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Novel 2*H*-1,3-benzoxazine ring formation by intramolecular heterocyclization of *N*-(α-aryloxyalkyl)imidoyl chlorides

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Abstract: A convenient synthetic approach to derivatives of 2-trichloromethyl and 2-dichlorometylene-2*H*-1,3-benzoxazines, based on intramolecular heterocyclization of readily accessible *N*-(α-aryloxytrichloroethyl)imidoyl chlorides, was developed. Base induced dehydrochlorination of 4-phenyl- or 4-trifluoromethyl-2-trichloromethylbenzoxazines allows preparation of 2-dichloromethylene-1,3-benzoxazines, whereas dehydrochlorination of 4-fluoromethyl analogs under similar conditions is accompanied by formal 1,5-*H*-shift to afford respective 2-dichloromethyl-4-fluoromethylene-1,3-benzoxazines.

Keywords: 2*H*-1,3-benzoxazines; dichloromethylene; imidoyl chlorides; intramolecular cyclization; polyfluoroalkyl; trichloromethyl.

Introduction

2*H*-1,3-Benzoxazines are of interest in medicine and material sciences. Specifically, they are useful as anti-inflammatory agents [1], photochromic substances [2] and photofading-preventive materials [3]. Derivatives of 1,3-benzoxazines I-III (Figure 1) are effective potassium channel regulators and are candidates as therapeutic agents for hypertension, angina pectoris, asthma and urinary incontinence [4–7]. 2,3-Disubstituted-1,3-benzoxazines show fungicidal activity [8]. Compounds incorporating hydrogenated benzo[*e*][1,3]oxazine or naphtho[2,1-*e*][1,3]oxazine fragment have been reported to show significant antimicrobial and cytotoxic activities [9]. A benzoxazinone fragment is considered a pharmaceutically privileged scaffold [6 and references cited therein]. 2*H*-1,3-Benzoxazines bearing a chloroalkyl group at the C-2 atom, to the best of our knowledge, have not been described so far. The importance of the CCl_3 group in natural biologically active products and synthetic molecules has been noted [10, 11]. Existing synthetic approaches to 1,3-benzoxazines have limitations and drawbacks [4, 6, 7]. Specifically, synthesis of benzoxazines from 2-hydroxyphenylketones involves generation of unstable N-H ketimines as key intermediates [7]; methods based on the use of salicylamides, *ortho*-hydroxybenzylamines [12, 13], or 1-chlorotrifluoroethylisocyanates [14] are limited to the synthesis of benzoxazin-4-ones. Recently reported method, utilizing oxidative C-O bond formation, requires synthesis of 1-(aminoalkyl)-2-naphthols or 2-(aminoalkyl)phenols and is limited to compounds incorporating 1,3-benzoxazine moiety in a complex condensed heterocyclic system [15]. Thus, elaboration of new synthetic methods for construction of a 1,3-benzoxazine skeleton remains a challenging task.

Results and discussion

We report a novel synthesis of 2*H*-1,3-benzoxazines with trichloromethyl group at the C-2 atom, based on readily accessible *N*-(α-aryloxytrichloroethyl)imidoyl chlorides (**1**). Thus, imidoyl chlorides **1** on heating in polyphosphoric acid (PPA) or in the presence of $AlCl_3$ (Lewis acid) undergo intramolecular heterocyclization ('intramolecular imidoylation') to afford benzoxazines **2** in 30–80% yields (Scheme 1). Apparently, electrophilic attack of the imine carbon atom on the *ortho* position of the benzene ring in imidoyl chlorides **1** is favored by electron-releasing mesomeric effect of the alkoxy substituent (Scheme 1). The presence of the electron-donating Me group(s) in *O*-benzene ring is beneficial for ring closure, whereas the electron-withdrawing C-4 fluorine atom in **1b** (which is in *meta* position to the reactive center) retards heterocyclization and reduces the yield of the respective oxazine **2b**. Heterocyclization of the dimethyl substrate **1e** proceeds regioselectively, with the involvement of a sterically less hindered C-6 atom of the oxybenzene ring. Remarkably,

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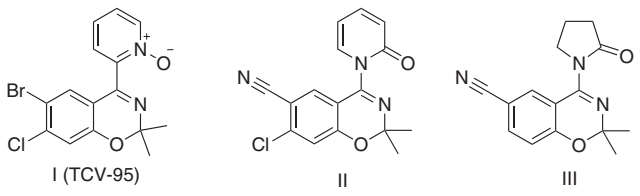
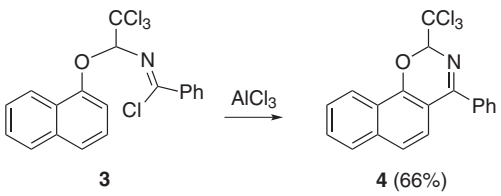


Figure 1 Biologically active 2*H*-1,3-benzoxazines, potassium channels regulators.

