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Synthesis of 3-Alkylbenzoxazolones from *N*-Alkyl-*N*-arylhydroxylamines by Contiguous *O*-Trichloroacetylation, Trichloroacetoxy *ortho*-Shift, and Cyclization Sequence

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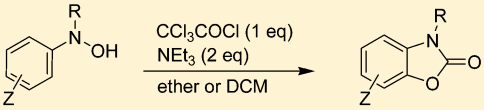
Supporting Information

ABSTRACT: Benzoxazolone pharmacophore is present in clinical pharmaceuticals, drug candidates, and many compounds having a wide spectrum of biological activities. The methods available for the synthesis of benzoxazolones have limited diversity due to problems in accessibility and air-sensitivity of diversely substituted *o*-aminophenols from which they are generally prepared by cyclocarbonylation with phosgene or its equivalents. The present paper describes a mild method for the synthesis of 3-alkylbenzoxazolones from easily accessible and air-stable nitroarenes. Nitroarenes were converted to *N*-alkyl-*N*-arylhydroxylamines in two steps involving partial reduction to arylhydroxylamines followed by selective *N*-alkylation. Treatment of *N*-alkyl-*N*-arylhydroxylamines with trichloroacetyl chloride and triethylamine afforded 3-alkylbenzoxazolones generally in good yields through an uninterrupted three-step sequence involving *O*-trichloroacetylation, $N \rightarrow C_{ortho}$ trichloroacetoxy shift, and cyclization in a single pot at ambient temperatures. The present method is mild, wide in scope, economical, and regioselective. Many sensitive groups like alkyl and aryl esters, amide, cyano, and the carbon−carbon double bond survive the reaction.



Z = H, Me, Cl, Br, CO_2R, CH_2CO_2Et, $CH_2CON(Me)Ph$, OCOMe etc.

R = Pr, $CH_2CH{=}CH_2$, $CH_2CH_2CO_2Et$, CH_2CH_2CN, CH_2Ph, $CH_2C_6H_4$-OMe-*p*

INTRODUCTION

The benzoxazolone nucleus **1** (Figure 1) is a privileged scaffold in medicinal chemistry for drug design and development.[1] It is a bioisostere of catechol, phenol, coumarin, and carbamate pharmacophores. It is metabolically more stable than catechol and phenol. Therefore, compounds containing the benzoxazolone nucleus are endowed with a broad spectrum of biological activities and improved pharmacokinetics. They serve as ligands for many receptor proteins involved in signal transduction, such as those of catechol amines[2,3] and other neurotransmitters,[3−8] as well as for other receptor proteins.[9−13] They are also inhibitors of many enzymes.[14−26] Therefore, they are useful in the treatment or alleviation of symptoms of a wide range of neurological, psychiatric, autoimmune, and metabolic disorders including Alzheimer disease,[7,10,14,15] schizophrenia,[3b,d,7] convulsion/epilepsy,[6,9d,11] various types of pain[6,8,11,18] and inflammation,[6,10,13,14,17,19−22] allergy,[8,10,21] cardiovascular[8,10−13,17,18] and cerebrovascular,[6,10,18] diseases, many types of cancer,[13,16,17,23,24] AIDS,[25,26] and hyperglycemia.[8,12,17,18,24] Because of their bioisosterism with coumarin and carbamate, they also exhibit antimicrobial,[27] insecticidal,[28] and herbicidal[29] (and therefore antimalarial[30]) activities. The parent (BOA) and a few simple benzoxazolones (e.g., 6-methoxy, MBOA) have been isolated from seeds, seedlings, roots, and other parts of many *monocotyledon* cereal, fodder, and some medicinal plants[31] and also from a marine sponge.[32] They serve as plant allelochemicals,[33] provide resistance to plants and seeds against pest attacks,[28,31b,d,e,32,34] and possess some of the activities mentioned previously,[31c,35−37] among others.[31a,32,33b] Some synthetic benzoxazolones have emerged as clinical drugs or drug candidates and agrochemicals. For example, chlorzoxazone (Paraflex,[19,38] **2**) (Figure 1) is a muscle relaxant, and phosalone[39] (**3**) is an agropesticide. Pardoprunox (SLV-308,[3a,c,40] **4**) and besonprodil

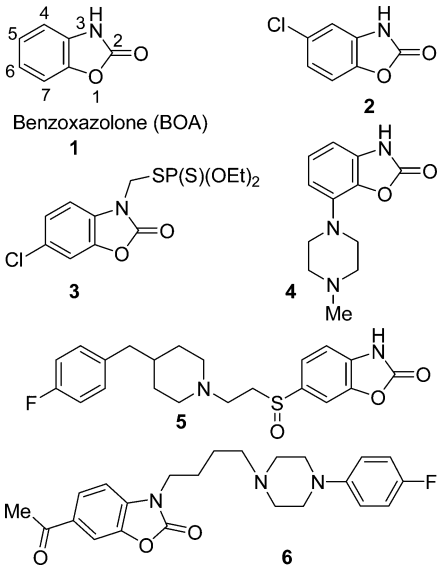


Figure 1. Some benzoxazolone drugs and drug candidates.

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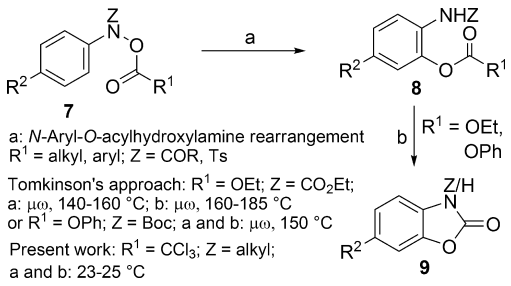
(CI-1041,[6b,41] **5**) are anti-Parkinson drugs undergoing clinical trials, and SN79[9a,b] (**6**) is a drug candidate useful in reducing the side effects of drug abuse.

Most of the benzoxazolone-based drug discovery programs are limited to investigations on *N*- and/or 6-substituted derivatives,[2b,3e,6a,9,20,23b,25,27b,d] plausibly because they are easily accessible by substitution reactions[1] of the commercially available parent benzoxazolone. However, for greater diversity, the heterocyclic ring needs to be constructed on variously substituted benzene rings. The heterocyclic ring is generally prepared by cyclocarbonylation of *o*-aminophenols[42] with phosgene[5,24] or other carbonyl group donors, such as molten urea,[20,21,25,27b,30] triphosgene,[7,11,19,29a,43] aryl chloroformates,[13,23b] carbonyl diimidazole,[2a,3b,6,7,18] etc.[44−47] Carbon monoxide has also been used for oxidative[48] and reductive[49] cyclocarbonylations of *o*-aminophenols and *o*-nitrophenols, respectively. Some examples of cyclization of *o*-hydroxyaryl isocyanates, generated in situ by Curtius,[50] Schimdt,[51] Hoffmann,[18,52] and Lossen[26b,29b] rearrangements of suitable salicylic acid derivatives, are also known. However, all of the aforesaid methods suffer from various drawbacks, such as air sensitivity of *o*-aminophenols, toxicity of phosgene, hazardous mixtures of CO and O_2 used in oxidative cyclocarbonylation, high temperatures and pressures, and undesirable side products. Most adversely, they have little diversity to offer because variously substituted phenols with an *ortho*-substitutent (generally an amino or nitro group) required to start with are not easily accessible. Generally, they are obtainable in many steps in low or poor yields due to associated problems of regioselectivity and oversubstitution of the aromatic ring.[43,49a,53] A few isolated reports deal with intramolecular cyclization of nitrene[54] and benzyne[55] reactive intermediates through C−N and C−O bond formation, respectively, at the unoccupied *ortho* position of the aromatic ring for constructing the heterocyclic ring, which reduces the severity of the latter problems to some extent. However, the high temperature pyrolytic[54] or subzero organometallic reaction conditions and acidic workup[55] limit the scope of these methods.

Recently, through an intelligent design of *N*-aryl-*O*-acylhydroxylamine rearrangement[56,57] (**7** to **8**; R^1 = alkyl, aryl) (Scheme 1) by way of replacing R^1 with a leaving group

Scheme 1. *N*-Aryl-*O*-acylhydroxylamine Rearrangement and Synthesis of Benzoxazolones



like OEt or OPh, Tomkinson and co-workers[58] constructed the heterocyclic ring through C−O and N−(CO) bond formation. The rearranged products **8** (R^1 = OEt, OPh; Z = CO_2Et, Boc), by virtue of the presence of an ethoxy/phenoxy leaving group in the migrated carbonate group, could be cyclized to the benzoxazolones **9** in high yields. However, the methodology is constrained by its failure with electron-deficient substrates, such as **7** (R^2 = CF_3), and sluggish reaction rates requiring prolonged microwave heating at high temperatures which could pose practical problems[59] and might be detrimental to sensitive groups present elsewhere in the molecule as observed by them in the case of *N*-Boc. Nevertheless, it is an attractive methodology owing to the robust synthetic chemistry involved and easy accessibility of the substrates through partial reduction of nitroarenes or by C−N coupling of protected hydroxylamines with aryl halides and, therefore, needs to be revisited.

Since the *N*-aryl-*O*-acylhydroxylamine rearrangement is known to be facilitated by increasing the electron-withdrawing ability of the acyl group and/or the electron-releasing ability of the nitrogen substituents,[56] we expected *N*-alkyl-*N*-aryl-*O*-trichloroacetylhydroxylamines **7** (R^1 = CCl_3; Z = alkyl) to be better substrates in the above reaction owing to their double activation by the complementary electronic effects of the *O*-trichloroacetyl and *N*-alkyl substituents. This double activation would facilitate not only the rearrangement step significantly[60] but also the cyclization step in view of higher reactivity of the electrophile−nucleophile pair in the rearranged product **8** and the well-known nucleofugality of the CCl_3 group.[61] Though the rearrangement of *N*-aryl-*O*-acylhydroxylamines has been well studied,[56,57] most of the reported cases describe the rearrangement of *N*-aryl-*N*,*O*-diacylhydroxylamines. We could not find an example of this rearrangement in the case of an *N*-alkyl-*N*-aryl-*O*-acylhydroxylamine. We now wish to report herein that *N*-alkyl-*N*-aryl-*O*-trichloroacetylhydroxylamines were indeed reactive enough to undergo the aforesaid rearrangement-cyclization sequence even during their preparation by *O*-trichloroacetylation of *N*-alkyl-*N*-arylhydroxylamines at ambient temperatures to afford the corresponding benzoxazolones in good to high yields.

RESULTS AND DISCUSSION

The *N*-alkyl-*N*-arylhydroxylamines **10** (Table 1) were prepared from nitroarenes in two steps involving partial reduction to *N*-arylhydroxylamines with Zn/NH_4Cl as reported,[62] followed by selective *N*-alkylation by known procedures with some modifications. *N*-Allylation was done with allyl acetate in the presence of $Pd(PPh_3)_4$ catalyst at room temperature (23−25 °C) under a nitrogen atmosphere.[63] *N*-(2-Cyano)ethylation and *N*-(2-ethoxycarbonyl)ethylation were performed by aza-Michel addition to acrylonitrile and ethyl acrylate, respectively, at room temperature in quantitative yields.[64] *N*-Benzyl and *N*-propyl derivatives were prepared by treatment of the *N*-arylhydroxylamines generated in situ (or isolated) with benzaldehyde and propanal, respectively, followed by reduction of the nitrones isolated (or generated in situ) with $NaBH_4$ in methanol at 0−10 °C.[65]

Treatment of a solution of a representative *N*-alkyl-*N*-arylhydroxylamine **10a** and Et_3N (2 equiv) in diethyl ether with trichloroacetyl chloride (1 equiv) at room temperature (23−25 °C) for 8 h directly furnished, to our delight, the benzoxazolone **12a** in 86% yield, ostensibly by an uninterrupted three-step *O*-trichloroacetylation, trichloroacetoxy *ortho*-shift, and cyclization sequence. This method (method A) was quite general and afforded other benzoxazolones consistently in good to high yields (Table 1). In the cases of the hydroxylamines **10e−g** (entries 6−9) having an active *N*-benzylic hydrogen atom, a competing base-promoted *β*-elimination of Cl_3CCO_2H in the *O*-trichloroacetylated derivatives also occurred to produce variable amounts of benzylideneanilines, which were susceptible to hydrolysis but could be isolated and identified (Scheme 2). The nature of the solvent also appeared to play a role in the

