ChemPubSoc Europe

DOI: 10.1002/ejoc.201600589

EurJOC European Journal of Organic Chemistry

Full Paper

Aminochlorination

A General $CuCl_2$-Promoted Alkene Aminochlorination Reaction

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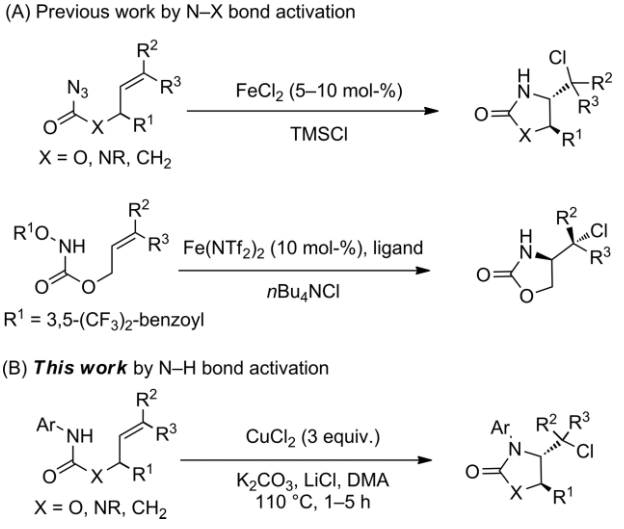
Abstract: A $CuCl_2$-promoted alkene aminochlorination reaction has been developed. A variety of anilides that contain a mono-, di-, or trisubstituted alkenyl moiety readily participated in this reaction to afford structurally diverse vicinal chloroamines. Studies suggest that the process proceeds by a radical-type mechanism and that $CuCl_2$ serves as both the oxidant to generate the amidyl radical as well as the chloride source.

Introduction

Cyclic vicinal chloroamines, which are found in a number of bioactive compounds and natural products, are versatile synthetic intermediates.[1] Among the many methods that have been developed to access these important structures, transition-metal-mediated intramolecular aminochlorinations of alkenes have attracted much attention.[2] These reactions typically proceed by an aminometallation step and subsequent cleavage of the carbon–metal bond by using a halide source to form the C–Cl bond.[2] Aminometallation reactions are sensitive to the steric hindrance of the alkene, and the organometallic intermediate that is derived from this process is usually prone to a β-hydride elimination.[3] Hence, many of the reported methods are limited to terminal alkenes.[4] The development of a chloroamination method that is applicable to a wide range of unactivated internal alkenes is of importance. In this context, Bach reported the versatile iron-catalyzed radical aminochlorination of a variety of alkenes and alkynes by starting from unstable acyl azides (Scheme 1A, top).[5] Recently, Xu reported an enantioselective aminochlorination of hydroxylamine derivatives, which is applicable to a host of internal alkenes (Scheme 1A, bottom).[6]

The oxidative cleavage of N–H bonds has recently been demonstrated as an attractive method for the generation of amidyl radicals.[7] Many chemical, photochemical, and electrochemical methods have been developed.[8] However, a general and efficient aminochlorination reaction that takes advantage of this radical-generating strategy remains elusive.[9] With our continued interest in the development of new amidyl radical-mediated reactions,[8j–8m] we report herein a simple but efficient $CuCl_2$-promoted radical aminochlorination reaction that employs stable and readily available anilides as the substrates



Scheme 1. Aminochlorination of unactivated internal alkenes (TMS = trimethylsilyl, Tf = trifluoromethanesulfonyl, DMA = *N*,*N*-dimethylacetamide).

(Scheme 1B). A variety of mono-, di-, and trisubstituted alkenes have participated in this reaction to afford structurally diverse vicinal chloroamines.

Results and Discussion

Carbamate **1a**, which contains a *p*-methoxyphenyl (PMP) group, was chosen as the model substrate to optimize the reaction. After extensive experimentation, the optimum conditions were determined to involve the treatment of **1a** with $CuCl_2$ (3 equiv.) in *N*,*N*-dimethylacetamide in the presence of K_2CO_3 and LiCl at 110 °C for 1 h. Under these conditions, the desired chloroamine **2a** was isolated in 85 % yield (Table 1, Entry 1). The use of $CuCl_2$ and a base were critical to the success of the reaction (Table 1, Entries 2 and 3). The additive LiCl, however, was not essential, but its omission let to a reduced yield (Table 1, Entry 4). Other bases such as Na_2CO_3 and KO*t*Bu as well as other solvents such as *N*,*N*-dimethylformamide (DMF) and MeCN were found to be less effective (Table 1, Entries 5–8, respectively). Finally, we

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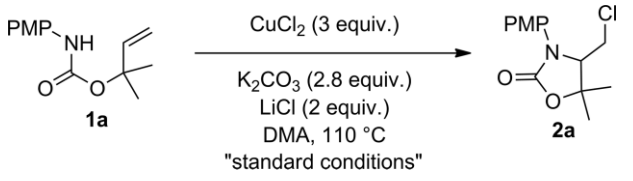
demonstrated that the reaction could be carried out on a gram scale without difficulty (Table 1, Entry 9).

Table 1. Optimization of reaction conditions.[a]



Entry	Deviation from standard conditions	Yield [%][b]
1	none	85
2	no $CuCl_2$	0
3	no K_2CO_3	trace
4	no LiCl	76
5	Na_2CO_3 instead of K_2CO_3	80
6	KO*t*Bu instead of K_2CO_3	63
7	DMF instead of DMA	65
8	MeCN instead of DMA	n.r.[c]
9	5.2 mmol (1.2 g) of **1a** instead of 0.3 mmol	84

[a] Reagents and conditions: **1a** (0.3 mmol), $CuCl_2$ (0.9 mmol), K_2CO_3 (0.84 mmol), DMA (3 mL), 110 C, 1 h. [b] Isolated yield. [c] n.r. = no reaction.