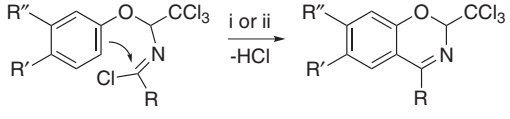


Scheme 2 Preparation of 2*H*-naphtho-1,3-oxazine **4**.

imidoyl chlorides with various substituents at the imine carbon atom are apt to heterocyclization expanding the scope of the reaction and allowing variation of substituents in the benzene and oxazine rings. Thus, benzoxazines with phenyl, methyl, fluoromethyl or trifluoromethyl group at C-4 atom are readily accessible by this approach. The simple preparative access to benzoxazines bearing a fluorine or trifluoromethyl substituent is of special importance, when taken into consideration that incorporation of a fluorinated group in organic molecules often imparts a variety of useful properties, including enhanced binding interactions in a biological system, metabolic stability and better performances of synthetic materials [16–21].

It is interesting to note that in the $AlCl_3$-catalyzed cyclization of fluoroacetimidoyl chloride **1g**, the formation of a small amount (~5%) of 4-chloromethyl-6-methyl-2-trichloromethyl-2*H*-1,3-benzoxazine (**2h**, R = CH_2Cl, R′ = Me, R″ = H; Scheme 1) was also detected and confirmed by analysis of ^1H and ^{13}C NMR spectra. Unexpected formation of compound **2h** can be accounted for by the $AlCl_3$-promoted chlorine-fluorine exchange in starting fluoroacetimidoyl chloride **1g** under the reaction conditions.

The developed methodology enables also the synthesis of more complex condensed systems incorporating the benzoxazine fragment as illustrated in Scheme 2.



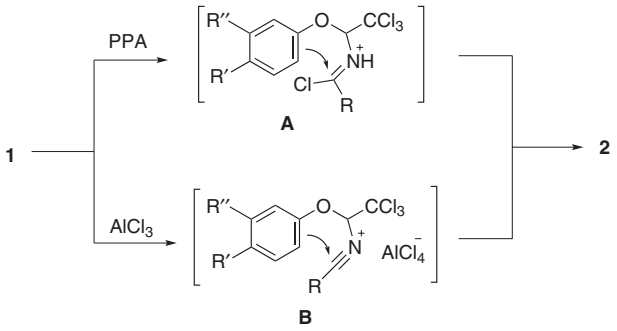
a: R = Ph; R′ = R″ = H
b: R = Ph; R′ = F; R″ = H
c: R = Ph; R′ = Me; R″ = H
d: R = CF_3; R′ = Me; R″ = H
e: R = Ph; R′ = R″ = Me
f: R = R′ = Me; R″ = H
g: R = CH_2F; R′ = Me; R″ = H

Scheme 1 Synthesis of 2*H*-1,3-benzoxazines. Reagents and conditions: (i) $AlCl_3$, dichloroethane; (ii) PPA, 80–100°C, 0.5 h, then 130–140°C, 0.5 h.

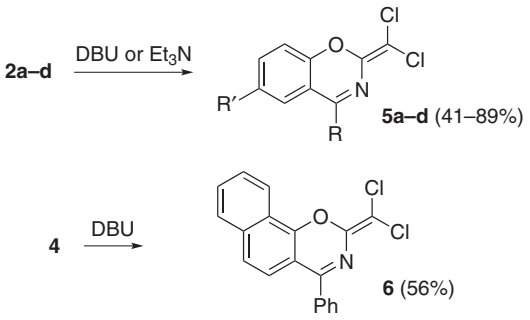
Promotion of intramolecular heterocyclization in Schemes 1 and 2 by $AlCl_3$ or PPA catalyst is connected most likely with generation of highly electrophilic iminium **A** and nitrilium **B** type intermediates that undergo electrophilic attack on the activated *ortho*-position of the aryloxy substituent (Scheme 3). A similar pattern has been reported previously for the preparation of dihydroisoquinolines from *N*-(2-arylethyl)imidoyl chlorides by the Bischler-Napieralski reaction [22].

To the best of our knowledge, 1,3-benzoxazines bearing a trichloromethyl group in the oxazine ring have not been reported so far. The presence of an electron-withdrawing CCl_3 group in compounds **2** increases C-H acidity of the neighboring carbon atom, offering additional synthetic opportunities. Thus, in the presence of base, such as triethylamine or DBU, benzoxazines **2a–d** and **4** readily undergo dehydrochlorination to afford the respective 2-(dichloromethylene)-2*H*-oxazines **5a–d** and **6** (Scheme 4). Compounds **5** and **6** are the first representatives of benzoxazines with 2-dichloromethylene group.