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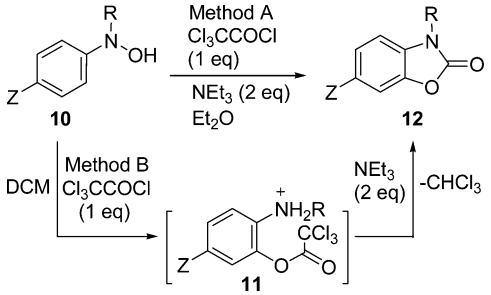
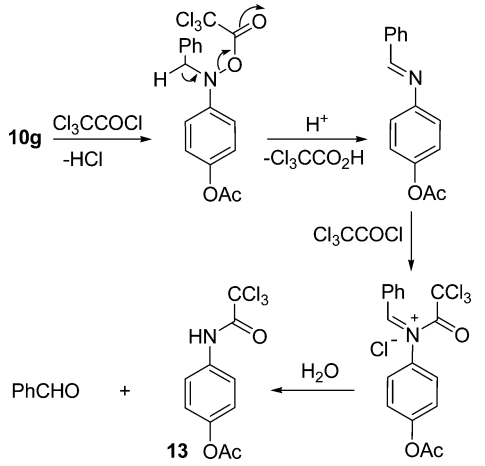
Table 1. One-Pot Synthesis of 3-Alkylbenzoxazalones 12 from *N*-Alkyl-*N*-arylhydroxylamines 10[a]



entry	10	Z	R	method	time (h)	12 yield (%)
1	a	H	$CH_2CH{=}CH_2$	A	8	86
2	a	H	$CH_2CH{=}CH_2$	A[b]	2	79
3	b	H	$CH_2CH_2CH_3$	A	8	90
4	c	H	CH_2CH_2COOEt	A	8	73
5	d	H	CH_2CH_2CN	A	8	85
6	e	H	Bn	A	8	20[c]
7	e	H	Bn	B	9[d]	84
8	f	H	(*p*-OMe)Bn	B	9[d]	78
9	g	*p*-OAc	Bn	B	9[d]	62[e]
10	h	*p*-Me	$CH_2CH{=}CH_2$	A	8	88
11	i	*p*-Me	CH_2CH_2COOEt	A	8	72
12	j	*p*-Cl	$CH_2CH{=}CH_2$	A	8	86
13	k	*p*-Cl	CH_2CH_2COOEt	A	8	71
14	l	*p*-Br	$CH_2CH{=}CH_2$	B	9[d]	81
15	m	*p*-CH_2COOEt	CH_2CH_2COOEt	A	8	71
16	n	*p*-$CH_2CON(Me)Ph$	CH_2CH_2COOEt	A[f]	4	68
17	o	*p*-COOEt	$CH_2CH{=}CH_2$	B	40[g]	61

[a]All of the reactions were performed with 2 mmol of **10** in 30 mL of the solvent at rt (23−25 °C). Additions of Cl_3CCOCl and Et_3N were done at 0−5 °C, and the temperature slowly rose to rt during 25 min. [b]DCM was taken as the solvent. [c]Benzylideneaniline was also isolated in 64% yield. [d]Et_3N was added after 6 h. [e]4-(2,2,2-Trichloroacetamido)phenyl acetate **13** was also isolated in 11% yield. [f]DCM was used as the solvent due to solubility reasons. [g]Et_3N was added after 36 h.

Scheme 2. Proposed Mechanism for the Formation of Trichloroacetanilide 13



formation of benzylideneaniline product. In the case of *N*-benzyl-*N*-phenylhydroxylamine **10e**, 3-benzylbenzoxazolone **12e** was formed along with the elimination product benzylideneaniline in a 1:3 ratio (calculated by NMR) in diethyl ether, in a 2:1 ratio in DCM, and in a 3:1 ratio in benzene. Electron-withdrawing substituents on the benzene ring, such as bromine or ester group (entries 14 and 17), also complicated the reaction even when other *N*-alkyl groups were present, arguably by slowing down the rearrangement. Curiously, the reaction with 1 equiv of Et_3N was not clean, showing many spots on TLC, and therefore was not pursued subsequently.

However, when the trichloroacetylation was performed in the absence of Et_3N at room temperature (23−25 °C) for a few hours, the reaction proceeded up to the rearrangement stage smoothly, indicating that even the hydrochloride salts of *N*-alkyl-*N*-aryl-*O*-trichloroacetylhydroxylamines formed on trichloroacetylation under these conditions could rearrange to the corresponding protonated *o*-trichloroacetoxy-*N*-alkylanilines **11**, which obviously could not cyclize. Deprotonation of the latter by Et_3N at this stage and stirring the reaction mixture further at room temperature for a few hours afforded the benzoxazolones in good to high yields. Dichloromethane was found to be the solvent of choice in this modification (method B) because in diethyl ether and benzene the hydrochloride salts precipitated out. No β-elimination to imines was observed in this modification except in the case of *N*-benzyl-*N*-(4-acetoxyphenyl)hydroxylamine **10g** (entry 9). In this case, the trichloroacetanilide derivative **13** (Scheme 2) was also isolated in 11% yield along with the expected benzoxazolone **12g** in 62% isolated yield. The product **13** arose probably due to *p*-acetoxy group assisted acid-catalyzed elimination of trichloroacetic acid in the *O*-trichloroacetylated intermediate product formed in the first step followed by *N*-trichloroacetylation of the imine in the reaction mixture and hydrolysis of the carbon−nitrogen double bond of the *N*-trichloroacetylated iminium chloride product during work up as shown in Scheme 2.

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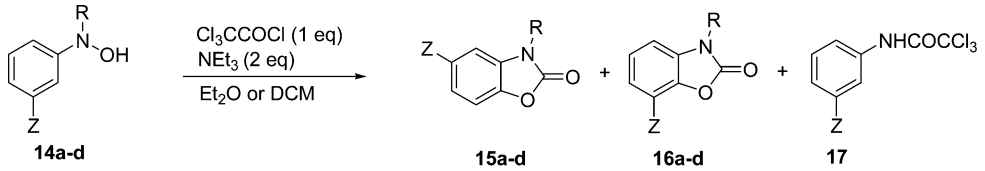
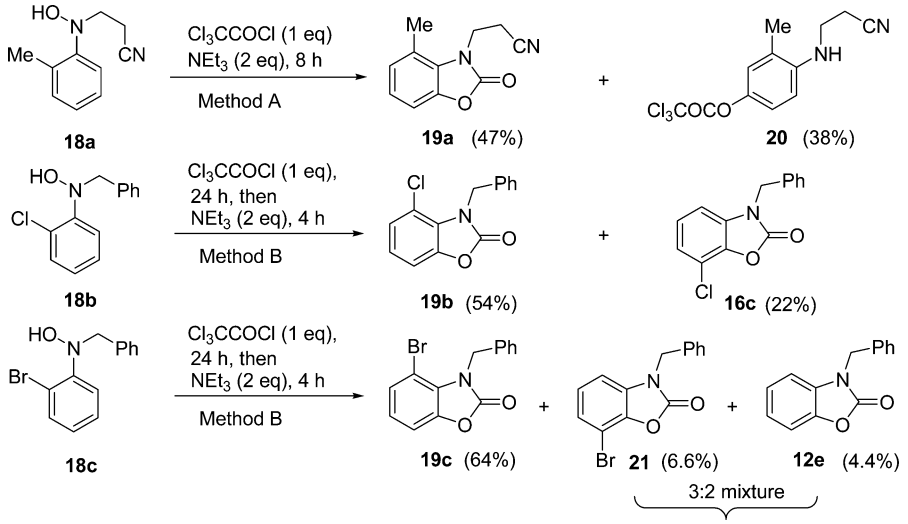
Scheme 3. Reaction of *Meta*-Substituted *N*-Alkyl-*N*-arylhydroxylamines



R	Z	Method	Time			
14a: CH_2CH_2COOEt	Me	A	8 h	44%	34%	-
				57:43 mixture		
14b: CH_2CH_2CN	COOMe	B	36+4 h	41%	26%	18%
14c: Bn	Cl	B	24+4 h	56%	8%	-
14d: $CH_2CH{=}CH_2$	Br	B	24+4 h	58%	-	-

Scheme 4. Reaction of *Ortho*-Substituted *N*-Alkyl-*N*-arylhydroxylamines



Nevertheless, this procedure (method B) was found to be more general, being applicable to substrates having electron-withdrawing as well as electron-donating substituents at the benzene ring and different types of *N*-alkyl substituents such as allyl, benzyl, 2-cyanoethyl, 2-ethoxycarbonylethyl, etc. The details are given in Table 1. Benzoxazolones having allyl,[35,66] benzyl,[13,23a] 2-cyanoethyl,[67] and 2-ethoxycarbonylethyl[67] substituents at position 3 are known to have significant biological activities.

In the case of *meta*-substituted substrates, the trichloroacetoxy group showed a tendency to migrate to the less hindered *ortho* position away from the *meta*-substituent selectively, leading to the formation of a mixture of regioisomeric 5- and 7-substituted benzoxazolones (Scheme 3) or 5-substituted benzoxazolones exclusively, depending on the nature of the *meta*-substituent. Thus, the reaction of *m*-methyl derivative **14a** resulted in the formation of an inseparable mixture of 5-methyl- and 7-methylbenzoxazolones **15a** and **16a** (57:43 ratio) with low regioselectivity in 78% yield. The mixture showed two distinctly separated signals for methyl protons in the ^{1}H NMR, which were used to calculate the ratio of the two regioisomers. Other signals were not well separated. However, the proton-decoupled ^{13}C NMR spectrum displayed almost all the signals as twins, indicating the isomeric nature of the components. On the basis of the chemical shifts and relative intensities, the twin signals could be assigned justifiably to the major (**15a**) and the minor (**16a**) isomers. The isomeric nature of **15a** and **16a** was also indicated by the appearance of a single $[M + Na]^+$ peak in the HRMS of the mixture. The *m*-methoxycarbonyl derivative **14b** provided the regioisomers 5-methoxycarbonylbenzoxazolone **15b** and 7-methoxycarbonylbenzoxazolone **16b** with relatively higher regioselectivity in 41% and 26% isolated yields, respectively, along with the trichloroacetanilide derivative **17** in 18% yield. The latter was formed probably by a mechanism similar to that shown in Scheme 2. The *m*-chloro derivative **14c** furnished the regioisomeric 5-chlorobenzoxazolone **15c** and 7-chlorobenzoxazolone **16c** with good regioselectivity in 56% and 8% isolated yields, respectively, whereas the *m*-bromo derivative **14d** produced the 5-bromobenzoxazolone **15d** exclusively in 58% isolated yield in a highly regioselective manner. The structure of **15d** was also supported by single crystal X-ray diffraction data. The ORTEP diagram is given in the Supporting Information. The reported method for the synthesis of benzoxazolones via carbonate migration[58] was nonregioselective for *meta*-substituted derivatives occurring on both sides in a 1:1 ratio, and the rearrangement products were not pursued further.

Ortho-substituted *N*-arylhydroxylamines **18** (Scheme 4) afforded the normal 4-substituted benzoxazolones **19** as the major products by acyloxy shift to the unoccupied *ortho* position. Other minor products, the nature of which depended on the nature of the *ortho*-substituent, were also formed probably through the cyclohexadienone imine intermediates **22** (Scheme 5) formed by acyloxy shift to the occupied *ortho* position. Thus, the reaction of the *o*-methyl derivative **18a** resulted in the formation of the normal 4-methylbenzoxazolone

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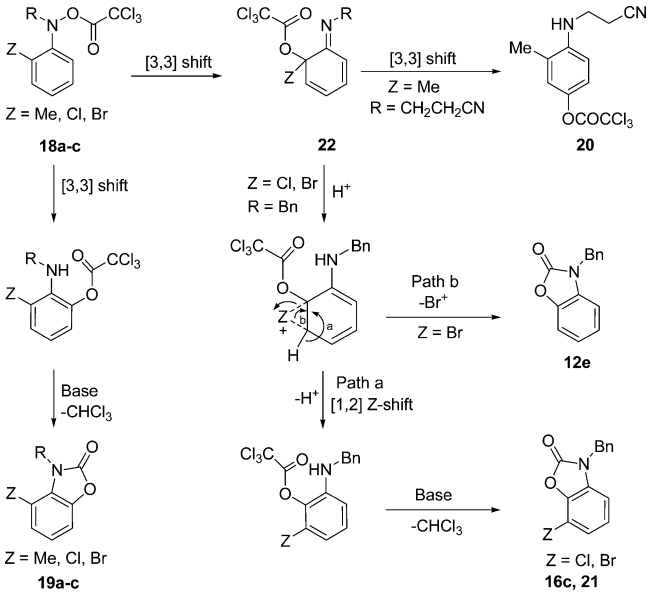
Scheme 5. Proposed Mechanism for the Formation of Products from *Ortho*-Substituted *N*-Alkyl-*N*-arylhydroxylamines