The scope of the chloroamination reaction was then explored. We were pleased to find that the reaction was not limited to terminal alkenes, as a host of di- and trisubstituted alkenes readily participated in the reaction (Table 2). Moreover, the reaction was flexible with regard to the linking tether, and a variety of allylic carbamates (Table 2, Entries 1–9), ureas (Table 2, Entries 10–12), and unsaturated amides (Table 2, Entries 13 and 14) were viable substrates. In terms of diastereoselectivity, the reactions with acyclic alkenes were not selective (Table 2, Entries 1 and 3), with the exception of those carried out with styrenyl substrates (Table 2, Entries 2 and 13), which afforded moderate to good diastereoselectivities. In contrast, the cyclic alkenes were difunctionalized with high stereochemical control to afford a variety of *cis*-fused rings and spirocyclic chloroamine derivatives with the *anti* configuration in high yields (Table 2, Entries 6–9, 11, 12 and 14).[8j] The *trans* configuration of **2g** was determined by single-crystal X-ray diffraction analysis (Figure 1) and different from that obtained by using acyl azides.[5] Although the chlorination step was not selective for the 1,2-disubstituted acyclic alkenes, the cyclization step of *cis*-alkenes **1f** and **1k** (Table 2, Entries 5 and 10, respectively) afforded only *trans*-configured five-membered heterocyclic compounds.[8l]

Since functionalized anilines are of importance in medicinal chemistry,[10] we explored the effect of the electronic properties of the *N*-aryl group on the difunctionalization reaction (Scheme 2). The copper-promoted reaction tolerated electronically diverse substituents on the *N*-aryl group, including the extremely electron-withdrawing nitro group. These results encouraged us to examine the use of a sulfonamide as the nitrogen-containing nucleophile. We were pleased to find that the aminochlorination of sulfonamide **5** proceeded in high yield. To the best of our knowledge, a chloroamination reaction that tolerates the use of both anilides and sulfonamides as the nucleophile has not been reported.

Table 2. Scope of alkenes in the aminochlorination reaction.[a]

Entry	Substrate	Product	*t* [h]	Yield [%],[b] *dr*[c]
1	**1b**, R = *n*Pr	**2b**	3	95, 1:1
2	**1c**, R = Ph	**2c**	3	94, 3.5:1
3	**1d**	**2d**	3	87, 1:1
4	**1e**	**2e**	1	89, NA
5	**1f**	**2f**	1	93, 1.3:1
6	**1g**	**2g**	3	86, >20:1
7	**1h**	**2h**	3	73, >20:1
8	**1i**	**2i**	3.5	67, >20:1
9	**1j**	**2j**	3.5	75, >20:1
10	**1k**	**2k**	1	95, 1:1
11	**1l**, R = Ph	**2l**	3	72, >20:1
12	**1m**, R = Bn	**2m**	3	59, >20:1
13	**1n**	**2n**	3	89, 9:1
14	**1o**	**2o**	3	85, >20:1

[a] Reagents and conditions: **1** (0.3 mmol), $CuCl_2$ (0.9 mmol), K_2CO_3 (0.84 mmol), LiCl (0.3 mmol), DMA (3 mL), 110 °C. [b] Isolated yield. [c] Diastereomeric ratio (*dr*) was determined by ^1H NMR analysis of the crude reaction mixture. In general, the isomers were separable by silica gel column chromatography.

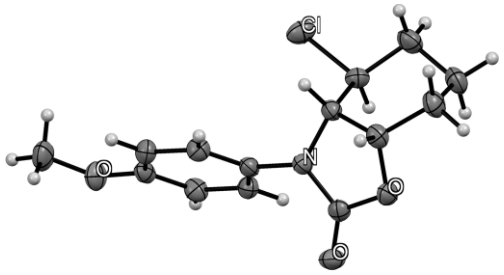
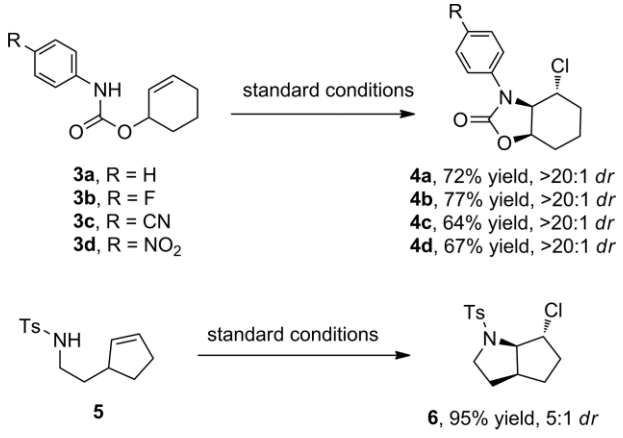


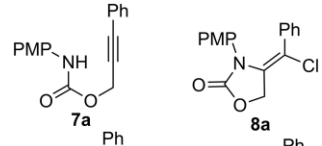
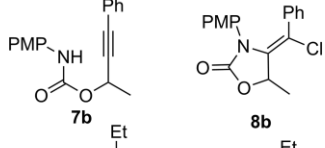
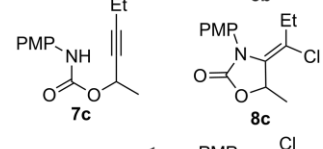
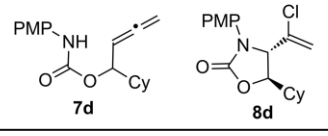
Figure 1. ORTEP representation of **2g** (thermal ellipsoids are shown at 50 % probability).



Scheme 2. Scope of N-nucleophiles (Ts = *para*-tolylsulfonyl).

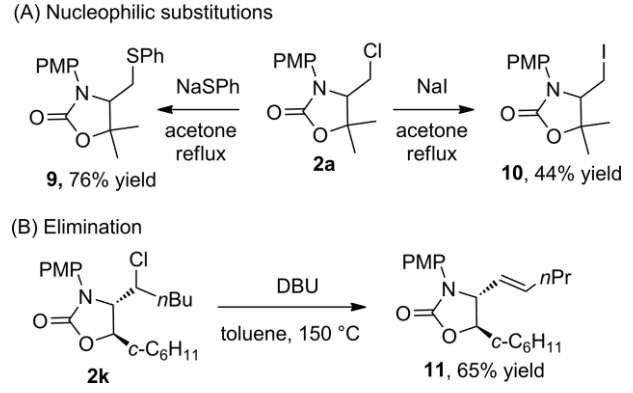
Further investigations revealed that the current protocol could be applied to the aminochlorination of alkynes[11,12] and allenes[13] (Table 3), which demonstrates the broad applicability of this simple aminochlorination protocol. The reactions of the alkynes afforded tetrasubstituted alkenes with the (*E*) configuration, for the most part, as assigned by NOESY experiments.