At the same time, reactions of benzoxazines **2f,g** with a methyl or fluoromethyl group at the C-4 atom, under the same conditions afforded the respective 4-methylene or 4-fluoromethylene substituted 6-methyl-2-dichloromethylbenzoxazine **7a,b**, apparently resulting from the formal 1,5-hydrogen shift in the primary dehydrochlorination products **C** (Scheme 5). Obviously, the driving force for the prototropic isomerization **C** → **7** is the formation of the energetically more favorable conjugated



Scheme 3 PPA or $AlCl_3$-promoted synthesis of 1,3-benzoxazines.



Scheme 4 Dehydrochlorination of 2*H*-1,3-benzoxazines.

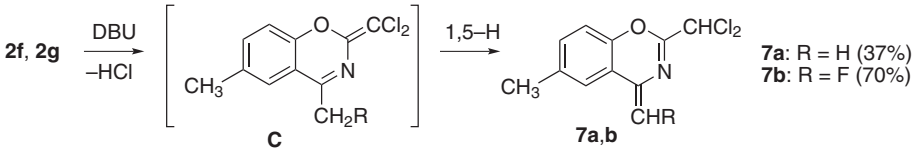
system C=NC=C. Noteworthy, proton shift in CH_2F-substituted compound **2g** proceeds stereoselectively affording mainly the *E*-isomer of **7b** (*E*/*Z* ~ 10:1). The assignment of geometry was based mainly on comparison of the value of a coupling constant between C-4 and fluorine nuclei in the ^{13}C NMR spectrum ($^2J_{CF} = 9$ Hz for *E* isomer) and the relative chemical shifts of =CHF in ^1H NMR spectrum ($\delta = 6.58$, $^2J_{HF} = 76.3$ Hz; $\delta = 7.11$, $^2J_{HF} = 78.8$ Hz for *E*- and *Z*-isomers, respectively), with our previous data for isomeric fluorovinylamides [23]. For the *Z* configuration, the value of the $^2J_{C\text{-}4,F}$ constant would be expected in the range of 30–40 Hz [23].

The starting imidoyl chlorides **1** and **3** were prepared according to Scheme 6. Readily accessible hydroxyamides **8** were converted into chlorides **9** [24, 25]. The latter species were allowed to react with the respective phenols in the presence of triethylamine to afford *N*-(α-aryloxytrichloroethyl)amides **10**. Reaction of amides **10** with phosphorus pentachloride or the Ph_3P-CCl_4 system led to the desired imidoyl chlorides **1** and **3**.

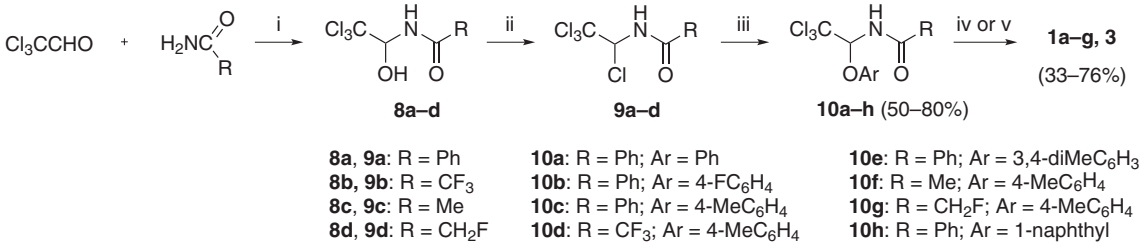
The spectral and analytical data of compounds **2** and **4–6** are in full agreement with their structures. In particular, analysis of APT ^{13}C NMR spectra of **2** and **5** confirm quaternary character of the C-4a atom involved in cyclization. The couplings of the C-5 atom of fluorine-containing products **2d**,**g** and **5d** ($\delta_C = 125.5$–125.9, $^4J_{CF} = 2$–5 Hz) and C-4 atom of **5b** ($\delta_C = 160.2$, $^4J_{CF} = 2$ Hz) indicate clearly the annelation of imino carbon atom with the phenoxy ring. The signal of the proton in the C-N=C triad of the benzoxazine system in compounds **2** and **4** is substantiated by the characteristic chemical shifts of sp^3 C-2 and sp^2 C-4 atoms ($\delta_C = 93.9$–94.7 and 155.6–167.8, respectively) and low-field resonance of the respective 2-C-proton ($\delta_H = 5.9$–6.4). In addition, the signals of C-4 atoms of compounds **2d** and **2g** reveal themselves in the ^{13}C NMR spectra as characteristic multiplets (155.6 ppm, $^2J_{CF} = 36$ Hz and 162.9, $^2J_{CF} = 17$ Hz) due to the splitting by interaction with fluorine atoms. The **2** → **5** transformation is accompanied by a substantial downfield shift of C-2 atom signal (from 93.9–94.7 ppm to 146.4–147.5 ppm) resulting from the sp^3- to sp^2 change of its hybridization.