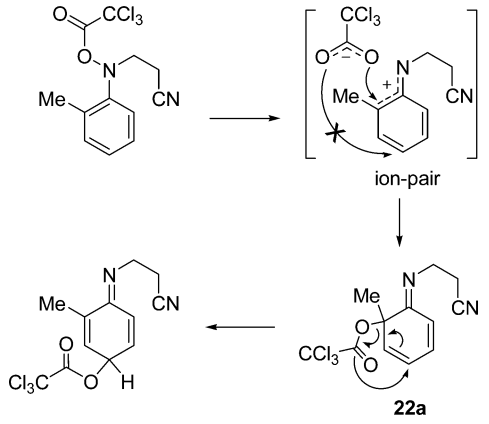
19a along with the *p*-trichloroacetoxyaniline derivative **20** in 47% and 38% isolated yields, respectively. The latter arose probably from the cyclohexadienone imine intermediate **22a** by a second acyloxy shift to the *para* position. Interestingly, the reaction of the *o*-chloro derivative **18b** furnished the normal 4-chlorobenzoxazolone **19b** as the major product in 54% isolated yield along with an unexpected minor product, which was identical to the one obtained as the minor product from the *m*-chloro derivative **14c**, i.e., the 7-chlorobenzoxazolone **16c**, in 22% isolated yield. It was formed probably by 1,2-shift of the chlorine atom to the *meta* position in the intermediate **22b** (Scheme 5). Similarly, the reaction of the *o*-bromo derivative **18c** provided the normal 4-bromobenzoxazolone **19c** as the major product in 64% isolated yield along with a small amount of an inseparable mixture of two compounds. By a detailed spectral analysis of this mixture, it was concluded that the major component was 3-benzyl-7-bromobenzoxazolone **21** formed as a result of 1,2-shift of the bromine atom to the *meta* position in the intermediate **22c** and the other minor component was a compound identical to the one obtained from the reaction of *N*-benzyl-*N*-phenylhydroxylamine **10e**, i.e., 3-benzylbenzoxazolone **12e** (3:2 ratio). The formation of **12e** was interesting. It was akin to reversal of electrophilic aromatic bromination and required loss of a bromonium ion, plausibly as BrCl. The structures of **19a–c** were further confirmed by single-crystal X-ray diffraction data. The product distribution in the reactions of *ortho*- and *meta*-substituted arylhydroxylamines suggested that the substituents follow the same trend in influencing the regioselectivity of the acyloxy shift in both the cases.

In the case of *N*-benzyl-*N*-(4-fluoro-2-methyl)hydroxylamine **23** (Scheme 6), where the *para* position was blocked, the migration occurred exclusively at the *ortho* position to afford the normal benzoxazolone **24** in 54% isolated yield along with the minor trichloroacetanilide derivative **25** in 11% isolated yield, the latter being reminiscent of Scheme 2. Likewise, the reaction of highly substituted *N*-arylhydroxylamine **26** occurred uneventfully to furnish the normal benzoxazolone **27** exclusively in 58% isolated yield.

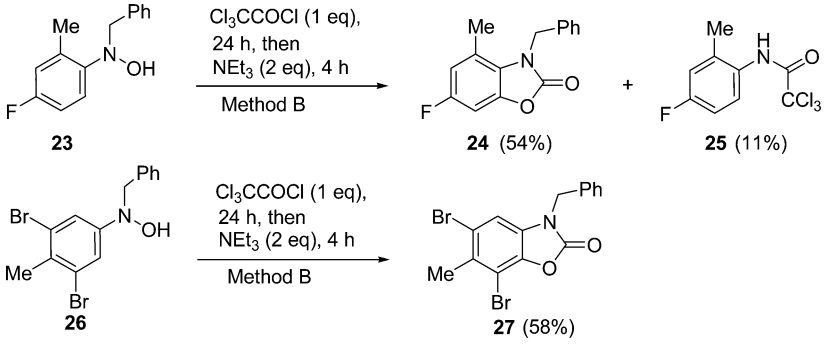
Although trichloroacetyl chloride is known to function as a carbonyl group donor,[61b–d] the reaction of *o*-aminophenol with trichloroacetyl chloride in the presence of Et_3N furnished only *o*-hydroxytrichloroacetanilide. The latter did not cyclize to benzoxazolone probably owing to lower electrophilicity of the trichloroacetamido carbonyl as well as lower nucleophilicity of the phenolic group as compared to those of trichloroacetoxy carbonyl and alkylamino group, respectively.

The aim of the present work was synthesis of benzoxazolones. However, some observations on the key rearrangement step of the synthesis are worth mentioning. The rearrangement of *N*-aryl-*O*-acylhydroxylamine is dominated by acyloxy *ortho*-shift. Isotopic labeling experiments have suggested that the acyloxy *ortho*-shift occurs by a concerted [3,3] sigmatropic acyloxy-shift and/or by heterolysis of the N–O bond to nitrenium cation–acyloxy anion pair (Scheme 7)

Scheme 7. Mechanism of Trichloroacetoxy *Para*-Shift



Scheme 6. Reactions of Polysubstituted *N*-Alkyl-*N*-arylhydroxylamines



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followed by recombination of the ions at the *ortho* position.[57] Stabilization of the ion pair by substituents promotes the ion-pair mechanism. For example, an *N*-phenyl substituent in $Ph_2NOCOPh$ and an *O*-dichloroacetyl substituent in PhN-$(COCH_3)OCOCHCl_2$ led the rearrangement to follow the ion-pair mechanism exclusively. In a rare example of this rearrangement of an *ortho*-substituted substrate *o*-TolN(Boc)-COPh, Tomkinson et al.[56] observed benzoyloxy shift at the *ortho* and *para* positions nonregioselectively. Although the mechanism of *ortho*-shift has been well studied, the precise mechanism of the *para*-shift is not understood. From the literature precedents,[57] it appears that the nature of the substrates studied in the present work would dictate the rearrangement to occur most probably by the ion-pair mechanism exclusively[57] because of appreciable stabilization of the nitrenium cation by the *N*-alkyl substituent and that of the trichloroacetate anion by the trichloromethyl group. The ion-pair may, in principle, recombine at the *ortho* as well as at the *para* positions. The absence of any indication of *para*-shift in the reactions of the *o*-chloro and *o*-bromo substrates **18b** and **18c** and also of the unsubstituted substrates **10a−f**, even when the unoccupied *para* position was available suggested that probably the ion-pair was too tight in the medium used (Et_2O or DCM) to realign and recombine at the *para* position. The same applies to the *o*-methyl derivative **18a** also. The fact that *para*-shift in the reaction of **18a** was indeed observed suggested that probably it occurred by two consecutive shifts, first to the substituted *ortho* position, most probably by the ion-pair mechanism to form the cyclohexadienone imine intermediate **22**. The second shift in **22** might occur by the ion-pair mechanism or by the concerted [3,3]-sigmatropic shift or by both. Clearly, more work is needed to clarify it. However, [3,3] sigmatropic shift appears to be more probable because ion-pair formation would now involve heterolysis of a stronger C−O bond instead of the weaker N−O bond. In the case of *o*-chloro and *o*-bromo derivatives **18b** and **18c**, the *para*-shift could not be observed, probably due to stabilization of the corresponding cyclohexadienone imine intermediate **22** by other faster competing pathways involving migration and/or elimination of the halogen atom. Obviously, an *o*-methyl group of **18a** could not behave in this manner and yielded the *para*-migration product **20**.

CONCLUSION

In conclusion, the present paper describes a method for the synthesis of 3-alkylbenzoxazolones from *N*-alkyl-*N*-arylhydroxylamines by a contiguous trichloroacetylation, trichloroacetoxy *ortho*-shift and cyclization sequence. It uses easily accessible and air-stable nitroarenes as the starting materials and inexpensive reagents. It is mild, wide in scope, economical in the number of synthetic steps, and regioselective. It is applicable to both electron-rich and electron-deficient substrates. Polysubstituted nitroarenes can also be employed in this reaction. In cases where the regioselectivity is not high, giving a mixture of regioisomeric benzoxazolones, it still retains its appeal by offering greater diversity which is highly desirable in medicinal chemistry. Many sensitive bystander groups including alkyl and aryl esters, amide, cyano, and carbon−carbon double bonds survive or are expected to survive under the mild reaction conditions. The *N*-benzylic groups such as benzyl[68] and *p*-methoxybenzyl[69] of the benzoxazolones could be removed by known methods, if needed, thus introducing a branching point in the synthesis and enhancing its synthetic value further.

EXPERIMENTAL SECTION

General Remarks. IR spectra were recorded on an FT-IR spectrometer by taking solid samples as KBr pellets and liquids as thin films on KBr disks. NMR spectra were recorded on a 300 MHz FT NMR spectrometer in $CDCl_3$ with TMS as internal standard. Multiplicities are indicated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), sext (sextet), m (multiplet), dd (doublet doublet), dt (doublet triplet), td (triplet doublet). DEPT spectra were routinely recorded to identify different types of carbons. Mass spectra were recorded on a high-resolution mass spectrometer (ESI-TOF) in positive-ion mode. Melting points were determined on an electrically heated apparatus by taking the samples in a glass capillary sealed at one end and are uncorrected. The progress of the reaction was monitored by TLC using a glass plate coated with a TLC grade silica gel. Iodine was used for visualizing the spots. For column chromatography, silica gel (60−120 mesh) was used as the stationary phase, and *n*-hexane−ethyl acetate mixtures were used as the mobile phase. Solvents were evaporated on a rotary evaporator under reduced pressure using an aspirator. *N*-Arylhydroxylamines were prepared by partial reduction of nitroarenes with Zn dust/NH_4Cl at 25−50 °C as reported.[62] Trichloroacetyl chloride was commercially available and used as received. Et_3N was dried over KOH pellets overnight and distilled over CaH_2. Et_2O was dried over fused $CaCl_2$, distilled, and stored over sodium wires. DCM was dried by distilling over anhydrous K_2CO_3.

Preparation of *N*-Allyl-*N*-arylhydroxylamines 10a, 10h, 10j, 10l, 10o, and 14d. These were prepared by allylation of *N*-arylhydroxylamines (4 mmol) with allyl acetate (4 mmol) in the presence of $Pd(PPh_3)_4$ catalyst (0.16 mmol, 4 mol %)) in THF at room temperature (23−25 °C) in 86−92% isolated yields according to a reported procedure.[63]

*N-Allyl-N-phenylhydroxylamine (**10a**):*[70] colorless liquid, 0.537g, 90%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24−7.29 (m, 2H), 7.13 (d, J = 8.7 Hz, 2H), 6.99 (t, J = 7.2 Hz, 1H), 6.83 (s, 1H, D_2O exchangeable), 5.88−6.02 (m, 1H), 5.16−5.28 (m, 2H), 3.88 (d, J = 6.6 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 152.0, 133.0, 128.7, 122.7, 119.0, 117.2, 62.6 ppm; IR (KBr) ν_{max} 3395 (s, br), 3370 (m), 2928 (w), 1643 (w), 1595 (s), 1490 (s), 1447 (m), 1337 (w), 1210 (m), 1106 (w), 1037 (w), 989 (m), 925 (w), 759 (s), 693 (s) cm^{-1}.

*N-Allyl-N-p-tolylhydroxylamine (**10h**):* colorless liquid, 0.601 g, 92%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08−7.16 (m, 4H), 6.64 (s, 1H, D_2O exchangeable), 5.94−6.09 (m, 1H), 5.22−5.34 (m, 2H), 3.90 (d, J = 6.0 Hz, 2H), 2.34 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 149.6, 133.1, 132.4, 129.2, 118.9, 117.6, 63.0, 20.6 ppm; IR (KBr) ν_{max} 3389 (s, br), 3027 (m), 2992 (m), 2867 (m), 2361 (m), 1613 (w), 1509 (s), 1443 (m), 1376 (w), 1339 (m), 1209 (m), 1042 (w), 991 (w), 925 (m), 819 (s), 754 (w) cm^{-1}; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{10}H_{13}NONa$ 186.0889, found 186.0896.

*N-Allyl-N-(4-chlorophenyl)hydroxylamine (**10j**):*[70] colorless liquid, 0.646 g, 88%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, J = 8.7 Hz, 2H), 7.06 (d, J = 8.7 Hz, 2H), 6.02 (s, 1H, D_2O exchangeable), 5.88−5.99 (m, 1H), 5.22−5.32 (m, 2H), 3.89 (d, J = 6.3 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 150.7, 132.6, 128.7, 127.5, 119.5, 118.1, 62.4 ppm; IR (KBr) ν_{max} 3388 (s, br), 3083 (m), 2928 (m), 2880 (m), 1593 (m), 1488 (s), 1412 (m), 1342 (w), 1286 (w), 1213 (m), 1096 (m), 1045 (w), 1002 (m), 927 (m), 829 (m) cm^{-1}.