Table 3. Alkyne and allene aminochlorination.[a]

Entry	Product	*t* [h]	Yield [%]	(*E*)/(*Z*)[c]
1		3	92	14:1
2		3	78	15:1
3		3	81	9:1
4		5	82	1.5:1 (*dr*)

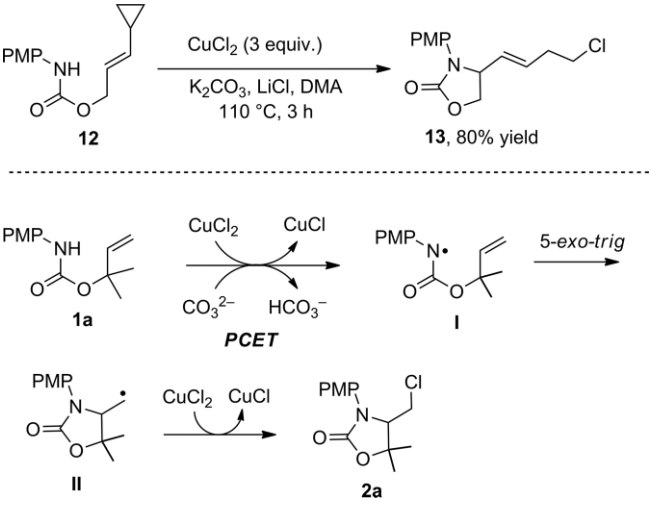
[a] Reagents and conditions: substrate (0.3 mmol), $CuCl_2$ (0.9 mmol), K_2CO_3 (0.84 mmol), LiCl (0.3 mmol), DMA (3 mL), 110 °C. [b] Isolated yield. [c] Determined by ^1H NMR analysis of the crude reaction mixture.

Notably, the C–Cl bond in the aminochlorination product can be converted into other important functional groups such as a thioether or an iodide by nucleophilic substitution reactions or an alkene through a 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) promoted regioselective elimination (Scheme 3).



Scheme 3. Transformations of aminochlorination products.

To probe the reaction mechanism, the radical clock substrate **12** was subjected to the standard conditions (Scheme 4, top)[14] to afford the ring-opening product **13** in 80 % yield, which suggests the involvement of a carbon-centered radical. This radical intermediate could be formed by cyclization of an amidyl radical or a sequence that involves alkene aminocupration and homolysis of the thus formed C–Cu bond.[3b] Considering that alkene aminocupration is usually difficult with sterically hindered alkenes[3b] and the broad tolerance of the current process to alkene substitutions, we believe that the copper-mediated aminochlorination most likely proceeds through a radical cyclization to form the C–N bond.[8k]



Scheme 4. Mechanistic studies and rationale (PCET = proton-coupled electron transfer).

A plausible mechanism was then proposed (Scheme 4, bottom). First, the proton-coupled electron transfer[8f] from *N*-arylcarbamate **1a** to $CuCl_2$ is assisted by the carbonate base to generate amidyl radical **I**.[15] Cyclization of the nitrogen-cen-

tered radical in a 5-*exo*-*trig* manner and the subsequent trapping of carbon-centered radical **II** by $CuCl_2$ then furnishes chloroamine **2a**.[16]

Conclusions

A general aminochlorination reaction that uses $CuCl_2$ as the oxidant and chloride source has been developed. The radical nature of this process allows for the participation of a variety of C–C multiple bonds, including those of alkenes, alkynes, and allenes. The reaction is operationally simple, scalable and provides convenient access to a diverse range of vicinal chloroamines.

Experimental Section

General Procedure for the Copper-Promoted Aminochlorination Reaction: The substrate (0.3 mmol, 1 equiv.), $CuCl_2$ (0.9 mmol, 3 equiv.), K_2CO_3 (0.84 mmol, 2.8 equiv.), and LiCl (0.6 mmol, 2 equiv.) were placed in a 10 mL round-bottomed flask. The flask was flushed with argon, and DMA (3 mL) was added. The resulting mixture was heated in an oil bath that was set at 110 °C until there was complete consumption of the starting material (progress monitored by TLC and ^{1}H NMR analysis). The reaction mixture was cooled to room temperature. Water (50 mL) and ethyl acetate (50 mL) were added, and the mixture was transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with ethyl acetate (2 × 50 mL). The combined organic phases were washed with brine (50 mL), dried with anhydrous $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure. The residue was then purified by chromatography on a silica gel column (hexane/ethyl acetate) to give the product.

4-(Chloromethyl)-3-(4-methoxyphenyl)-5,5-dimethyloxazolidin-2-one (2a): White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.24 (m, 2 H), 7.00–6.83 (m, 2 H), 4.11 (dd, *J* = 7.3, 3.3 Hz, 1 H), 3.80 (s, 3 H), 3.62–3.50 (m, 2 H), 1.61 (d, *J* = 5.2 Hz, 6 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.2, 155.1, 129.0, 125.6, 114.8, 79.9, 66.5, 55.6, 40.5, 29.2, 21.4 ppm. IR (neat): $\tilde{\nu}$ = 2974, 1747, 1514, 1250, 1112, 832, 758 cm^{-1}. HRMS (ESI): calcd. for [M + Na]$^+$ 292.0711; found 292.0715.

4-(1-Chlorobutyl)-3-(4-methoxyphenyl)oxazolidin-2-one (2b): Two separable diastereomers were obtained (isomer 1/isomer 2, 1:1). Data for isomer 1 of **2b**: White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.22 (m, 2 H), 6.89–6.81 (m, 2 H), 4.65–4.59 (m, 1 H), 4.47–4.36 (m, 2 H), 3.91 (dt, *J* = 10.0, 3.3 Hz, 1 H), 3.73 (s, 3 H), 1.61–1.47 (m, 3 H), 1.23–1.12 (m, 1 H), 0.75 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.9, 156.1, 128.8, 124.5, 114.8, 63.4, 60.7, 56.0, 55.6, 32.2, 19.6, 13.4 ppm. IR (neat): $\tilde{\nu}$ = 2961, 1751, 1514, 1406, 1250, 1032, 832, 756 cm^{-1}. HRMS (ESI): calcd. for [M + Na]$^+$ 306.0873; found 306.0870. Data for isomer 2 of **2b**: White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.25 (m, 2 H), 6.98–6.87 (m, 2 H), 4.52–4.41 (m, 3 H), 4.06–3.93 (m, 1 H), 3.81 (s, 3 H), 1.63–1.50 (m, 3 H), 1.44–1.28 (m, 1 H), 0.89 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.4, 156.5, 128.3, 126.4, 114.8, 62.6, 61.3, 60.9, 55.6, 35.6, 19.9, 13.5 ppm. IR (neat): $\tilde{\nu}$ = 2962, 1755, 1514, 1250, 1138, 1031, 832, 755 cm^{-1}. HRMS (ESI): calcd. for [M + Na]$^+$ 306.0873; found 306.0870.