Conclusions

A simple synthesis of 2-trichloromethyl- and 2-dichlorometylene-substituted 6-aryl-2*H*-1,3-benzoxazines, based on intramolecular heterocyclization of readily accessible



Scheme 5 Dehydrochlorination and prototropic isomerization of 4-methyl- and 4-fluoromethyl-2*H*-1,3-benzoxazines.



Scheme 6 Preparation of imidoyl chlorides **1** and **3**. Reagents and conditions: (i) H_2SO_4, 95°C; (ii) PCl_5, benzene; (iii) ArOH, Et_3N, benzene, reflux, 3 h; (iv) PCl_5, 100–110°C, 1 h; (*v*) Ph_3P, CCl_4, dichloroethane, reflux 8 h.

N-(α-aryloxytrichloroethyl)benzimidoyl chlorides, catalyzed by Lewis ($AlCl_3$) or Bronsted (PPA) acid, was developed. Remarkably, imidoyl chlorides with various substituents at the imine carbon atom are apt to heterocyclization expanding the scope of the reaction and allowing variation of substituents in the benzene and oxazine rings. Benzoxazines with aryl, methyl, fluorine, fluoromethyl, trifluoromethyl, trichloromethyl, dichloromethyl, methylene, fluoromethylene and dichloromethylene groups are readily accessible by this approach. The simple preparative access to benzoxazines bearing fluorine-containing substituents is of special importance because incorporation of a fluorinated group in organic molecules modulates their pharmacological properties.

Experimental

^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a Varian VXR-300 spectrometer at 299.95 MHz and ^{19}F NMR spectra were recorded on a Gemini 200 Varian instrument at 188.14 MHz. ^{13}C NMR spectra were obtained on a Bruker Avance DRX 500 spectrometer operating at 125.76 MHz. Chemical shifts are reported relative to internal transmission magnetic spectroscopy (TSM) (^{1}H, ^{13}C), and $CFCl_3$ (^{19}F). APCI MS spectra were recorded using an Agilent 1100 instrument. Melting points are uncorrected. Solvents were dried before use according to standard methods. Elemental analysis was carried out on a Carlo Erba 1106 instrument in the analytical laboratory of Institute of Organic Chemistry, NAS of Ukraine. Compounds **8a,c** [26], **8b,d** [27], **9a** [28], **9c** [29], **9d** [30] have been described previously.

General procedure for the preparation of imidoyl chlorides 1a–c,e

A mixture of the appropriate amide **10** and a 5% molar excess of PCl_5 was heated at 100–110°C for 1 h. After removal of $POCl_3$, the residue was distilled under reduced pressure (**1a–c**) or used in subsequent synthesis without purification (**1e**).

***N*-(2,2,2-Trichloro-1-phenoxyethyl)benzimidoyl chloride (1a)** Yield 72%; colorless oil; bp 162–164°C/0.02 mm Hg; ^{1}H NMR ($CDCl_3$): δ 6.22 (s, 1H, CHN), 7.08 (t, 1H, $^3J_{HH}$ = 7 Hz, Ph), 7.12 (d, 2H, $^3J_{HH}$ = 8 Hz, Ph), 7.31 (t, 2H, $^3J_{HH}$ = 8 Hz, Ph), 7.45 (t, 2H, $^3J_{HH}$ = 7 Hz, Ph), 7.56 (t, 1H, $^3J_{HH}$ = 7 Hz, Ph), 8.14 (d, 2H, $^3J_{HH}$ = 7 Hz, Ph); ^{13}C NMR ($CDCl_3$): δ 97.1 (CHN), 98.8 (CCl_3), 117.7 ($C^{2,6}{}_{PhO}$), 123.5 ($C^4{}_{PhO}$), 128.5 ($C^{3,5}{}_{\underline{Ph}C}$), 129.7 ($C^{2,6}{}_{\underline{Ph}C}$), 129.9 ($C^{3,5}{}_{PhO}$), 133.1 ($C^4{}_{\underline{Ph}C}$), 134.44 ($C^1{}_{\underline{Ph}C}$), 151.2 (C=N), 156.6 ($C^1{}_{PhO}$). Anal. Calcd for $C_{15}H_{11}Cl_4NO$: C, 49.62; H, 3.05; Cl, 39.06; N, 3.86. Found: C, 49.81; H, 3.11; Cl, 39.34; N, 3.93.