*N-Allyl-N-(4-bromophenyl)hydroxylamine (**10l**):* colorless liquid, 0.803 g, 88%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 6.50 (s, 1H, D_2O exchangeable), 5.77−5.89 (m, 1H), 5.12−5.22 (m, 2H), 3.79 (d, J = 6.3 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 151.0, 132.4, 131.6, 119.5, 118.6, 115.1, 62.3 ppm; IR (KBr) ν_{max} 3405 (s), 2909 (m), 1586 (m), 1485 (s), 1410 (m), 1216 (m), 1133 (w), 1068 (w), 996 (m), 929 (m), 822 (s), 695 (w) cm^{-1}; HRMS (ESI-TOF) m/z [M − 2H + Na]$^+$ calcd for $C_9H_8BrNONa$ 247.9681, found 247.9702.

*N-Allyl-N-(4-ethoxylcarbonylphenyl)hydroxylamine (**10o**):* colorless liquid, 0.761 g, 86%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, J = 8.1 Hz, 2H), 7.05 (d, J = 8.1 Hz, 2H), 7.00 (s, 1H, D_2O exchangeable), 5.85−5.97 (m, 1H), 5.19−5.31 (m, 2H), 4.31 (q, J = 7.2 Hz, 2H), 4.04

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(d, J = 5.1 Hz, 2H), 1.35 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 166.9, 155.6, 132.2, 130.6, 122.3, 119.0, 114.4, 60.6, 60.1, 14.2 ppm; IR (KBr) ν_{max} 3383 (m, br), 3081 (w), 2983 (w), 1686 (s), 1603 (s), 1509 (w), 1421 (m), 1369 (m), 1282 (s), 1228 (s), 1179 (m), 1112 (m), 1018 (w), 924 (w), 849 (w), 772 (w) cm^{-1}; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{12}H_{16}NO_3$ 222.1125, found 222.1132.

*N-Allyl-N-(3-bromophenyl)hydroxylamine (**14d**):* colorless liquid, 0.794 g, 87%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (s, 1H), 7.08−7.17 (m, 2H), 7.00 (d, J = 7.5 Hz, 1H), 5.88−6.02 (m, 1H), 5.78 (s, 1H, D_2O exchangeable), 5.24−5.34 (m, 2H), 3.93 (d, J = 6.3 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 153.4, 132.5, 130.0, 125.0, 122.8, 119.5, 115.0, 61.9 ppm; IR (KBr) ν_{max} 3400 (s, br), 3078 (m), 2926 (w), 2856 (w), 1587 (s), 1471 (s), 1424 (m), 1341 (w), 1214 (w), 1065 (w), 990 (m), 927 (m), 776 (m), 684 (m) cm^{-1}; HRMS (ESI-TOF) m/z [M − 2H + Na]$^+$ calcd for $C_9H_8BrNONa$ 247.9681, found 247.9633.

Preparation of *N*-Propyl-*N*-phenylhydroxylamine 10b. Compound **10b** was prepared by reaction of phenylhydroxylamine with propanal followed by reduction of the nitrone with $NaBH_4$ according to a reported procedure for reduction of nitrones with some modifications.[65b] The nitrone was not isolated but reduced in situ as it tends to dimerize with passage of time. A solution of phenylhydroxylamine (0.436 g, 4 mmol) and propanal (0.232g, 0.29 mL, 4 mmol) in ethanol (10 mL) was stirred for 10 min at 0−5 °C. Thin-layer chromatography indicated the disappearance of phenylhydroxylamine after this time. Sodium borohydride (0.152 g, 4 mmol) was added portionwise to this solution at the same temperature. The reaction mixture was stirred for 30 min, and the temperature of the reaction mixture was maintained at 0−5 °C. The volatiles were then removed under reduced pressure. The residual mass was taken up in ethyl acetate (50 mL) and washed with brine (3 × 20 mL). The organic layer was dried (Na_2SO_4), filtered, and evaporated under reduced pressure. The crude product thus obtained was purified by column chromatography (*n*-hexane−ethyl acetate, 4:1 v/v) to obtain *N*-phenyl-*N*-propylhydroxylamine[71] **10b** (0.556 g, 92%) as a colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (t, J = 7.8 Hz, 2H), 7.19 (d, J = 7.8 Hz, 2H), 7.03 (t, J = 7.2 Hz, 1H), 6.98 (s, 1H, D_2O exchangeable), 3.22 (t, J = 7.2 Hz, 2H), 1.72 (sext, J = 7.2 Hz, 2H), 0.97 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 152.9, 128.6, 122.6, 117.3, 62.3, 19.6, 11.5 ppm; IR (KBr) ν_{max} 3375 (m, br), 2965 (s), 2876 (m), 1597 (m), 1489 (m), 1456 (m), 1380 (w), 1221 (w), 1136 (w), 1063 (w), 760 (s), 695 (m) cm^{-1}.

Preparation of *N*-Ethoxycarbonylethyl-*N*-arylhydroxylamines 10c, 10i, 10k, 10m, 10n, and 14a. These were prepared by Michael addition of arylhydroxylamines (4 mmol) to ethyl acrylate (8 mmol) in diethyl ether at room temperature (23−25 °C) under a nitrogen atmosphere in quantitative yields following a reported procedure.[64a] The reaction time varied from 2 h for **10c**, **10i**, **10m**, **10n**, and **14a** to 48 h for **10k**. The products obtained from the reaction mixture were adequately pure and used as such without further purification.

*N-(2-Ethoxycarbonylethyl)-N-phenylhydroxylamine (**10c**):* colorless liquid, 0.837 g, 100%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (t, J = 7.8 Hz, 2H), 7.14 (d, J = 8.1 Hz, 2H), 6.99 (t, J = 7.2 Hz, 1H), 6.68 (s, 1H, D_2O exchangeable), 4.13 (q, J = 7.2 Hz, 2H), 3.55 (t, J = 6.6 Hz, 2H), 2.66 (t, J = 6.6 Hz, 2H), 1.24 (t, J = 6.9 Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 172.8, 152.2, 128.7, 122.6, 116.8, 60.7, 55.6, 32.0, 14.1 ppm; IR (KBr) ν_{max} 3425 (s, br), 3066 (m), 2985 (m), 2904 (w), 1728 (s), 1597 (m), 1491 (m), 1450 (m), 1381 (m), 1179 (s), 1093 (m), 1036 (m), 925 (w), 762 (m), 696 (m) cm^{-1}; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{11}H_{15}NO_3Na$ 232.0944, found 232.0952.

*N-(2-Ethoxycarbonylethyl)-N-(p-tolyl)hydroxylamine (**10i**):* colorless liquid, 0.892 g, 100%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06 (s, 4H), 6.90 (s, 1H, D_2O exchangeable), 4.12 (q, J = 7.2 Hz, 2H), 3.48 (t, J = 6.6 Hz, 2H), 2.64 (t, J = 6.6 Hz, 2H), 2.28 (s, 3H), 1.23 (t, J = 7.2 Hz 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 172.8, 149.9, 132.3, 129.2, 117.3, 60.6, 55.9, 31.8, 20.5, 14.1 ppm; IR (KBr) ν_{max} 3440 (s, br), 2986 (m), 2919 (m), 1731 (s), 1615 (m), 1508 (s), 1450 (s), 1381 (s), 1174 (s), 1033 (s), 929 (m), 821 (s), 688 (m), 530 (m) cm^{-1}; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{12}H_{17}NO_3Na$ 246.1101, found 246.1100.

*N-(4-Chlorophenyl)-N-(2-ethoxycarbonylethyl)hydroxylamine (**10k**):* colorless liquid, 0.974 g, 100%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, J = 8.7 Hz, 2H), 7.07 (d, J = 8.7 Hz, 2H), 6.15 (s, 1H, D_2O exchangeable), 4.15 (q, J = 7.2 Hz, 2H), 3.54 (t, J = 6.6 Hz, 2H), 2.67 (t, J = 6.6 Hz, 2H), 1.26 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 172.8, 150.8, 128.5, 127.5, 118.1, 60.7, 55.5, 31.7, 14.0 ppm; IR (KBr) ν_{max} 3415 (s, br), 2984 (m), 2905 (w), 1729 (s), 1591 (m), 1487 (s), 1445 (m), 1378 (m), 1178 (m), 1094 (m), 1057 (m), 1029 (m), 925 (w), 830 (m), 651 (w) cm^{-1}; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{11}H_{14}ClNO_3Na$ 266.0554, found 266.0550.

*N-(2-Ethoxycarbonylethyl)-N-(4-ethoxycarbonylmethylphenyl)-hydroxylamine (**10m**):* colorless liquid, 1.181 g, 100%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (d, J = 8.7 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 5.47 (s, 1H, D_2O exchangeable), 4.15 (q, J = 7.2 Hz, 4H), 3.55−3.60 (m, 4H), 2.69 (t, J = 6.6 Hz, 2H), 1.23−1.29 (m, 6H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 172.7, 171.9, 151.1, 129.4, 127.9, 116.8, 60.7, 60.5, 55.3, 40.4, 31.6, 14 ppm; IR (KBr) ν_{max} 3421 (s, br), 2884 (s), 1735 (s), 1615 (m), 1512 (s), 1375 (m), 1174 (s), 1029 (s), 928 (w), 817 (m) cm^{-1}; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{15}H_{21}NO_5Na$ 318.1312, found 318.1325.

*N-(2-Ethoxycarbonylethyl)-N-[4-(N′-methyl-N′-phenyl)-aminocarbonylmethyl]phenylhydroxylamine (**10n**):* colorless liquid, 1.426 g, 100%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34−7.41(m, 3H), 7.12(d, J = 6.6 Hz, 2H), 7.01 (d, J = 8.1 Hz, 2H), 6.95 (d, J = 8.1 Hz, 2H), 6.50 (s, 1H, D_2O exchangeable), 4.15 (q, J = 7.2 Hz, 2H), 3.55 (t, J = 6.6 Hz, 2H), 3.40 (s, 2H), 3.27 (s, 3H), 2.68 (t, J = 6.6 Hz, 2H), 1.26 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 172.5, 171.3, 150.5, 143.8, 129.6, 129.3, 127.9, 127.5, 116.9, 60.5, 55.4, 40.0, 37.5, 31.6, 14.1 ppm; IR (KBr) ν_{max} 3327 (s, br), 2981 (w), 2929 (w), 1730 (s), 1643 (s), 1597 (m), 1503 (m), 1430 (m), 1382 (s), 1179 (m), 1120 (m), 1059 (w), 817 (w), 776 (w), 702 (w) cm^{-1}; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{20}H_{24}N_2O_4Na$ 379.1628, found 379.1641.

*N-(2-Ethoxylcarbonylethyl)-N-(m-tolyl)hydroxylamine (**14a**):* colorless liquid, 0.891 g, 100%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (t, J = 7.5 Hz, 1H), 6.96−7.01 (m, 2H), 6.84 (d, J = 6.9 Hz, 1H), 6.08 (s, 1H, D_2O exchangeable), 4.18 (q, J = 7.2 Hz, 2H), 3.59 (t, J = 6.9 Hz, 2H), 2.71 (t, J = 6.6 Hz, 2H), 2.34 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 172.8, 152.2, 138.4, 128.5, 123.4, 117.6, 114.0, 60.6, 55.6, 31.8, 21.5, 14.1 ppm; IR (KBr) ν_{max} 3427 (s, br), 2983 (m), 2917 (m), 1732 (s), 1599 (m), 1485 (m), 1449 (m), 1378 (m), 1248 (m), 1189 (s), 1094 (w), 1057 (m), 859 (w), 783 (m), 698 (m) cm^{-1}; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{12}H_{17}NO_3Na$ 246.1101, found 246.1109.

Preparation of *N*-Cyanoethyl-*N*-arylhydroxylamines 10d, 14b, and 18a. These were prepared by Michael addition of arylhydroxylamines (4 mmol) to acrylonitrile (4 mmol) in diethyl ether at room temperature (23−25 °C) under a nitrogen atmosphere in quantitative yields following a reported procedure.[64b] The reaction time varied from 1 h for **10d**, **18a** to 8 h for **14b**. The products obtained from the reaction mixture were adequately pure and used as such without further purification.

*N-(2-Cyanoethyl)-N-phenylhydroxylamine (**10d**):*[64b] colorless liquid, 0.647 g, 100%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (t, J = 7.2 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 7.05 (t, J = 7.2 Hz, 1H), 5.95 (s, 1H, D_2O exchangeable), 3.52 (t, J = 6.6 Hz, 2H), 2.71 (t, J = 6.6 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 151.4, 128.9, 123.2, 118.8, 117.0, 55.1, 15.2 ppm; IR (KBr) ν_{max} 3362 (s), 3063 (w), 2913 (w), 2259 (w), 1597 (m), 1491 (s), 1449 (m), 1423 (m), 1373 (w), 1249 (m), 1206 (w), 1059 (w), 917 (w), 891 (w), 758 (s), 690 (s) cm^{-1}.