4-[Chloro(phenyl)methyl]-3-(4-methoxyphenyl)oxazolidin-2-one (2c): Two separable diastereomers were obtained (isomer 1/isomer 2, 1:3.5). Data for isomer 1 of **2c**: White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43–7.38 (m, 2 H), 7.37–7.30 (m, 3 H), 7.24–7.20 (m, 2 H), 6.99–6.93 (m, 2 H), 5.15 (d, *J* = 4.0 Hz, 1 H), 4.98–4.93 (m, 1 H), 4.53 (dd, *J* = 9.6, 3.7 Hz, 1 H), 4.46 (t, *J* = 9.1 Hz, 1 H), 3.84 (s, 3 H ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 157.4, 155.3, 134.1, 129.5 (2 signals), 128.8, 127.8, 123.3, 114.8, 62.7, 61.5, 59.6, 55.7 ppm. IR (neat): $\tilde{\nu}$ = 2933, 1756, 1514, 1250, 1131, 830, 701 cm^{-1}. HRMS (ESI): calcd. for [M + Na]$^+$ 340.0716; found 340.0714. Data for isomer 2 of **2c**: White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.27 (m, 7 H), 6.98–6.91 (m, 2 H), 5.11 (d, *J* = 3.2 Hz, 1 H), 4.68 (ddd, *J* = 8.8, 4.8, 3.2 Hz, 1 H), 4.60 (dd, *J* = 9.2, 4.8 Hz, 1 H), 4.34 (t, *J* = 9.0 Hz, 1 H), 3.83 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.5, 156.4, 135.8, 129.1 (2 signals), 128.3, 127.2, 126.3, 115.0, 63.0, 62.7, 61.6, 55.7 ppm. IR (neat): $\tilde{\nu}$ = 2916, 1756, 1514, 1250, 1133, 1030, 832, 700 cm^{-1}. HRMS (ESI): calcd. for [M + Na]$^+$ 340.0716; found 340.0713.

4-(1-Chloropropyl)-3-(4-methoxyphenyl)oxazolidin-2-one (2d): Two separable diastereomers were obtained (isomer 1/isomer 2, 1:1). Data for isomer 1 of **2d**: White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39–7.30 (m, 2 H), 6.99–6.87 (m, 2 H), 4.70 (dt, *J* = 8.6, 3.8 Hz, 1 H), 4.53 (dd, *J* = 18.1, 8.6 Hz, 1 H), 4.46 (dd, *J* = 9.5, 4.1 Hz, 1 H), 3.90 (dt, *J* = 11.3, 3.0 Hz, 1 H), 3.81 (s, 3 H), 1.83–1.74 (m, 1 H), 1.62–1.53 (m, 1 H), 1.00 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 158.0, 156.1, 129.0, 124.5, 114.9, 63.5, 62.5, 60.8, 55.6, 23.9, 11.3 ppm. IR (neat): $\tilde{\nu}$ = 2971, 1755, 1514, 1250, 1130, 1036, 832, 755 cm^{-1}. HRMS (ESI): calcd. for [M + Na]$^+$ 292.0716; found 292.0711. Data for isomer 2 of **2d**: White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36–7.27 (m, 2 H), 6.99–6.86 (m, 2 H), 4.51–4.36 (m, 3 H), 3.93–3.89 (m, 1 H), 3.81 (s, 3 H), 1.69–1.54 (m, 2 H), 1.02 (t, *J* = 7.3 Hz, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 158.5, 156.5, 128.4, 126.5, 114.9, 62.9, 62.7, 61.3, 55.6, 27.1, 11.3 ppm. IR (neat): $\tilde{\nu}$ = 2971, 1755, 1514, 1250, 1139, 1026, 833, 754 cm^{-1}. HRMS (ESI): calcd. for [M + Na]$^+$ 292.0716; found 292.0709.

4-(2-Chloropropan-2-yl)-3-(4-methoxyphenyl)oxazolidin-2-one (2e): White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.21 (m, 2 H), 7.01–6.80 (m, 2 H), 4.60–4.45 (m, 3 H), 3.80 (s, 3 H), 1.50 (s, 3 H), 1.32 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.2, 157.0, 130.6, 126.2, 114.7, 70.7, 65.6, 65.1, 55.5, 31.2, 26.2 ppm. IR (neat): $\tilde{\nu}$ = 2954, 1737, 1516, 1248, 1135, 824 cm^{-1}. HRMS (ESI): calcd. for [M + Na]$^+$ 292.0716; found 292.0710.

4-(1-Chloropentyl)-5-cyclohexyl-3-(4-methoxyphenyl)oxazolidin-2-one (2f): Two separable diastereomers were obtained (isomer 1/isomer 2, 1.3:1). Data for isomer 1 of **2f**: White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38–7.31 (m, 2 H), 6.96–6.89 (m, 2 H), 4.36–4.33 (m, 2 H), 3.95 (dt, *J* = 11.0, 2.5 Hz, 1 H), 3.81 (s, 3 H), 1.91–1.77 (m, 4 H), 1.76–1.50 (m, 5 H), 1.31–1.15 (m, 8 H), 0.84 (t, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 157.8, 155.8, 129.0, 124.3, 114.8, 78.4, 63.4, 60.7, 55.6, 42.8, 30.3, 28.7, 28.1, 26.6, 26.2, 25.9, 25.7, 22.0, 13.9 ppm. IR (neat): $\tilde{\nu}$ = 2929, 2855, 1752, 1514, 1249, 1135, 831, 624 cm^{-1}. HRMS (ESI): calcd. for [M + Na]$^+$ 402.1806; found 402.1806. Data for isomer 2 of **2f**: White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34–7.30 (m, 2 H), 6.95–6.91 (m, 2 H), 4.36–4.33 (m, 1 H), 4.08 (t, *J* = 2.7 Hz, 1 H), 3.97–3.91 (m, 1 H), 3.81 (s, 3 H), 1.92–1.70 (m, 7 H), 1.58–1.51 (m, 3 H), 1.31–1.24 (m, 7 H), 0.88 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 158.3, 156.1, 128.6, 126.1, 114.8, 78.2, 64.2, 62.0, 55.6, 42.7, 33.3, 28.9, 28.4, 26.8, 26.2, 26.0, 25.8, 22.2, 13.9 ppm. IR (neat): $\tilde{\nu}$ = 2929, 2855, 1746, 1514, 1249, 1140, 828, 756 cm^{-1}. HRMS (ESI): calcd. for [M + Na]$^+$ 402.1806; found 402.1807.