***N*-[2,2,2-Trichloro-1-(4-fluorophenoxy)ethyl]benzimidoyl chloride (1b)** Yield 51%; colorless oil; bp 133–135°C/0.2 mm Hg; ^{1}H NMR ($CDCl_3$): δ 6.11 (s, 1H, CHN), 7.0 (t, 2H, $^1J_{HH}$ = $^3J_{HF}$ = 8 Hz, Ar), 7.1 (m, 2H, Ar), 7.47 (t, 2H, $^3J_{HH}$ = 7 Hz, Ar), 7.58 (t, 1H, $^3J_{HH}$ = 7 Hz, Ar), 8.14 (d, 2H, $^3J_{HH}$ = 7 Hz, Ar); ^{19}F NMR ($CDCl_3$): δ –119.9. Anal. Calcd for $C_{15}H_{11}Cl_4NO$: C, 47.28; H, 2.65; Cl, 37.22; N, 3.68. Found: C, 47.55; H, 2.80; Cl, 37.34; N, 3.80.

***N*-[2,2,2-Trichloro-1-(4-methylphenoxy)ethyl]benzimidoyl chloride (1c)** Yield 76%; colorless oil; bp 150°C/0.07 mm Hg; ^{1}H NMR ($CDCl_3$): δ 2.29 (s, 3H, Me), 6.17 (s, 1H, CHN), 7.02 (d, 2H, $^3J_{HH}$ = 8.7 Hz, Ar), 7.1 (d, 2H, $^3J_{HH}$ = 8.7 Hz, Ar), 7.45 (t, 2H, $^3J_{HH}$ = 8 Hz, Ar), 7.56 (t, 1H, $^3J_{HH}$ = 7 Hz, Ar), 8.14 (d, 2H,$^3J_{HH}$ = 8 Hz, Ar). Anal. Calcd for $C_{16}H_{13}Cl_4NO$: C, 50.96; H, 3.47; Cl, 37.60; N, 3.71. Found: C, 51.06; H, 3.60; Cl, 37.56; N, 3.90.

***N*-[2,2,2-Trichloro-1-(3,4-dimethylphenoxy)ethyl]benzimidoyl chloride (1e)** Crude compound was used; yield 73%; colorless oil; ^{1}H NMR ($CDCl_3$): δ 2.18 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 6.17 (s, 1H, CH), 6.86 (d, 1H, $^3J_{HH}$ = 8 Hz, Ar), 6.93 (s, 1H, Ar), 7.03 (d, 1H, $^3J_{HH}$ = 8 Hz, Ar), 7.44 (t, 2H, $^3J_{HH}$ = 7.5 Hz, Ar), 7.55 (t, 1H, $^3J_{HH}$ = 7.5 Hz, Ar), 8.14 (d, 2H, $^3J_{HH}$ = 7.5 Hz, Ar).

General procedure for the preparation of imidoyl chlorides 1d,f,g and 3

A mixture of respective amide **10** (1 mmol), Ph_3P (0.39 g, 1.5 mmol) and CCl_4 (0.29 mL, 3 mmol) in dichloroethane (10 mL) was heated at reflux for 8 h. After cooling to room temperature the volatiles were removed under reduced pressure and the residue was extracted with hexane (5 × 3 mL).

***N*-[2,2,2-Trichloro-1-(4-tolyloxyethyl)trifluoroacetimidoyl chloride (1d)** Yield 57%; colorless oil; bp 65–67°C/0.045 mm Hg; ^{1}H NMR ($CDCl_3$): δ 2.32 (s, 3H, Me), 5.92 (s, 1H, CHN), 6.95 (d, 2H, $^3J_{HH}$ = 8.7 Hz, $CH^{2,6}{}_{Ph}$), 7.14 (d, 2H, $^3J_{HH}$ = 8.7 Hz, $CH^{3,5}{}_{Ph}$); ^{13}C NMR ($CDCl_3$): δ 20.7 (Me), 96.9 (CHN), 97.1 (CCl_3), 116.4 (q, $^1J_{CF}$ = 277 Hz, CF_3), 118.2 ($C^{2,6}{}_{Ar}$), 130.5 ($C^{3,5}{}_{Ar}$), 134.4 ($C^4{}_{Ar}$), 154.01 ($C^1{}_{Ar}$), 140.9 (q, $^2J_{CF}$ = 44 Hz, C=N); ^{19}F NMR ($CDCl_3$): δ –72.33. Anal. Calcd for $C_{11}H_8Cl_4F_3NO$: C, 35.80; H, 2.19; Cl, 38.43; N, 3.80. Found: C, 35.94; H, 2.33; Cl, 38.34; N, 3.97.