*N-(2-Cyanoethyl)-N-(3-methoxycarbonylphenyl)hydroxylamine (**14b**):* colorless liquid, 0.881 g, 100%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.71−7.45 (m, 1H), 7.34−7.43 (m, 2H), 5.91 (s, 1H, D_2O exchangeable), 3.93 (s, 3H), 3.60 (t, J = 6.6 Hz, 2H), 2.77 (t, J = 6.6 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 167.1, 151.8, 130.6, 129.0, 123.9, 121.2, 118.6, 117.5, 54.7, 52.2, 15.3 ppm; IR (KBr) ν_{max} 3385 (m, br), 2954 (w), 2253 (w), 1718 (s), 1593 (m), 1442 (m),

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1297 (m), 1258 (m), 1198 (w), 1110 (m), 990 (w), 758 (m) cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{11}H_{12}N_2O_3Na$ 243.0740, found 243.0736.

*N-(2-Cyanoethyl)-N-(o-tolyl)hydroxylamine (**18a**):* colorless liquid, 0.704 g, 100%; ^1H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, J = 7.8 Hz, 1H), 7.22 (t, J = 8.1 Hz, 1H), 7.06−7.17 (m, 2H), 5.70 (s, 1H, D_2O exchangeable), 3.16 (t, J = 6.3 Hz, 2H), 2.76 (t, J = 6.3 Hz, 2H), 2.04 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 150.4, 130.8, 130.2, 126.7, 125.6, 119.5, 118.7, 55.1, 17.5, 16.4 ppm; IR (KBr) ν_{max} 3413 (s), 2896 (w), 2253 (w), 1485 (m) 1440 (m), 1413 (m), 1185 (m), 1054 (m), 900 (w), 772 (m), 728 (w), 574 (w) cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{10}H_{12}N_2ONa$ 199.0842, found 199.0843.

Preparation of *N*-Benzyl-*N*-arylhydroxylamines 10e−g, 14c, 18b, 18c, 23, and 26. These were prepared from nitroarenes in two steps following a reported procedure.[65] A solution of the nitroarene (20 mmol) and NH_4Cl (10 mmol) in H_2O−EtOH (1:1 v/v) was treated with Zn dust (40 mmol) at 25−50 °C for 2 h, and the *N*-arylhydroxylamine thus formed was treated with a solution of benzaldehyde (20 mmol) in AcOH in situ at room temperature for 1 h to give *N*-benzylidenearylamine oxide (nitrone) in 75−84% isolated yields. The nitrones (4 mmol) were then reduced with $NaBH_4$ (6 mmol) in methanol at 5−10 °C for 1 h to afford the *N*-benzyl-*N*-arylhydroxylamines in 82−88% yields. The nitrones (*N*-benzylidenebenzenamine oxide,[72] *N*-(4-methoxybenzylidene)benzenamine oxide,[72] and *N*-benzylidene-3-chlorobenzenamine oxide[73]) are reported in the literature with their spectral data.

*N-Benzyl-N-phenylhydroxylamine (**10e**):* colorless needles, 0.654 g, 82%; mp 86 °C (*n*-hexane−chloroform) (lit.[74] mp 87−88 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 7.22−7.28 (m, 7H), 7.11(d, J = 7.8 Hz, 2H), 6.98 (t, J = 7.2 Hz, 1H), 6.20 (s, 1H, D_2O exchangeable), 4.26 (s, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 152.3, 136.8, 129.3, 128.7, 128.3, 127.5, 122.7, 117.2, 64.4 ppm; IR (KBr) ν_{max} 3367 (m, br), 3030 (w), 2886 (w), 2840 (w), 1590 (m), 1485 (m), 1448 (m), 1346 (m), 1178 (m), 1155 (w), 997 (m), 899 (w), 752 (m), 691 (s), 541 (m) cm^{-1}.

*N-(4-Methoxybenzyl)-N-phenylhydroxylamine (**10f**):*[75] colorless flakes, 0.807 g, 88%; mp 74 °C (*n*-hexane−chloroform); ^1H NMR (300 MHz, $CDCl_3$) δ 7.19−7.28 (m, 4H), 7.12 (d, J = 8.1 Hz, 2H), 6.98 (t, J = 7.2 Hz, 1H), 6.78 (d, J = 8.1 Hz, 2H), 6.25 (s, 1H, D_2O exchangeable), 4.22 (s, 2H), 3.73 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 158.9, 152.4, 130.6, 128.9, 128.6, 122.6, 117.3, 113.6, 63.8, 55.1 ppm; IR (KBr) ν_{max} 3292 (s, br), 3003 (m), 2889 (m), 2836 (m), 1608 (m), 1512 (s), 1461 (m), 1349 (m), 1251 (s), 1181 (m), 1031 (m), 899 (m), 824 (m), 788 (m), 692 (m), 550 (s) cm^{-1}.

4-Acetoxy-N-benzylidenebenzenamine oxide: colorless flakes, 3.981 g, 78%; mp 80 °C (*n*-hexane−chloroform); ^1H NMR (300 MHz, $CDCl_3$) δ 8.38−8.41 (m, 2H), 7.90 (s, 1H), 7.81 (d, J = 9.0 Hz, 2H), 7.47−7.50 (m, 3H), 7.22 (d, J = 8.7 Hz, 2H), 2.33 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 168.9, 151.5, 146.4, 134.7, 131.1, 130.5, 129.1, 128.6, 122.9, 122.3, 21.0 ppm; IR (KBr) ν_{max} 3054 (w), 1757 (s), 1497 (m), 1435 (m), 1368 (m), 1194 (s), 1068 (m), 1011 (m), 907 (m), 683 (m) cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{15}H_{13}NO_3Na$ 278.0788, found 278.0796.

*N-(4-Acetoxyphenyl)-N-benzylhydroxylamine (**10g**):* colorless flakes, 0.886 g, 86%; mp 72 °C (*n*-hexane−chloroform); ^1H NMR (300 MHz, $CDCl_3$) δ 7.31−7.41 (m, 5H), 7.23 (d, J = 8.7 Hz, 2H), 7.04 (d, J = 8.7 Hz, 2H), 5.25 (s, 1H, D_2O exchangeable), 4.37 (s, 2H), 2.30 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 169.8, 150.5, 145.9, 129.1, 128.4, 127.6, 121.6, 118,0, 64.7, 21.0 ppm; IR (KBr) ν_{max} 3287 (m, br), 3000 (w), 2854 (w), 1748 (s), 1499 (m), 1427 (m), 1371 (m), 1186 (s), 1019 (m), 907 (m), 844 (m), 738 (m), 703 (m) cm^{-1}; HRMS (ESI-TOF) m/z $[M - 2H + Na]^+$ calcd for $C_{15}H_{13}NO_3Na$ 278.0788, found 278.0797.

*N-Benzyl-N-(3-chlorophenyl)hydroxylamine (**14c**):* colorless flakes, 0.804 g, 86%; mp 42 °C (*n*-hexane−chloroform); ^1H NMR (300 MHz, $CDCl_3$) δ 7.31 (s, 5H), 7.13−7.22 (m, 2H), 6.94−6.97 (m, 2H), 5.90 (s, 1H, D_2O exchangeable), 4.30 (s, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 153.6, 136.5, 134.6, 129.7, 129.1, 128.4, 127.7, 122.3, 116.9, 114.8, 63.9 ppm; IR (KBr) ν_{max} 3219 (m, br), 3062 (w), 3032 (w), 2880 (m), 1588 (s), 1462 (m), 1348 (w), 1185 (m), 1073 (m), 1025 (m), 914 (m), 877 (m), 776 (m), 744 (m), 693 (s), 576 (m) cm^{-1}; HRMS (ESI-TOF) m/z $[M - 2H + H]^+$ calcd for $C_{13}H_{11}ClNO$ 232.0524, found 232.0522.

N-Benzylidene-2-chlorobenzenamine oxide:[76] colorless flakes, 3.753 g, 81%; mp 38 °C (*n*-hexane−chloroform); ^1H NMR (300 MHz, $CDCl_3$) δ 8.34−8.38 (m, 2H), 7.56−7.60 (m, 2H), 7.46−7.50 (m, 4H), 7.35−7.40 (m, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 146.4, 138.9, 131.1, 130.5, 130.4, 129.8, 129.0, 128.5, 127.7, 127.1, 125.5 ppm; IR (KBr) ν_{max} 3236 (m), 3060 (m), 1698 (m), 1586 (m), 1475 (m), 1447 (m), 1405 (s), 1300 (m), 1196 (m), 1095 (m), 1045 (m), 887 (m), 757 (s), 689 (m), 654 (m) cm^{-1}.

*N-Benzyl-N-(2-chlorophenyl)hydroxylamine (**18b**):* colorless needles, 0.795 g, 85%; mp 85 °C (*n*-hexane−chloroform); ^1H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, J = 7.8 Hz, 1H), 7.46 (d, J = 6.6 Hz, 2H), 7.24−7.37 (m, 5H), 7.08 (t, J = 7.5 Hz, 1H), 6.20 (s, 1H, D_2O exchangeable), 4.16 (s, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 149.6, 137.0, 129.8, 129.5, 128.2, 127.6, 127.5, 125.6, 121.1, 64.1 ppm; IR (KBr) ν_{max} 3212 (m, br), 3062 (m), 3031 (m), 2891 (m), 1585 (w), 1458 (m), 1337 (w), 1184 (m), 1124 (m), 1046 (m), 752 (s), 701 (s), 556 (w) cm^{-1}; HRMS (ESI-TOF) m/z $[M - 2H + H]^+$ calcd for $C_{13}H_{11}ClNO$ 232.0524, found 232.0523.

N-Benzylidene-2-bromobenzenamine oxide:[76] colorless flakes, 4.528 g, 82%; mp 36 °C (*n*-hexane−chloroform); ^1H NMR (300 MHz, $CDCl_3$) δ 8.35−8.38 (m, 2H), 7.66 (d, J = 7.8 Hz, 1H), 7.58 (d, J = 6.9 Hz, 1H), 7.56 (s, 1H), 7.47−7.52 (m, 3H), 7.41 (t, J = 7.8 Hz, 1H), 7.27−7.32 (m, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 147.9, 139.0, 133.6, 131.2, 130.6, 129.7, 129.1, 128.6, 128.4, 125.5, 116.3 ppm; IR (KBr) ν_{max} 3061 (w), 2924 (w), 1699 (w), 1586 (m), 1530 (m), 1469 (s), 1401 (m), 1196 (m), 1085 (m), 1033 (m), 886 (w), 756 (s), 693 (m) cm^{-1}.

*N-Benzyl-N-(2-bromophenyl)hydroxylamine (**18c**):* colorless needles, 0.934 g, 84%; mp 78 °C (*n*-hexane−chloroform); ^1H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, J = 8.1 Hz, 1H), 7.49−7.55 (m, 3H), 7.25−7.31 (m, 4H), 7.01 (t, J = 7.5 Hz, 1H), 5.83 (s, 1H, D_2O exchangeable), 4.16 (s, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 150.9, 137.1, 133.0, 129.4, 128.2, 128.2, 127.6, 126.2, 121.6, 116.0, 64.4 ppm; IR (KBr) ν_{max} 3213 (m, br), 3058 (m), 3030 (m), 2888 (w), 1581 (w), 1494 (w), 1457 (s), 1336 (w), 1185 (m), 1082 (w), 1018 (m), 893 (m), 751 (s), 696 (s), 555 (m) cm^{-1}; HRMS (ESI-TOF) m/z $[M - 2H + Na]^+$ calcd for $C_{13}H_{10}BrNONa$ 297.9838, found 297.9835.

N-Benzylidene-4-fluoro-2-methylbenzenamine oxide: colorless cubes, 3.438 g, 75%; mp 80 °C (*n*-hexane−chloroform); ^1H NMR (300 MHz, $CDCl_3$) δ 8.33−8.37 (m, 2H), 7.56 (s, 1H), 7.48−7.51 (m, 3H), 7.39 (dd, J_{HF} = 8.4 Hz, J_{HH} = 5.1 Hz, 1H), 6.93−7.03 (m, 2H), 2.44 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 162.28 (d, J_{CF} = 249.1 Hz), 145.0, 137.7, 134.62 (d, J_{CF} = 8.3 Hz), 131.0, 130.2, 128.7, 128.6, 125.12 (d, J_{CF} = 9.5 Hz), 117.98 (d, J_{CF} = 22.6 Hz), 113.35 (d, J_{CF} = 22.6 Hz), 17.2 ppm; IR (KBr) ν_{max} 3061 (w), 3026 (w), 1618 (w), 1583 (m), 1444 (s), 1396 (s), 1268 (m), 1187 (s), 1152 (m), 1111 (m), 1064 (m), 878 (m), 814 (m), 761 (m), 722 (m), 535 (m) cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{14}H_{12}FNONa$ 252.0795, found 252.0793.