4-Chloro-3-(4-methoxyphenyl)hexahydrobenzo[*d*]oxazol-2(3*H*)-one (2g): White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.27 (m, 2 H), 6.97–6.88 (m, 2 H), 4.85 (dt, *J* = 6.8, 4.7 Hz, 1 H), 4.37 (dd, *J* = 6.9, 4.6 Hz, 1 H), 4.11 (dt, *J* = 6.7, 4.2 Hz, 1 H), 3.81 (s, 3 H), 2.10–

1.96 (m, 3 H), 1.86–1.63 (m, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.2, 156.2, 129.5, 125.5, 114.7, 73.3, 63.0, 57.1, 55.6, 29.0, 25.5, 16.4 ppm. IR (neat): $\tilde{\nu}$ = 2935, 1754, 1514, 1248, 1137, 832, 754 cm^{-1}. HRMS (ESI): calcd. for $[M + Na]^+$ 304.0716; found 304.0712.

(3a*R*,4*R*,6*S*,7a*R*)-4-Chloro-3-(4-methoxyphenyl)-3a-methyl-6-(prop-1-en-2-yl)hexahydrobenzo[*d*]oxazol-2(3*H*)-one (2h): White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.20–7.04 (m, 2 H), 6.99–6.85 (m, 2 H), 4.84 (dd, *J* = 8.8, 0.8 Hz, 2 H), 4.50 (dd, *J* = 8.2, 6.1 Hz, 1 H), 4.22 (dd, *J* = 4.9, 3.2 Hz, 1 H), 3.81 (s, 3 H), 2.67–2.58 (m, 1 H), 2.32–2.24 (m, 1 H), 2.14–2.00 (m, 2 H), 1.83–1.74 (m, 4 H), 1.57 (s, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 159.6, 156.9, 146.7, 130.4, 127.2, 114.8, 110.7, 79.3, 64.5, 60.5, 55.5, 34.4, 34.2, 31.7, 23.5, 21.1 ppm. IR (neat): $\tilde{\nu}$ = 2937, 1759, 1513, 1250, 1075, 832, 761 cm^{-1}. HRMS (ESI): calcd. for $[M + Na]^+$ 358.1186; found 358.1183.

4-Chloro-3-(4-methoxyphenyl)hexahydro-2*H*-cyclopenta[*d*]-oxazol-2-one (2i): White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.52–7.32 (m, 2 H), 7.02–6.82 (m, 2 H), 5.25–5.10 (m, 1 H), 4.80–4.75 (m, 1 H), 4.33–4.27 (m, 1 H), 3.80 (s, 3 H), 2.46–2.17 (m, 3 H), 2.16–2.00 (m, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 157.1, 154.8, 129.9, 121.8, 114.8, 77.7, 70.1, 61.0, 55.6, 32.0, 31.2 ppm. IR (neat): $\tilde{\nu}$ = 2936, 1752, 1514, 1396, 1252, 1136, 825, 750 cm^{-1}. HRMS (ESI): calcd. for $[M + Na]^+$ 290.0560; found 290.0554.

6-Chloro-1-(4-methoxyphenyl)-3-oxa-1-azaspiro[4.5]decan-2-one (2j): White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33–7.26 (m, 2 H), 6.98–6.93 (m, 2 H), 4.61–4.59 (m, 1 H), 4.22 (d, *J* = 8.8 Hz, 1 H), 3.82 (s, 3 H), 3.76–3.72 (m, 1 H), 2.26–2.16 (m, 1 H), 2.14–2.03 (m, 1 H), 1.82–1.48 (m, 4 H), 1.32–1.06 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 159.9, 157.4, 131.3, 126.1, 114.8, 68.3, 65.9, 62.8, 55.6, 36.9, 33.6, 25.1, 22.0 ppm. IR (neat): $\tilde{\nu}$ = 2941, 1756, 1514, 1249, 1153, 834, 758 cm^{-1}. HRMS (ESI): calcd. for $[M + Na]^+$ 318.0873; found 318.0872.

1-Benzyl-4-(1-chloropentyl)-5-cyclohexyl-3-(4-methoxyphenyl)-imidazolidin-2-one (2k): Two separable diastereomers were obtained (isomer 1/isomer 2, 1:1). Data for isomer 1 of **2k**: White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42–7.27 (m, 7 H), 6.94–6.86 (m, 2 H), 4.96 (d, *J* = 14.9 Hz, 1 H), 4.17–4.14 (m, 1 H), 3.99 (d, *J* = 14.9 Hz, 1 H), 3.86–3.81 (m, 1 H), 3.80 (s, 3 H), 3.38–3.35 (m, 1 H), 1.88–0.94 (m, 17 H), 0.79 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 157.3, 156.7, 137.0, 131.3, 129.0, 128.7, 127.8, 123.4, 114.6, 61.5, 60.0, 56.8, 55.6, 45.3, 38.9, 30.2, 29.0, 28.6, 26.6, 26.5, 26.2, 25.9, 22.1, 13.9 ppm. IR (neat): $\tilde{\nu}$ = 2926, 2853, 1700, 1513, 1437, 1246, 830, 747 cm^{-1}. HRMS (ESI): calcd. for $[M + Na]^+$ 491.2436; found 491.2433. Data for isomer 2 of **2k**: White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43–7.24 (m, 7 H), 6.93–6.87 (m, 2 H), 4.82 (d, *J* = 15.3 Hz, 1 H), 4.19 (d, *J* = 15.3 Hz, 1 H), 3.97 (t, *J* = 2.5 Hz, 1 H), 3.90–3.85 (m, 1 H), 3.78 (s, 3 H), 3.37 (t, *J* = 2.6 Hz, 1 H), 1.83–1.55 (m, 5 H), 1.51–1.38 (m, 4 H), 1.29–1.13 (m, 5 H), 1.11–0.95 (m, 3 H), 0.82 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 157.8, 157.0, 137.3, 130.9, 128.6, 128.4, 127.4, 125.2, 114.5, 63.3, 60.7, 58.4, 55.5, 46.1, 39.1, 33.3, 28.9, 28.7, 26.5, 26.4, 26.2, 26.0, 22.1, 13.9 ppm. IR (neat): $\tilde{\nu}$ = 2927, 2854, 1696, 1514, 1446, 1246, 831, 708 cm^{-1}. HRMS (ESI): calcd. for $[M + Na]^+$ 491.2436; found 491.2435.