***N*-[2,2,2-Trichloro-1-(4-tolyloxyethyl)acetimidoyl chloride (1f)** Yield 38%; colorless oil; bp 99–101°C/0.06 mm Hg; ^{1}H NMR ($CDCl_3$): δ 2.30 (s, 3H, Me), 2.55 (s, 3H, Me), 5.89 (s, 1H, CHN), 6.96 (d, 2H, $^3J_{HH}$ = 8.5 Hz, $C^{2,6}{}_{Ph}$), 7.11 (d, 2H, $^3J_{HH}$ = 8.5 Hz, $C^{3,5}{}_{Ph}$); ^{13}C NMR ($CDCl_3$): δ 20.7 (<u>Me</u>Ar), 30.5 (<u>Me</u>C=N), 97.3 (CHN), 98.5 (CCl_3), 117.7 ($C^{2,6}{}_{Ar}$), 130.2 ($C^{3,5}{}_{Ar}$), 133.2 ($C^4{}_{ArC}$), 151.6 (C=N), 154.4 ($C^1{}_{Ar}$). Anal. Calcd for $C_{11}H_{11}Cl_4NO$: C, 42.10; H, 3.69; Cl, 45.02; N, 4.45. Found: C, 41.94; H, 3.52; Cl, 45.21; N, 4.67.

***N*-[2,2,2-Trichloro-1-(4-tolyloxyethyl)fluoroacetimidoyl chloride (1g)** Yield 33%; colorless oil; bp 70–75°C/0.05 mm Hg; ^{1}H NMR ($CDCl_3$): δ 2.35 (s, 3H, Me), 5.09 (d, 2H, $^2J_{HF}$ = 47 Hz, CH_2F), 6.04 (s, 1H, CHN), 7.01 (d, 2H, $^3J_{HH}$ = 8 Hz, Ar), 7.17 (m, 2H, Ar); ^{19}F NMR ($CDCl_3$): δ –215.4 (t, $^2J_{FH}$ = 47 Hz); ^{13}C NMR ($CDCl_3$): δ 20.6 (Me), 82.1 (d, $^1J_{CF}$ = 189 Hz, CH_2F), 96.4 (CHN), 97.9 (CCl_3), 117.7 ($C^{2,6}{}_{Ar}$), 130.3 ($C^{3,5}{}_{Ar}$), 133.5 ($C^4{}_{Ar}$), 149.6 (d, $^2J_{CF}$ = 22 Hz, C=N) 154.1 ($C^1{}_{Ar}$). Anal. Calcd for $C_{11}H_{10}Cl_4FNO$: C, 39.67; H, 3.03; Cl, 42.58; N, 4.21. Found: C, 39.80; H, 3.21; Cl, 42.69; N, 4.36.

***N*-[2,2,2-Trichloro-1-(1-naphthyloxy)ethyl]benzimidoyl chloride (3)** Yield 60%; colorless powder; mp 93–94°C; ^{1}H NMR ($CDCl_3$): δ 6.44 (s, 1H, CHN), 7.05 (d, 1H, $^3J_{HH}$ = 8 Hz, Ar), 7.34–7.57 (m, 5H, Ar), 7.65 (d, 1H, $^3J_{HH}$ = 7.2 Hz, Ar), 7.69 (d, 1H, $^3J_{HH}$ = 7.2 Hz, Ar), 7.80 (m, 1H, Ar), 8.13 (d, 2H, $^3J_{HH}$ = 7.2 Hz, Ar), 8.45 (m, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ 96.9 (CHN), 98.8 (CCl_3), 109.2 ($C^2{}_{naphth}$), 122.7, 123.0, 125.4, 125.8, 126.7,

127.4 (naphthyl), 126.2 (C^{8a}_{naphth}), 128.5 ($C^{3,5}_{Ph}$), 130.0 ($C^{2,6}_{Ph}$), 132.1 (C^{4}_{Ph}), 134.5 (C^{4a}_{naphth}), 134.7 (C^{1}_{Ph}), 152.3 (C^{1}_{naphth}). Anal. Calcd for $C_{19}H_{13}Cl_4NO$: C, 55.24; H, 3.17; Cl, 34.33; N, 3.39. Found: C, 55.39; H, 3.24; Cl, 34.38; N, 3.55.

General procedures for the preparation of 1,3-benzoxazines 2a–g and 4

Method A A mixture of the imidoyl chloride **1a–d, 1d–g** (1 mmol) and $AlCl_3$ (0.27 g, 2 mmol) in dichloroethane (5 mL) was stirred at room temperature for 24 h. The mixture was poured into ice water (15 mL), extracted with CH_2Cl_2, dried over $MgSO_4$ and crystallized from ethanol (**2b,e**) or purified by column chromatography (silica-gel, hexane-EA, 9:1) (**2d,f,g**). Compound **4** was obtained from imidoyl chloride **3**.

