; Baldinger, H; Karpitschka, E. M.; Knoflach, J. O-Diphenylphosphinylhydroxylamine (DPH), ein elektrophiles N-Aminierungsmittel. *Synthesis* **1982**, 592–594.
11. (a) Erdik, E.; Ay, M. Electrophilic amination of carbanions. *Chem. Rev.* **1989**, *89*, 1947–1980; (b) Radhakrishna, A. S.; Loudon, G. M.; Miller, M. J. Amination of ester enolates with O-(2,4-dinitrophenyl)hydroxylamine. *J. Org. Chem.* **1979**, *44*, 4836–4841.
12. Legault, C.; Charette, A. B. Highly efficient synthesis of O-(2,4-dinitrophenyl)hydroxylamine. Application to the synthesis of substituted N-benzoyliminopyridinium ylides. *J. Org. Chem.* **2003**, *68*, 7119–7122.
13. Chen, G.; Sasaki, M.; Yudin, A. K. Facile preparation of allyl amines and pyrazoles by hydrazinolysis of 2-ketoaziridines. *Tetrahedron Lett.* **2006**, *47*, 255–259.