4-Chloro-3-(4-methoxyphenyl)-1-phenyloctahydro-2*H*-benzo-[*d*]imidazol-2-one (2l): White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59–7.50 (m, 2 H), 7.38–7.31 (m, 2 H), 7.29–7.22 (m, 2 H), 7.16–7.07 (m, 1 H), 6.98–6.90 (m, 2 H), 4.56–4.45 (m, 1 H), 4.40–4.30 (m, 2 H), 3.82 (s, 3 H), 2.21–2.13 (m, 1 H), 2.06–1.95 (m, 1 H), 1.92–1.75 (m, 2 H), 1.69–1.53 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 158.1, 157.1, 138.5, 130.7, 129.2, 126.4, 124.1, 121.0, 114.7, 60.4, 56.3, 55.6, 52.6, 28.5, 25.8, 16.2 ppm. IR (neat): $\tilde{\nu}$ = 2932, 1713, 1513, 1389, 1247, 757, 693 cm^{-1}. HRMS (ESI): calcd. for $[M + Na]^+$ 379.1189; found 379.1186.

1-Benzyl-4-chloro-3-(4-methoxyphenyl)octahydro-2*H*-benzo-[*d*]imidazol-2-one (2m): White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43–7.22 (m, 7 H), 6.97–6.87 (m, 2 H), 4.86 (d, *J* = 15.1 Hz, 1 H), 4.27–4.21 (m, 1 H), 4.14 (dd, *J* = 7.0, 3.5 Hz, 1 H), 4.05 (d, *J* = 15.1 Hz, 1 H), 3.80 (s, 3 H), 3.71–3.66 (m, 1 H), 1.99–1.90 (m, 2 H), 1.80–1.73 (m, 1 H), 1.69–1.60 (m, 2 H), 1.54–1.46 (m, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.5, 157.6, 137.1, 131.3, 128.8, 128.5, 127.7, 125.7, 114.6, 61.0, 57.1, 55.6, 51.2, 45.4, 29.2, 24.7, 16.4 ppm. IR (neat): $\tilde{\nu}$ = 2943, 1705, 1513, 1246, 829, 701 cm^{-1}. HRMS (ESI): calcd. for $[M + Na]^+$ 393.1346; found 393.1345.

5-[Chloro(phenyl)methyl]-1-(4-methoxyphenyl)pyrrolidin-2-one (2n): Two separable diastereomers were obtained (isomer 1/isomer 2, 1:9). Data for isomer 1 of **2n**: White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.50–7.45 (m, 2 H), 7.36–7.27 (m, 5 H), 7.02–6.95 (m, 2 H), 5.08 (d, *J* = 3.3 Hz, 1 H), 4.84–4.77 (m, 1 H), 3.84 (s, 3 H), 2.31–2.23 (m, 2 H), 2.15–2.08 (m, 1 H), 1.53–1.43 (m, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 174.4, 157.5, 135.3, 130.3, 129.0, 128.6, 127.8, 124.5, 114.7, 65.2, 60.6, 55.7, 30.6, 30.5 ppm. IR (neat): $\tilde{\nu}$ = 2954, 1709, 1514, 1219, 1032, 828 cm^{-1}. HRMS (ESI): calcd. for $[M + Na]^+$ 338.0924; found 338.0920. Data for isomer 2 of **2n**: White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.29 (m, 7 H), 7.02–6.95 (m, 2 H), 5.10 (d, *J* = 2.5 Hz, 1 H), 4.46 (ddd, *J* = 8.8, 3.8, 2.7 Hz, 1 H), 3.83 (s, 3 H), 2.82–2.71 (m, 1 H), 2.56–2.46 (m, 1 H), 2.35–2.26 (m, 1 H), 2.08–1.97 (m, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.8, 158.5, 136.9, 129.4, 128.7, 128.5, 127.2, 127.1, 114.8, 66.2, 63.8, 55.5, 31.0, 18.2 ppm. IR (neat): $\tilde{\nu}$ = 2934, 1698, 1512, 1248, 832, 699 cm^{-1}. HRMS (ESI): calcd. for $[M + Na]^+$ 338.0924; found 338.0921.

7-Chloro-1-(4-methoxyphenyl)octahydro-2*H*-indol-2-one (2o): White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.21–7.12 (m, 2 H), 6.99–6.87 (m, 2 H), 4.29–4.13 (m, 2 H), 3.80 (s, 3 H), 2.80–2.68 (m, 1 H), 2.56 (dd, *J* = 16.4, 7.1 Hz, 1 H), 2.26 (dd, *J* = 16.4, 3.7 Hz, 1 H), 1.89–1.65 (m, 4 H), 1.59–1.42 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 175.0, 158.3, 129.7, 126.6, 114.6, 64.3, 57.2, 55.5, 38.4, 30.7, 29.5, 27.2, 18.1 ppm. IR (neat): $\tilde{\nu}$ = 2937, 1703, 1512, 1248, 1032, 833 cm^{-1}. HRMS (ESI): calcd. for $[M + Na]^+$ 302.0924; found 302.0918.

4-Chloro-3-phenylhexahydrobenzo[*d*]oxazol-2(3*H*)-one (4a): Product **4a** was contaminated with a small amount of the oxidative amination product.[8k] White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.47–7.42 (m, 2 H), 7.42–7.36 (m, 2 H), 7.25–7.19 (m, 1 H), 4.87–4.83 (m, 1 H), 4.49 (dd, *J* = 6.7, 4.7 Hz, 1 H), 4.16–4.12 (m, 1 H), 2.09–1.96 (m, 3 H), 1.84–1.73 (m, 2 H), 1.72–1.65 (m, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 155.6, 136.7, 129.3, 126.0, 122.8, 73.2, 62.1, 57.0, 28.7, 24.9, 16.2 ppm. IR (neat): $\tilde{\nu}$ = 2947, 1756, 1501, 1393, 1194, 759, 693 cm^{-1}. HRMS (ESI): calcd. for $[M + Na]^+$ 274.0611; found 274.0605.