Method B A mixture of the imidoyl chloride **1a–c** (1.5 mmol) and PPA (2.5 g) was heated at 80–100°C for 0.5 h and then at 130–140°C for 0.5 h. After cooling, the mixture was poured into ice water. The precipitated product was separated by filtration and washed successively with water, aqueous $NaHCO_3$, and water. Analytically pure sample was obtained by crystallization from ethanol.

4-Phenyl-2-trichloromethyl-2*H*-1,3-benzoxazine (2a) Yield 42% (method A), 58% (method B); light yellow solid; mp 94–96°C; ^{1}H NMR ($CDCl_3$): δ 5.95 (s, 1H, CHN), 7.02 (t, 1H, $^3J_{HH}$ = 8 Hz, Ar), 7.11 (d, 1H, $^3J_{HH}$ = 8 Hz, Ar), 7.33 (d, 1H, $^3J_{HH}$ = 8 Hz, Ar), 7.51 (m, 4H, Ar), 7.66 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$): δ 94.1 (C-2), 99.2 (CCl_3), 116.5 (C-8), 117.2 (C-4a), 122.1 (C-5), 128.3 (C^{4}_{Ph}), 128.4 ($C^{3,5}_{Ph}$), 129.1 ($C^{2,6}_{Ph}$), 130.5 (C-6), 134.5 (C-7), 135.7 (C^{1}_{Ph}), 154.9 (C-8a), 167.1 (C-4); LC-APCI-MS: *m/z* 292 [M-1]. Anal. Calcd for $C_{15}H_{10}Cl_3NO$: C, 55.16; H, 3.09; Cl, 32.56; N, 4.29. Found: C, 55.31; H, 3.17; Cl, 32.12; N, 4.29.

6-Fluoro-4-phenyl-2-trichloromethyl-2*H*-1,3-benzoxazine (2b) Yield 30% (method A), 20% (method B); gray solid; mp 91.5–93°C; ^{1}H NMR ($CDCl_3$): δ 5.92 (s, 1H, CHN), 7.07 (m, 2H, Ar), 7.2 (m, 1H, Ar), 7.5 (m, 3H, Ar), 7.66 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$): δ 94.6 (C-2), 99.1 (CCl_3), 114.4 (d, $^2J_{CF}$ = 24 Hz, C-5), 117.8 (d, $^3J_{CF}$ = 7 Hz, C-4a), 118.0 (d, $^3J_{CF}$ = 7 Hz, C-8), 121.2 (d, $^2J_{CF}$ = 24 Hz, C-7), 128.7, 129.0 ($C^{2,6}_{Ph}$, $C^{3,5}_{Ph}$), 130.8 (C^{4}_{Ph}), 135.4 (C^{1}_{Ph}), 151.0 (d, $^4J_{CF}$ = 2 Hz, C-8a), 157.2 (d, $^1J_{CF}$ = 243 Hz, C-6), 166.1 (C-4); ^{19}F NMR ($CDCl_3$): δ –119.7; LC-APCI-MS: *m/z* 344 [M+1]. Anal. Calcd for $C_{15}H_9Cl_3FNO$: C, 52.28; H, 2.63; Cl, 30.86; N, 4.06. Found: C, 52.41; H, 2.77; Cl, 31.05; N, 4.26.

6-Methyl-4-phenyl-2-trichloromethyl-2*H*-1,3-benzoxazine (2c) Yield 78% (method B); white solid; mp 91–92°C; ^{1}H NMR ($CDCl_3$): δ 2.28 (s, 3H, Me), 5.89 (s, 1H, CHN), 7.0 (d, 1H, $^3J_{HH}$ = 8.1 Hz, Ar), 7.11 (s, 1H, Ar), 7.3 (d, 1H, $^3J_{HH}$ = 8.1 Hz, Ar), 7.51 (m, 3H, Ar), 7.65 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$): δ 20.8 (Me), 94.3 (C-2), 99.5 (CCl_3), 116.3 (C-5), 117.1 (C-4a), 128.4 (C-8), 128.5, 129.2 ($C^{2,3}_{Ph}$), 130.5 (C^{4}_{Ph}), 131.6 (C-6), 135.1 (C-7), 136.1 (C^{1}_{Ph}), 152.9 (C-8a), 167.2 (C-4). Anal. Calcd for $C_{16}H_{12}Cl_3NO$: C, 56.42; H, 3.55; Cl, 31.22; N, 4.11. Found: C, 56.59; H, 3.67; Cl, 30.75; N, 4.30.