*N-Benzyl-N-(4-fluoro-2-methylphenyl)hydroxylamine (**23**):* colorless flakes, 0.778 g, 84%; mp 66 °C (*n*-hexane−chloroform); ^1H NMR (300 MHz, $CDCl_3$) δ 7.54 (dd, J_{HF} = 8.7 Hz, J_{HF} = 5.7 Hz, 1H), 7.32−7.41 (m, 5H), 6.85−6.94 (m, 2H), 6.09 (s, 1H, D_2O exchangeable), 4.01 (s, 2H), 2.31 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 160.03 (d, J_{CF} = 243.1 Hz), 147.23 (d, J_{CF} = 3.0 Hz), 137.0, 132.59 (d, J_{CF} = 7.5 Hz), 129.3, 128.3, 127.5, 121.65 (d, J_{CF} = 9.1 Hz), 116.68 (d, J_{CF} = 21.9 Hz), 113.06 (d, J_{CF} = 21.9 Hz), 65.1, 17.74 (d, J_{CF} = 0.8 Hz) ppm; IR (KBr) ν_{max} 3362 (s, br), 3034 (w), 2898 (w), 2851 (m), 1590 (w), 1490 (s), 1446 (m), 1351 (m), 1267 (m), 1225 (m), 1178 (m), 987 (m), 863 (m), 726 (m), 568 (m) cm^{-1}; HRMS (ESI-TOF) m/z $[M - 2H + Na]^+$ calcd for $C_{14}H_{12}FNONa$ 252.0795, found 252.0792.

N-Benzylidene-3,5-dibromo-4-methylbenzenamine oxide: colorless needles, 5.609 g, 76%; mp 112 °C (*n*-hexane−chloroform); ^1H NMR (300 MHz, $CDCl_3$) δ 8.37−8.41 (m, 2H), 8.01 (s, 2H), 7.88 (s, 1H), 7.50−7.52 (m, 3H), 2.64 (s, 3H) ppm; ^{13}C NMR (75.5 MHz,

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$CDCl_3$) δ 147.4, 139.6, 134.6, 131.4, 130.2, 129.2, 128.7, 125.0, 124.9, 23.5 ppm; IR (KBr) ν_{max} 3094 (w), 3051 (m), 1579 (m), 1547 (m), 1445 (s), 1418 (s), 1375 (m), 1301 (w), 1206 (w), 1177 (m), 1089 (s), 998 (m), 872 (m), 856 (m), 760 (m), 735 (m), 689 (s) cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{14}H_{11}Br_2NONa$ 389.9100, found 389.9083.

*N-Benzyl-N-(3,5-dibromo-4-methylphenyl)hydroxylamine (**26**):* colorless liquid, 1.276 g, 86%, purified by column chromatography using *n*-hexane−ethyl acetate (8:2 v/v); ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (s, 7H), 6.00 (s, 1H, D_2O exchangeable), 4.20 (s, 2H), 2.44 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 151.7, 136.3, 130.6, 129.1, 128.5, 127.8, 125.0, 120.0, 63.9, 22.8 ppm; IR (KBr) ν_{max} 3244 (m, br), 3025 (m), 2886 (m), 2844 (m), 1591 (w), 1481 (m), 1379 (w), 1339 (w), 1175 (m), 1110 (w), 1043 (m), 1014 (m), 902 (m), 748 (m), 727 (m), 689 (s), 562 (m) cm^{-1}; HRMS (ESI-TOF) m/z $[M - 2H + Na]^+$ calcd for $C_{14}H_{11}Br_2NONa$ 389.9100, found 389.9085.

Synthesis of Benzoxazolones. *Typical Procedures. Method A. 3-Allylbenzoxazolone (**12a**).* A solution of *N*-allyl-*N*-phenylhydroxylamine (**10a**) (0.298 g, 2 mmol) in dry diethyl ether (30 mL) was protected from atmospheric moisture by a guard tube ($CaCl_2$). The solution was magnetically stirred and cooled to 0−5 °C in a small ice bath. Triethylamine (0.405 g, 0.56 mL, 4 mmol) was injected into the stirred solution through a rubber septum, and then trichloroacetyl chloride (0.364 g, 0.23 mL, 2 mmol) was injected slowly. The stirring was continued. The reaction mixture attained room temperature (23−25 °C) gradually during about 25 min. The stirring was continued at this temperature, and the progress of the reaction was monitored by TLC, which indicated completion of the reaction after a total time of 8 h. The reaction mixture was diluted with ethyl acetate (50 mL) and washed with brine (2 × 30 mL). The organic layer was dried (Na_2SO_4), filtered, and evaporated under reduced pressure. The crude product thus obtained was further purified by column chromatography using *n*-hexane−ethyl acetate mixture (9:1 v/v) as the solvent for elution to obtain 3-allylbenzoxazolone (0.301 g, 86%) as colorless flakes: mp 41 °C (*n*-hexane−ethyl acetate) (lit.[77] mp 40−41.5 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 7.01−7.20 (m, 3H), 6.90 (d, J = 7.2 Hz, 1H), 5.77−5.91 (m, 1H), 5.24 (d, J = 14.1 Hz, 2H), 4.39 (d, J = 4.5 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 154.2, 142.5, 130.7, 130.4, 123.7, 122.4, 118.6, 109.8, 108.8, 44.4 ppm; IR (KBr) ν_{max} 3069 (w), 2926 (w), 1778 (s), 1694 (w), 1603 (w), 1487 (m), 1436 (w), 1362 (m), 1245 (m), 1158 (w), 1079(w), 1018 (w), 928 (w), 752 (m), 696 (w) cm^{-1}.

*Method B. 3-Benzylbenzoxazolone (**12e**).* A solution of *N*-benzyl-*N*-phenylhydroxylamine (**10e**) (0.398 g, 2 mmol) in dry DCM (30 mL) was protected from atmospheric moisture using a guard tube ($CaCl_2$) and cooled to 0−5 °C in a small ice−water bath. Trichloroacetyl chloride (0.364 g, 0.23 mL, 2 mmol) was slowly injected into this solution with stirring through a rubber septum. The stirring was continued, and the reaction mixture was allowed to attain room temperature (23−25 °C) slowly, which took about 25 min. The stirring was continued at this temperature. After treatment with trichloroacetyl chloride in this manner for a total time of 6 h, the reaction mixture was cooled again to 0−5 °C in a small ice bath. Triethylamine (0.405 g, 0.56 mL, 4 mmol) was injected slowly to the stirred solution, and stirring was continued. The reaction temperature reached room temperature (23−25 °C) in about 25 min. The stirring was continued at this temperature, and the progress of the reaction was monitored by TLC, which indicated completion of the reaction after a total of 3 h of treatment with triethylamine. The reaction mixture was diluted with ethyl acetate (50 mL) and washed with brine (2 × 30 mL). The organic layer was dried (Na_2SO_4), filtered, and evaporated under reduced pressure. The residual mass was purified by column chromatography using *n*-hexane−ethyl acetate mixture (9:1 v/v) as the solvent for elution to obtain 3-benzylbenzoxazolone (0.378 g, 84%) as colorless needles: mp 126 °C (*n*-hexane−ethyl acetate) (lit.[78] mp 130 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 7.29−7.35 (m, 5H), 7.16−7.21 (m, 1H), 7.09 (d, J = 3.6 Hz, 1H), 7.07 (d, J = 3.6 Hz, 1H), 6.82−6.86 (m, 1H), 4.99 (s, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 154.7, 142.6, 134.6, 130.7, 128.9, 128.2, 127.6, 123.8, 122.5, 110.0, 108.9, 46.0 ppm; IR (KBr) ν_{max} 3073 (m), 3032 (w), 2356 (w), 1757 (s), 1614 (m), 1483 (s), 1355 (s), 1234 (s), 1146 (m), 1073 (m), 1008 (m), 910 (m), 742 (s), 688 (s), 561 (w) cm^{-1}.

*3-(2-Cyanoethyl)-5-methoxycarbonylbenzoxazolone (**15b**), 3-(2-Cyanoethyl)-7-methoxycarbonylbenzoxazolone (**16b**), and Methyl 3-(2,2,2-Trichloroacetamido)benzoate (**17**): Reaction of N-(2-Cyanoethyl)-N-(3-methoxycarbonyl)phenylhydroxylamine **14b** (Method B).* The reaction was performed by taking **14b** (0.440 g, 2 mmol), trichloroacetyl chloride (0.364 g, 0.23 mL, 2 mmol), and Et_3N (0.405 g, 0.56 mL, 4 mmol) in DCM (30 mL). Initially, **14b** was treated with trichloroacetyl chloride for 36 h, and then the resulting reaction mixture was treated with Et_3N for 4 h. Usual workup followed by purification of the crude product by column chromatography using *n*-hexane−ethyl acetate mixture (4:1 v/v) as the solvent for elution first gave methyl 3-(2,2,2-trichloroacetamido)benzoate (**17**) (0.107 g, 18%) as colorless flakes, mp 58 °C (*n*-hexane−ethyl acetate): ^1H NMR (300 MHz, $CDCl_3$) δ 8.36 (s, 1H, D_2O exchangeable), 8.06 (s, 1H), 7.82−7.87 (m, 2H), 7.43 (t, J = 7.8 Hz, 1H), 3.87 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 166.2, 159.4, 136.2, 131.3, 129.5, 127.0, 124.6, 121.4, 92.6, 52.4 ppm; IR (KBr) ν_{max} 3334 (s), 3080 (w), 1708 (s), 1552 (m), 1448 (w), 1436 (w), 1297 (m), 1203 (m), 1122 (w), 1002 (w), 903 (w), 842 (m), 811 (m), 753 (m), 651 (m) cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{10}H_8Cl_3NO_3Na$ 317.9462, found 317.9468.

Further elution of the column with *n*-hexane−ethyl acetate (3:7 v/v) provided a mixture of **15b** and **16b** as a colorless solid, which was separated by recrystallization from *n*-hexane−ethyl acetate. The less soluble 3-(2-cyanoethyl)-7-methoxycarbonylbenzoxazolone (**16b**) recrystallized first almost completely as colorless cubes (0.128 g, 26%): mp 158 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.81 (dd, J = 6.6, 2.7 Hz, 1H), 7.29−7.36 (m, 2H), 4.19 (t, J = 6.6 Hz, 2H), 4.01 (s, 3H), 2.92 (t, J = 6.6 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 164.0, 153.6, 142.1, 131.2, 125.0, 123.9, 116.6, 114.7, 112.1, 52.6, 38.5, 16.9 ppm; IR (KBr) ν_{max} 3088 (w), 3052 (m), 2963 (m), 2254 (w), 1770 (s), 1720 (s), 1611 (m), 1468 (m), 1363 (m), 1306 (m), 1256 (m), 1206 (m), 1141 (m), 984 (m), 918 (m), 755 (s) cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{12}H_{10}N_2O_4Na$ 269.0533, found 269.0533.

The mother liquor was evaporated under reduced pressure, and the solid thus obtained was recrystallized from *n*-hexane−chloroform to obtain 3-(2-cyanoethyl)-5-methoxycarbonylbenzoxazolone (**15b**) (0.202 g, 41%) as colorless needles: mp 156 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, J = 8.4 Hz, 1H), 7.77 (s, 1H), 7.29 (d, J = 8.4 Hz, 1H), 4.18 (t, J = 6.9 Hz, 2H), 3.94 (s, 3H), 2.91 (t, J = 6.9 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 165.9, 153.7, 145.8, 130.3, 126.7, 125.7, 116.4, 110.2, 109.3, 52.5, 38.4, 16.7 ppm; IR (KBr) ν_{max} 3067 (w), 2952 (m), 2250 (w), 1772 (s), 1718 (s), 1618 (m), 1492 (m), 1464 (m), 1362 (m), 1254 (s), 1108 (m), 1078 (m), 973 (w), 909 (w), 761 (m) cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{12}H_{10}N_2O_4Na$ 269.0533, found 269.0536.

*3-Benzyl-4-chlorobenzoxazolone (**19b**) and 3-Benzyl-7-chlorobenzoxazolone (**16c**): Reaction of N-Benzyl-N-(2-chloro)-phenylhydroxylamine (**18b**) (Method B).* The reaction was performed by taking **18b** (0.467 g, 2 mmol), trichloroacetyl chloride (0.364 g, 0.23 mL, 2 mmol), and Et_3N (0.405 g, 0.56 mL, 4 mmol) in DCM (30 mL). Initially, **18b** was treated with trichloroacetyl chloride for 24 h and then the resulting reaction mixture was treated with Et_3N for 4 h. Usual workup followed by purification of the crude product by column chromatography using *n*-hexane−ethyl acetate (8:2 v/v) as the solvent for elution gave a mixture of **19b** and **16c** as a colorless solid, which was separated by recrystallization from *n*-hexane-chloroform. 3-Benzyl-4-chlorobenzoxazolone (**19b**) was less soluble and recrystallized first as colorless plates (0.280 g, 54%): mp 81 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.29−7.37 (m, 5H), 7.03−7.18 (m, 3H), 5.37 (s, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 154.6, 143.8, 136.1, 128.8, 127.9, 127.5, 127.1, 125.7, 123.1, 114.9, 108.8, 46.5 ppm; IR (KBr) ν_{max} 3067 (w), 3036 (m), 2935 (w), 1758 (s), 1598 (m), 1456 (m), 1355 (s), 1258 (m), 1060 (m), 1008 (m), 945 (m), 783 (m), 747 (m), 702 (s), 640 (m), 531 (m) cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{14}H_{10}Cl_1NO_2Na$ 282.0292, found 282.0292.