4-Chloro-3-(4-fluorophenyl)hexahydrobenzo[*d*]oxazol-2(3*H*)-one (4b): Product **4b** was contaminated with a small amount of the oxidative amination product.[8k] White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44–7.36 (m, 2 H), 7.14–7.06 (m, 2 H), 4.86 (dt, *J* = 6.8, 4.4 Hz, 1 H), 4.42–4.38 (m, 1 H), 4.11–4.06 (m, 1 H), 2.15–1.94 (m, 3 H), 1.85–1.64 (m, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 160.7 (d, *J* = 246.3 Hz), 155.8, 132.8 (d, *J* = 3.0 Hz), 125.3 (d, *J* = 8.4 Hz), 116.2 (d, *J* = 22.8 Hz), 73.6, 63.0, 57.5, 29.5, 25.3, 16.8 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –115.40 ppm. IR (neat): $\tilde{\nu}$ = 2949, 1755, 1511, 1395, 837, 756 cm^{-1}. HRMS (ESI): calcd. for $[M + Na]^+$ 292.0516; found 292.0512.

4-[4-Chloro-2-oxohexahydrobenzo[*d*]oxazol-3(2*H*)-yl]benzo-nitrile (4c): Product **4c** was contaminated with a small amount of the oxidative amination product.[8k] White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77–7.61 (m, 4 H), 4.87 (dt, *J* = 7.0, 3.6 Hz, 1 H), 4.56 (t, *J* = 6.1 Hz, 1 H), 4.13–4.06 (m, 1 H), 2.26–1.93 (m, 3 H), 1.89–1.69

(m, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 154.6, 141.2, 133.3, 121.3, 119.1, 108.3, 74.2, 62.0, 57.9, 29.8, 24.5, 16.8 ppm. IR (neat): $\tilde{\nu}$ = 2932, 2222, 1753, 1388, 1190, 839, 743 cm^{-1}. HRMS (ESI): calcd. for $[M + Na]^+$ 299.0563; found 299.0556.

4-Chloro-3-(4-nitrophenyl)hexahydrobenzo[*d*]oxazol-2(3*H*)-one (4d): Product **4d** was contaminated with a small amount of the oxidative amination product.[8k] White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30–8.21 (m, 2 H), 7.83–7.74 (m, 2 H), 4.89 (dt, *J* = 6.9, 3.5 Hz, 1 H), 4.61 (t, *J* = 6.2 Hz, 1 H), 4.13–4.08 (m, 1 H), 2.29–2.20 (m, 1 H), 2.13–2.09 (m, 1 H), 2.04–1.93 (m, 1 H), 1.92–1.68 (m, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.5, 143.0, 125.2, 124.9, 120.8, 74.4, 62.3, 58.1, 30.0, 24.5, 16.9 ppm. IR (neat): $\tilde{\nu}$ = 2748, 1759, 1595, 1514, 1502, 1194, 754, 752 cm^{-1}. HRMS (ESI): calcd. for $[M + Na]^+$ 319.0462; found 319.0460.

6-Chloro-1-tosyloctahydrocyclopenta[*b*]pyrrole (6): Two separable diastereomers were obtained (isomer 1/isomer 2, 5.2:1). Data for isomer 1 of **6**: White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78–7.69 (m, 2 H), 7.41–7.31 (m, 2 H), 4.70 (d, *J* = 3.7 Hz, 1 H), 3.74 (d, *J* = 7.6 Hz, 1 H), 3.44 (dt, *J* = 10.3, 6.2 Hz, 1 H), 3.01 (dt, *J* = 10.1, 7.3 Hz, 1 H), 2.76 (p, *J* = 7.0 Hz, 1 H), 2.44 (s, 3 H), 2.21–2.07 (m, 2 H), 1.99–1.91 (m, 1 H), 1.75–1.66 (m, 1 H), 1.55–1.45 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.0, 133.1, 129.9, 128.1, 73.1, 65.8, 50.0, 42.0, 33.5, 30.8, 29.4, 21.7 ppm. IR (neat): $\tilde{\nu}$ = 2966, 2873, 1348, 1305, 1228, 1160, 826 cm^{-1}. HRMS (ESI): calcd. for $[M + Na]^+$ 322.0639; found 322.0643. Data for isomer 2 of **6**: White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82–7.71 (m, 2 H), 7.34–7.28 (m, 2 H), 4.45 (td, *J* = 4.7, 2.1 Hz, 1 H), 4.19 (dd, *J* = 10.0, 5.1 Hz, 1 H), 3.57 (ddd, *J* = 9.9, 7.4, 4.3 Hz, 1 H), 3.33 (ddd, *J* = 9.9, 8.6, 7.1 Hz, 1 H), 2.62–2.50 (m, 1 H), 2.44 (d, *J* = 6.4 Hz, 3 H), 2.19–1.68 (m, 6 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 143.7, 135.5, 129.7, 127.7, 68.2, 64.3, 51.7, 42.3, 37.3, 33.1, 28.6, 21.7 ppm. IR (neat): $\tilde{\nu}$ = 2966, 2873, 1347, 1162, 1093, 663, 549 cm^{-1}. HRMS (ESI): calcd. for $[M + Na]^+$ 322.0639; found 322.0641.

(*E*)-4-[Chloro(phenyl)methylene]-3-(4-methoxyphenyl)oxazolidin-2-one (8a, Major Isomer): White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.04–6.98 (m, 1 H), 6.95–6.90 (m, 2 H), 6.90–6.83 (m, 2 H), 6.80–6.75 (m, 2 H), 6.55–6.44 (m, 2 H), 5.20 (s, 2 H), 3.66 (s, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 159.0, 157.0, 134.2, 131.5, 129.2, 128.0, 127.8, 127.5, 126.6, 113.9, 105.3, 68.0, 55.6 ppm. HRMS (ESI): calcd. for $[M + Na]^+$ 338.0560; found 338.0555.

(*E*)-4-[Chloro(phenyl)methylene]-3-(4-methoxyphenyl)-5-methyloxazolidin-2-one (8b, Major Isomer): White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.03–6.97 (m, 1 H), 6.95–6.86 (m, 4 H), 6.80–6.74 (m, 2 H), 6.51–6.45 (m, 2 H), 5.50 (q, *J* = 6.3 Hz, 1 H), 3.65 (s, 3 H), 1.80 (d, *J* = 6.3 Hz, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.8, 156.0, 136.4, 134.7, 129.3, 128.0, 127.7, 127.5, 127.0, 113.9, 106.5, 76.0, 55.6, 19.1 ppm. HRMS (ESI): calcd. for $[M + Na]^+$ 352.0716; found 352.0714.