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The mother liquor was evaporated under reduced pressure, and the solid thus obtained was recrystallized from *n*-hexane−ethyl acetate to obtain 3-benzyl-7-chlorobenzoxazolone (**16c**) (0.114 g, 22%) as colorless needles: mp 114 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (s, 5H), 7.00−7.11 (m, 2H), 6.74 (d, J = 7.5 Hz, 1H), 5.01 (s, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 153.9, 139.2, 134.2, 131.9, 129.1, 128.5, 127.6, 124.5, 123.2, 115.7, 107.3, 46.5 ppm; IR (KBr) ν_{max} 3056 (w), 2924 (w), 1764 (s), 1617 (m), 1473 (m), 1344 (m), 1212 (w), 1137 (w), 1020 (m), 755 (m), 705 (m) cm^{-1}; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{14}H_{10}Cl_1NO_2Na$ 282.0292, found 282.0291.

3-Propylbenzoxazolone (**12b**):[79] colorless liquid, 0.319 g, 90%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07−7.21 (m, 3H), 6.98 (d, J = 7.5 Hz, 1H), 3.79 (t, J = 6.6 Hz, 2H), 1.82 (sext, J = 7.2 Hz, 2H), 1.00 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 154.6, 142.6, 131.2, 123.7, 122.2, 109.9, 108.2, 43.8, 21.1, 11.1 ppm; IR (KBr) ν_{max} 2968 (m), 2938 (m), 2877 (w), 1782 (s), 1614 (m), 1486 (m), 1363 (m), 1245 (m), 1128 (w), 1073 (m), 1015 (m), 964 (m), 752 (m), 682 (w) cm^{-1}.

3-(2-Ethoxycarbonylethyl)benzoxazolone (**12c**): colorless flakes; mp 42 °C (*n*-hexane−ethyl acetate) (lit.[80] mp 42−44 °C); 0.343 g, 73%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (t, J = 7.2 Hz, 2H), 7.12 (t, J = 7.5 Hz, 2H), 4.08−4.17 (m, 4H), 2.84 (t, J = 6.9 Hz, 2H), 1.22 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 170.8, 154.3, 142.6, 130.8, 123.8, 122.4, 110.0, 108.6, 61.0, 38.0, 32.4, 14.0 ppm; IR (KBr) ν_{max} 2984 (w), 1779 (s), 1732 (s), 1625 (w), 1486 (m), 1365 (m), 1253 (m), 1194 (m), 1149 (w), 1094 (w), 1050 (w), 1021 (w), 944 (w), 752 (m) cm^{-1}.

3-(2-Cyanoethyl)benzoxazolone (**12d**): colorless cubes; mp 118 °C (*n*-hexane−ethyl acetate) (lit.[80] mp 120 °C); 0.320 g, 85%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10−7.27 (m, 4H), 4.14 (t, J = 6.6 Hz, 2H), 2.88 (t, J = 6.6 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 153.9, 142.4, 130.0, 124.2, 123.1, 116.8, 110.4, 108.2, 38.1, 16.8 ppm; IR (KBr) ν_{max} 3045 (w), 2979 (w), 2936 (w), 2251 (w), 1777 (s), 1613 (w), 1482 (m), 1447 (m), 1363 (s), 1249 (m), 1222 (m), 1152 (w), 1095 (w), 1048 (w), 940 (w), 904 (w), 756 (s), 673 (w) cm^{-1}.

3-(4-Methoxybenzyl)benzoxazolone (**12f**): colorless plates; mp 108 °C (*n*-hexane−ethyl acetate); 0.398 g, 78%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, J = 8.4 Hz, 2H), 7.17−7.21 (m, 1H), 7.06−7.10 (m, 2H), 6.84−6.88 (m, 3H), 4.94 (s, 2H), 3.78 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 159.5, 154.7, 142.7, 130.8, 129.1, 126.8, 123.7, 122.4, 114.3, 110.0, 108.9, 55.3, 45.6 ppm; IR (KBr) ν_{max} 3019 (w), 2960 (w), 2835 (w), 1756 (s), 1612 (m), 1511 (m), 1482 (m), 1356 (m), 1242 (s), 1175 (m), 1147 (m), 1072 (m), 1023 (m), 826 (m), 754 (s), 676 (m) cm^{-1}; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{15}H_{13}NO_3Na$ 278.0788, found 278.0788.

3-Benzyl-6-acetoxybenzoxazolone (**12g**): colorless flakes; mp 92 °C (*n*-hexane−ethyl acetate); 0.351 g, 62%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (s, 5H), 7.03 (d, J = 1.5 Hz, 1H), 6.8−6.83 (m, 2H), 5.00 (s, 2H), 2.29 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 169.5, 154.8, 146.0, 142.5, 134.3, 129, 128.5, 128.4, 127.6, 117.0, 108.8, 105.1, 46.2, 20.9 ppm; IR (KBr) ν_{max} 3084 (w), 2942 (w), 1787 (s), 1751 (s), 1625 (w), 1496 (s), 1449 (m), 1369 (m), 1341 (m), 1223 (s), 1159 (m), 1002 (m), 897 (w), 737 (w), 660 (w) cm^{-1}; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{16}H_{13}NO_4Na$ 306.0737, found 306.0724.

3-Allyl-6-methylbenzoxazolone (**12h**): colorless liquid, 0.333 g, 88%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.02 (s, 1H), 6.95 (d, J = 7.8 Hz, 1H), 6.83 (d, J = 8.1 Hz, 1H), 5.81−5.92 (m, 1H), 5.24−5.29 (m, 2H), 4.42 (d, J = 5.4 Hz, 2H), 2.40 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 154.5, 142.6, 132.6, 130.5, 128.4, 124.1, 118.5, 110.5, 108.4, 44.5, 21.3 ppm; IR (KBr) ν_{max} 2923 (w), 1777 (s), 1683 (w), 1642 (w), 1503(m), 1445 (m), 1366 (m), 1290 (w), 1264(m), 1183 (w), 1081 (w), 1007 (w), 936 (m), 862 (w), 805 (m), 749 (w), 702 (w), 592 (w) cm^{-1}; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{11}H_{12}NO_2$ 190.0863, found 190.0869.

3-(2-Ethoxycarbonylethyl)-6-methylbenzoxazolone (**12i**): colorless liquid, 0.359 g, 72%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.97−7.01 (m, 3H), 4.07−4.15 (m, 4H), 2.80 (t, J = 6.6 Hz, 2H), 2.38 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 170.7, 154.4, 142.6, 132.6, 128.4, 124.1, 110.6, 108.2, 61.0, 38.0, 32.4, 21.3, 14.0 ppm; IR (KBr) ν_{max} 2983 (w), 2931 (w), 1776(s), 1733(s), 1620 (w), 1504(m), 1449(m), 1365(m), 1266(m), 1196(m), 1094 (w), 1028 (w), 946(m), 805(m), 751 (w), 594 (w) cm^{-1}; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{13}H_{15}NO_4Na$ 272.0893, found 272.0884.

3-Allyl-6-chlorobenzoxazolone (**12j**):[81] colorless liquid, 0.360 g, 86%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, J = 1.8 Hz, 1H), 7.15 (dd, J = 8.4, 1.8 Hz, 1H), 6.88 (d, J = 8.1 Hz, 1H), 5.82−5.95 (m, 1H), 5.27−5.34 (m, 2H), 4.45 (dt, J = 5.7, 1.5 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 153.8, 142.7, 130.0, 129.5, 127.8, 123.8, 119.0, 110.8, 109.4, 44.6 ppm; IR (KBr) ν_{max} 3073 (w), 2924 (w), 1777 (s), 1606 (m), 1489 (s), 1360 (m), 1297 (m), 1254 (m), 1179 (w), 1059 (w), 988 (m), 914 (m), 851 (w), 808 (m), 760 (w), 703 (w) cm^{-1}.

3-(2-Ethoxycarbonylethyl)-6-chlorobenzoxazolone (**12k**): colorless flakes; mp 80 °C (*n*-hexane−ethyl acetate) (lit.[80] mp 78 °C); 0.383 g, 71%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, J = 1.5 Hz, 1H), 7.21(dd, J = 8.4, 1.8 Hz, 1H), 7.06 (d, J = 8.7 Hz, 1H), 4.10−4.17 (m, 4H), 2.83 (t, J = 6.6 Hz, 2H), 1.23 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 170.6, 153.7, 142.5, 129.5, 127.6, 123.7, 110.6, 109.3, 60.9, 38.0, 32.1, 13.8 ppm; IR (KBr) ν_{max} 3070 (w), 2986 (m), 1780 (s), 1726 (s), 1617 (m), 1489 (s), 1358 (s), 1321 (m), 1276 (m), 1192 (s), 1091 (m), 1030 (m), 944 (m), 910 (m), 808 (m), 753 (w), 706 (w), 594 (w) cm^{-1}.

3-Allyl-6-bromobenzoxazolone (**12l**): colorless liquid, 0.412 g, 81%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (s, 1H), 7.31 (d, J = 8.4 Hz, 1H), 6.85 (d, J = 8.4 Hz, 1H), 5.82−5.95 (m, 1H), 5.34 (d, J = 4.5 Hz, 1H), 5.29 (d, J = 11.4 Hz, 1H), 4.44 (d, J = 5.4 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 153.8, 143.0, 130.1, 130.0, 126.8, 119.1, 114.8, 113.6, 109.9, 44.7 ppm; IR (KBr) ν_{max} 3081 (w), 2926 (w), 1785 (s), 1684 (w), 1615 (w), 1485 (m), 1436 (w), 1360 (m), 1260 (w), 1076 (w), 1004 (w), 930 (w), 806 (w), 756 (w), 702 (w) cm^{-1}; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{10}H_9BrNO_2$ 253.9811, found 253.9812.

3-(2-Ethoxycarbonylethyl)-6-(ethoxycarbonylmethyl)-benzoxazolone (**12m**): colorless liquid, 0.456 g, 71%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (s, 1H), 7.11 (d, J = 8.1 Hz, 1H), 7.05 (d, J = 8.1 Hz, 1H), 4.09−4.19 (m, 6H), 3.63 (s, 2H), 2.81 (t, J = 6.6 Hz, 2H), 1.19−1.28 (m, 6H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 171.3, 170.7, 154.3, 142.6, 129.8, 128.7, 124.8, 111.0, 108.5, 61.0, 41.0, 38.0, 32.3, 14.1, 14.0 ppm; IR (KBr) ν_{max} 2981 (m), 1779 (s), 1733 (s), 1577 (m), 1505 (m), 1451 (m), 1367 (m), 1266 (m), 1193 (m), 1093 (m), 1031 (m), 956 (w), 795 (w), 756 (w) cm^{-1}; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{16}H_{19}NO_6Na$ 344.1105, found 344.1109.

3-(2-Ethoxycarbonylethyl)-6-[(N-methyl-N-phenyl)-aminocarbonylmethyl]benzoxazolone (**12n**): colorless liquid, 0.521 g, 68%; ^{1}H NMR (300 MHz, CDCl3) δ 7.39−7.46 (m, 3H), 7.16 (d, J = 6.9 Hz, 2H), 6.88−6.98 (m, 3H), 4.07−4.15 (m, 4H), 3.46 (s, 2H), 3.28 (s, 3H), 2.80 (t, J = 6.6 Hz, 2H), 1.22 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 170.72, 170.66, 154.3, 143.6, 142.5, 130.1, 129.8, 129.4, 128.1, 127.4, 124.6, 110.9, 108.2, 61.0, 40.4, 38.0, 37.6, 32.4, 14.0 ppm; IR (KBr) ν_{max} 2982 (w), 1776 (s), 1731 (s), 1654 (s), 1594 (m), 1500 (m), 1450 (m), 1376 (m), 1267 (m), 1196 (m), 1118 (m), 955 (w), 774 (w), 702 (w), 558 (w) cm^{-1}; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{21}H_{22}N_2O_5Na$ 405.1421, found 405.1415.