(*Z*)-4-[Chloro(phenyl)methylene]-3-(4-methoxyphenyl)-5-methyloxazolidin-2-one (8b, Minor Isomer): White solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.42–7.32 (m, 5 H), 7.32–7.28 (m, 2 H), 7.01–6.94 (m, 2 H), 5.36 (q, *J* = 6.3 Hz, 1 H), 3.84 (s, 3 H), 1.19 (d, *J* = 6.3 Hz, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 159.7, 156.4, 137.4, 136.0, 129.5, 129.3, 129.2, 129.1, 128.0, 114.2, 104.0, 75.6, 55.6, 19.9 ppm. HRMS (ESI): calcd. for $[M + Na]^+$ 352.0716; found 352.0714. The stereochemistry was determined by nuclear Overhauser effect (NOE) analysis. The two separable *trans* and *cis* isomers were obtained (isomer 1/isomer 2, 15:1).

(*E*)-4-(1-Chloropropylidene)-3-(4-methoxyphenyl)-5-methyloxazolidin-2-one (8c, Major Isomer): White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26–7.13 (m, 2 H), 7.02–6.90 (m, 2 H), 5.35–5.24 (m, 1 H), 3.83 (s, 3 H), 1.86–1.71 (m, 2 H), 1.66 (d, *J* = 6.3 Hz, 3 H), 0.82 (t, *J* = 7.3 Hz, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.9, 156.2, 135.2, 128.8, 128.4, 114.9, 112.5, 75.7, 55.6, 26.1, 19.1, 11.9 ppm. HRMS (ESI): calcd. for $[M + Na]^+$ 304.0716; found 304.0713. The stereochemistry was determined by nuclear Overhauser effect (NOE) analysis.

(*Z*)-4-(1-Chloropropylidene)-3-(4-methoxyphenyl)-5-methyloxazolidin-2-one (8c, Minor Isomer): White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.23–7.14 (m, 2 H), 6.98–6.89 (m, 2 H), 5.26 (q, *J* = 6.3 Hz, 1 H), 3.83 (s, 3 H), 2.22 (ddd, *J* = 14.6, 7.3, 2.3 Hz, 2 H), 1.59 (d, *J* = 6.3 Hz, 3 H), 1.13 (t, *J* = 7.3 Hz, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 159.5, 156.4, 132.9, 129.3, 128.3, 114.1, 108.6, 74.7, 55.6, 28.5, 21.3, 12.6 ppm. HRMS (ESI): calcd. for $[M + Na]^+$ 304.0716; found 304.0711.

4-(1-Chlorovinyl)-5-cyclohexyl-3-(4-methoxyphenyl)oxazolidin-2-one (8d): Two separable diastereomers were obtained (isomer 1/isomer 2, 1.5:1). Data for isomer 1 of **8d**: White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.30 (m, 2 H), 6.95–6.83 (m, 2 H), 5.44 (d, *J* = 2.1 Hz, 1 H), 5.39 (d, *J* = 2.1 Hz, 1 H), 4.59 (d, *J* = 4.2 Hz, 1 H), 4.26 (dd, *J* = 5.9, 4.3 Hz, 1 H), 3.78 (s, 3 H), 1.93–1.65 (m, 6 H), 1.37–1.07 (m, 5 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.7, 155.6, 139.4, 129.4, 124.1, 116.9, 114.5, 81.0, 65.9, 55.6, 42.3, 27.9, 27.2, 26.2, 25.8, 25.6 ppm. IR (neat): $\tilde{\nu}$ = 2929, 2854, 1751, 1515, 1398, 1249, 1135, 826 cm^{-1}. HRMS (ESI): calcd. for $[M + Na]^+$ 358.1180; found 358.1185. Data for isomer 2 of **8d**: White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.35 (m, 2 H), 6.95–6.83 (m, 2 H), 5.50 (d, *J* = 1.7 Hz, 1 H), 5.43 (d, *J* = 1.7 Hz, 1 H), 4.80 (d, *J* = 7.1 Hz, 1 H), 4.30 (dd, *J* = 10.6, 7.1 Hz, 1 H), 3.79 (s, 3 H), 2.20–1.65 (m, 6 H), 1.37–0.93 (m, 5 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.5, 155.8, 137.1, 129.8, 124.2, 119.6, 114.5, 80.9, 66.5, 55.6, 37.1, 29.5, 29.3, 26.3, 25.2, 25.1 ppm. IR (neat): $\tilde{\nu}$ = 2924, 2852, 1731, 1516, 1407, 1250, 1143, 826 cm^{-1}. HRMS (ESI): calcd. for $[M + Na]^+$ 358.1180; found 358.1183.

CCDC 1473268 (for **2g**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Acknowledgments

Financial support from Xiamen University, the National Natural Science Foundation of China (NSFC) (no. 21402164), the Fundamental Research Funds for the Central Universities, and the "Thousand Youth Talents Plan" are acknowledged.

Keywords: Synthetic methods · Alkenes · Cyclization · Copper · Radicals · Aminochlorination

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[15] The reaction may also proceed through deprotonation followed by an electron transfer to produce nitrogen-centered radical **I**, as previously proposed for the oxidation of *N*-arylamides (see ref.[8l]). $CuCl_2$ should be a competent oxidant for the conjugate base of the substrates, judging from its reduction potential (0.45 V vs. Fc/Fc^+, PhCN).

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Received: March 13, 2016
Published Online: ■

Aminochlorination

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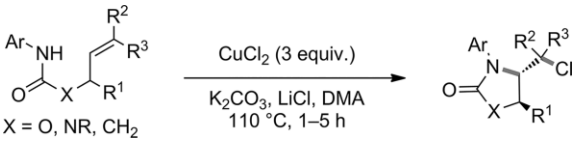
A General $CuCl_2$-Promoted Alkene Aminochlorination Reaction



A $CuCl_2$-promoted alkene aminochlorination reaction has been developed. A variety of mono-, di-, and trisubstituted alkenes readily participated in this reaction to afford structurally diverse vicinal chloroamines. DMA = *N*,*N*-dimethylacetamide.

DOI: 10.1002/ejoc.201600589