3-Allyl-6-ethoxycarbonylbenzoxazolone (**12o**): colorless plates; mp 72 °C (*n*-hexane−ethyl acetate); 0.301 g, 61%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, J = 8.1 Hz, 1H), 7.89 (s, 1H), 7.01 (d, J = 8.1 Hz, 1H), 5.85−5.98 (m, 1H), 5.29−5.35 (m, 2H), 4.49 (d, J = 5.4 Hz, 2H), 4.39 (q, J = 7.2 Hz, 2H), 1.41 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 165.7, 154.2, 142.2, 134.7, 130.0, 126.3, 125.2, 119.2, 111.1, 108.2, 61.3, 44.8, 14.3 ppm; IR (KBr) ν_{max} 3079 (w), 2970 (m), 1787 (s), 1704 (s), 1608 (m), 1501 (m), 1451 (s), 1362 (s), 1284 (s), 1216 (m), 1172 (m), 1114 (m), 1072 (m), 1019 (m), 995 (m), 934 (m), 894 (w), 836 (m), 763 (s), 700 (m) cm^{-1}; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{13}H_{13}NO_4Na$ 270.0737, found 270.0741.

4-(2,2,2-Trichloroacetamido)phenyl acetate (**13**): white powder; mp 74 °C (*n*-hexane−ethyl acetate); 0.065 g, 11%; ^{1}H NMR (300

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MHz, $CDCl_3$) δ 8.34 (s, 1H, D_2O exchangeable), 7.61 (d, J = 8.7 Hz, 2H), 7.16 (d, J = 8.7 Hz, 2H), 2.32 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 169.3, 159.3, 148.2, 133.5, 122.5, 121.4, 92.7, 21.0 ppm; IR (KBr) ν_{max} 3298 (s), 3141 (w), 3065 (w), 1744 (s), 1723 (s), 1611 (w), 1541 (m), 1513 (m), 1410 (w), 1371 (m), 1237 (s), 1198 (s), 882 (m), 843 (m), 817 (m), 657 (m) cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{10}H_8Cl_3NO_3Na$ 317.9462, found 317.9447.

*3-(2-Ethoxycarbonylethyl)-5-methylbenzoxazolone (**15a**) and 3-(2-ethoxycarbonylethyl)-7-methylbenzoxazolone (**16a**) mixture:* colorless liquid (ratio 57:43), 0.389 g, 78%; ^1H NMR (300 MHz, $CDCl_3$) δ 7.00–7.07 (m, 1H), 6.84–6.89 (m, 2H), 4.03–4.12 (m, 4H), 2.77 (t, J = 6.6 Hz, 2H), 2.36 (s, 1.7H), 2.33 (s, 1.3H), 1.18 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) **15a** (major) δ 170.6, 154.4, 140.5, 133.7, 130.6, 122.7, 109.4, 109.0, 60.9, 37.9, 32.3, 21.4, 13.9; **16a** (minor) δ 170.6, 154.3, 141.1, 130.3, 123.9, 123.4, 120.4, 106.0, 60.9, 37.9 38.0, 32.3, 14.2, 13.9 ppm; IR (KBr) ν_{max} 2983 (w), 1777 (s), 1733 (s), 1618 (w), 1471 (m), 1377 (m), 1254 (m), 1192 (m), 1059 (w), 1026 (w), 963 (w), 804 (w), 763 (w), 671 (w) cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{13}H_{15}NO_4Na$ 272.0893, found 272.0905.

*3-Benzyl-5-chlorobenzoxazolone (**15c**):* colorless needles; mp 172 °C (*n*-hexane-ethyl acetate) (lit.[27a] mp 172–174 °C); 0.291 g, 56%; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35 (s, 5H), 7.03–7.12 (m, 2H), 6.83 (s, 1H), 4.97 (s, 2H) ppm; ^{13}C NMR (75.5 MHz, CDCl3) δ 154.5, 141.1, 134.1, 131.8, 129.3, 129.1, 128.5, 127.6, 122.4, 110.8, 109.3, 46.2 ppm; IR (KBr) ν_{max} 3063 (w), 2938 (w), 1770 (s), 1610 (m), 1485 (s), 1371 (m), 1343 (m), 1247 (m), 1080 (m), 1014 (m), 923 (m), 810 (m), 743 (m), 700 (m), 664 (m) cm^{-1}.

*3-Allyl-5-bromobenzoxazolone (**15d**):* colorless flakes; mp 66 °C (*n*-hexane–ethyl acetate); 0.295 g, 58%; ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, J = 9.3 Hz, 1H), 7.1 (s, 1H), 7.09 (d, J = 9.6 Hz, 1H), 5.82–5.95 (m, 1H), 5.36 (d, J = 3.6 Hz, 1H), 5,31 (d, J = 11.1 Hz, 1H), 4.43 (d, J = 5.1 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 153.9, 141.5, 132.1, 129.9, 125.3, 119.2, 116.3, 112.1, 111.3, 44.7 ppm; IR (KBr) ν_{max} 3071 (w), 2930 (w), 1771 (s), 1604 (m), 1483 (s), 1373 (m), 1340 (m), 1242 (m), 1177 (m), 1076 (w), 1003 (m), 940 (m), 888 (w), 796 (m), 703 (w) cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{10}H_8BrNO_2Na$ 275.9631, found 275.9637.

*3-(2-Cyanoethyl)-4-methylbenzoxazolone (**19a**):* colorless needles; mp 112 °C (*n*-hexane–ethyl acetate); 0.190 g, 47%; ^1H NMR (300 MHz, $CDCl_3$) δ 7.10 (d, J = 7.8 Hz, 1H), 7.05 (t, J = 7.8 Hz, 1H), 6.97 (d, J = 7.2 Hz, 1H), 4.33 (t, J = 6.9 Hz, 2H), 2.90 (t, J = 6.9 Hz, 2H), 2.60 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 154.5, 142.7, 127.9, 127.3, 122.9, 119.6, 116.4, 108.4, 39.2, 17.67, 17.65 ppm; IR (KBr) ν_{max} 2974 (w), 2940 (w), 2257 (w), 1765 (s), 1682 (w), 1497 (w), 1457 (m), 1365 (m), 1260 (m), 1177 (w), 1111 (w), 1088 (w), 1021 (w), 960 (w), 783 (m), 753 (w), 726 (w) cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{11}H_{10}N_2O_2Na$ 225.0634, found 225.0635.

*3-Benzyl-4-bromobenzoxazolone (**19c**):* colorless flakes; mp 75 °C (*n*-hexane–ethyl acetate); 0.389 g, 64%; ^1H NMR (300 MHz, $CDCl_3$) δ 7.32 (s, 5H), 7.27 (d, J = 8.1 Hz, 1H) 7.19 (d, J = 8.1 Hz, 1H), 6.99 (t, J = 8.1 Hz, 1H), 5.39 (s, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 154.7, 143.8, 136.0, 128.9, 128.7, 127.8, 126.9, 123.6, 109.3, 101.5, 46.1 ppm; IR (KBr) ν_{max} 3058 (w), 1776 (s), 1590 (m), 1482 (m), 1450 (s), 1362 (m), 1326 (m), 1258 (m), 1109 (m), 1077 (m), 916 (m), 758 (m), 696 (m), 616 (m) cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{14}H_{10}BrNO_2Na$ 325.9787, found 325.9784.

*4-(2-Cyanoethylamino)-3-methylphenyl 2,2,2-trichloroacetate (**20**):* colorless liquid, 0.244 g, 38%; ^1H NMR (300 MHz, $CDCl_3$) δ 6.97–7.01 (m, 2H), 6.57 (d, J = 8.4 Hz, 1H), 4.12 (s, 1H, D_2O exchangeable), 3.57 (t, J = 6.3 Hz, 2H), 2.68 (t, J = 6.3 Hz, 2H), 2.18 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 161.1, 142.9, 142.2, 124.1, 122.4, 118.6, 118.0, 109.7, 89.7, 39.7, 18.0, 17.4 ppm; IR (KBr) ν_{max} 3420 (m), 2926 (m), 2250 (w), 1767 (s), 1675 (m), 1561 (m), 1524 (m), 1318 (m), 1223 (s), 1155 (w), 1004 (w), 968 (w), 832 (m), 814 (m), 683 (m) cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{12}H_{11}Cl_3N_2O_2Na$ 342.9778, found 342.9775.

*3-Benzyl-7-bromobenzoxazolone (**21**):* white solid mixture (3:2) with 3-benzylbenzoxazolone **12e**, 0.040 g, 6.6% (calculated from ^1H NMR); (spectral data were discerned by comparing the spectra of **12e** with those of the mixture) ^1H NMR (300 MHz, $CDCl_3$) δ 7.33 (s, 5H) (overlapped with **12e**), 7.18–7.25 (m, 1H) (overlapped with **12e**), 6.96 (t, J = 7.8 Hz, 1H), 6.75 (d, J = 7.8 Hz, 1H), 4.98 (s, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 153.8, 140.8, 134.2, 131.6, 129.1, 128.5, 127.6, 125.9, 124.9, 107.8, 102.6, 46.5 ppm; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{14}H_{10}BrNO_2Na$ 325.9787, found 325.9791.

*3-Benzyl-6-fluoro-4-methylbenzoxazolone (**24**):* colorless flakes; mp 68 °C (*n*-hexane–ethyl acetate); 0.278 g, 54%; ^1H NMR (300 MHz, $CDCl_3$) δ 7.28–7.37 (m, 3H), 7.19 (d, J = 7.2 Hz, 2H), 6.85 (d, J_{HF} = 7.5 Hz, 1H), 6.61 (d, J_{HF} = 10.2 Hz, 1H), 5.20 (s, 2H), 2.26 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 158.21 (d, J_{CF} = 242.4 Hz), 155.4, 142.74 (d, J_{CF} = 14.3 Hz), 136.1, 128.9, 127.8, 125.7, 124.9, 121.18 (d, J_{CF} = 9.1 Hz), 113.12 (d, J_{CF} = 23.4 Hz), 96.79 (d, J_{CF} = 27.9 Hz), 46.6, 17.1 ppm; IR (KBr) ν_{max} 3090 (m), 3060 (w), 2980 (w), 1765 (s), 1641 (m), 1496 (m), 1450 (s), 1357 (m), 1177 (m), 1110 (m), 1048 (m), 1017 (m), 968 (m), 865 (m), 805 (m), 719 (s), 584 (m) cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{15}H_{12}FNO_2Na$ 280.0744, found 280.0748.

*N-(4-Fluoro-2-methylphenyl)trichloroacetamide (**25**):* colorless plates; mp 118 °C (*n*-hexane–ethyl acetate) (lit.[82] mp 119–121 °C); 0.060 g, 11%; ^1H NMR (300 MHz, $CDCl_3$) δ 8.18 (s, 1H, D_2O exchangeable), 7.66 (dd, J_{HF} = 9.6 Hz, J_{HH} = 5.1 Hz, 1H), 6.98 (d, J = 7.5 Hz, 2H), 2.31 (s, 3H), ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 160.86 (d, J_{CF} = 246.9 Hz), 159.8, 133.45 (d, J_{CF} = 8.3 Hz), 129.66 (d, J_{CF} = 3.0 Hz), 125.29 (d, J_{CF} = 8.3 Hz), 117.47 (d, J_{CF} = 22.6 Hz), 113.74 (d, J_{CF} = 21.9 Hz), 92.8, 17.6 ppm; IR (KBr) ν_{max} 3293 (s), 3009 (w), 2925 (m), 1703 (s), 1618 (m), 1522 (s), 1266 (s), 1227 (m), 1151 (w), 1041 (w), 1007 (w), 871 (m), 822 (s), 730 (w), 687 (m) cm^{-1}.

*3-Benzyl-5,7-dibromo-6-methylbenzoxazolone (**27**):* colorless needles; mp 101 °C (*n*-hexane–ethyl acetate); 0.460 g, 58%; ^1H NMR (300 MHz, $CDCl_3$) δ 7.24–7.29 (m, 5H), 6.89 (s, 1H), 4.85 (s, 2H), 2.41 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 153.5, 140.5, 133.9, 131.3, 129.6, 129.1, 128.5, 127.5, 118.6, 111.4, 105.4, 46.4, 22.5 ppm; IR (KBr) ν_{max} 3070 (w), 2926 (w), 1777 (s), 1622 (w), 1592 (m), 1463 (s), 1336 (m), 1255 (w), 1132 (w), 1014 (m), 973 (w), 920 (w), 709 (m), 655 (m) cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{15}H_{11}Br_2NO_2Na$ 417.9049, found 417.9039.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^1H NMR and ^{13}C NMR spectra of all compounds including the nitrones; ORTEP diagrams and CIFs of **15d**, **19a**, **19b**, and **19c**. This material is available free of charge via the Internet at http://pubs.acs.org/. Crystallographic data for compounds **15d** (CCDC 955230), **19a** (CCDC 955233), **19b** (CCDC 955232), and **19c** (CCDC 955231) may also be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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