6-Methyl-2-trichloromethyl-4-trifluoromethyl-2*H*-1,3-benzoxazine (2d) Yield 41% (method A); colorless oil; ^{1}H NMR ($CDCl_3$): δ 2.34 (s, 3H, Me), 5.99 (q, 1H, $^5J_{HH}$ = 1.5 Hz, CHN), 6.97 (d, 1H, $^3J_{HH}$ = 8.7 Hz, Ar), 7.3 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$): δ = 20.8 (Me), 93.9 (C-2), 97.8 (CCl_3), 111.7 (C-4a), 115.5 (C-8), 119.2 (q, $^1J_{CF}$ = 279 Hz, CF_3), 125.9 (q, $^4J_{CF}$ = 2.5 Hz, C-5), 132.7 (C-6), 136.9 (C-7), 152.9 (C-8a), 155.6 (q, $^2J_{CF}$ = 36 Hz, C-4); ^{19}F NMR ($CDCl_3$): δ –69.37. Anal. Calcd for $C_{11}H_7Cl_3F_3NO$: C, 39.73; H, 2.12; Cl, 31.98; N, 4.21. Found: C, 39.94; H, 2.30; Cl, 31.81; N, 4.25.

6,7-Dimethyl-4-phenyl-2-trichloromethyl-2*H*-1,3-benzoxazine (2e) Yield 39% (method A); yellow powder; mp 106–108°C; ^{1}H NMR ($CDCl_3$): δ 2.18 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 5.90 (s, 1H, CHN), 6.91 (s, 1H, Ar), 7.06 (s, 1H, Ar), 7.5 (m, 3H, Ar), 7.64 (d, 2H, $^3J_{HH}$ = 7.8 Hz, Ar);^{13}C NMR ($CDCl_3$): δ 19.1 (Me), 20.4 (Me), 94.3 (C-2), 99.6 (CCl_3), 115.1 (C-4a), 117.3 (C-8), 128.5 ($C^{3,5}_{Ph}$), 128.7 (C-6), 128.8 (C-5), 129.2 ($C^{2,6}_{Ph}$), 130.4 (C^{4}_{Ph}), 136.2 (C^{1}_{Ph}), 144.4 (C-7), 153.1 (C-8a), 167.1 (C-4). Anal. Calcd for $C_{17}H_{14}Cl_3NO$: C, 57.57; H, 3.98; Cl, 29.99; N, 3.95. Found: C, 57.71; H, 4.12; Cl, 30.21; N, 4.12.

4,6-Dimethyl-2-trichloromethyl-2*H*-1,3-benzoxazine (2f) Yield 45% (method A); colorless oil; ^{1}H NMR ($CDCl_3$): δ 2.32 (s, 3H, Me), 2.45 (s, 3H, Me), 5.79 (s, 1H, CHN), 6.88 (d, 1H, $^3J_{HH}$ = 8.8 Hz, Ar), 7.2 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$): δ 20.7 (6-Me), 22.0 (4-Me), 94.1 (C-2), 99.5 (CCl_3), 115.9 (C-8), 126.0 (C-5), 135.0 (C-7), 117.2 (C-4a), 131.7 (C-6), 151.5 (C-8a), 165.7 (C-4). Anal. Calcd for $C_{11}H_{10}Cl_3NO$: C, 47.43; H, 3.62; Cl, 38.18; N, 5.03. Found: C, 47.62; H, 3.85; Cl, 38.25; N, 5.23.

4-(Fluoromethyl)-6-methyl-2-trichloromethyl-2*H*-1,3-benzoxazine (2g) Yield 30% (method A); colorless oil; ^{1}H NMR ($CDCl_3$): δ 2.24 (s, 3H, Me), 5.29 (d, 2H, $^2J_{HF}$ = 47 Hz, CH_2F), 5.77 (s, 1H, CHN), 6.83 (d, 1H, $^3J_{HH}$ = 8 Hz, Ar), 7.16 (d, 1H, $^3J_{HH}$ = 8 Hz, Ar), 7.23 (s, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ 20.7 (Me), 83.1 (d, $^1J_{CF}$ = 174 Hz, CF), 94.0 (C-2), 98.7 (CCl_3), 114.8 (C-4a), 116.1 (C-8), 125.8 (d, $^4J_{CF}$ = 5 Hz, C-5), 132.1 (C-6), 135.7 (C-7), 151.8 (C-8a), 162.9 (d, $^2J_{CF}$ = 17 Hz, C-4); ^{19}F-{H} NMR ($CDCl_3$): δ –223.6. Anal. calcd for $C_{11}H_9Cl_3FNO$: C, 44.55; H, 3.06; Cl, 35.86; N, 4.72. Found: C, 44.74; H, 3.21; Cl, 35.99; N, 4.87.

4-Chloromethyl-6-methyl-2-trichloromethyl-2*H*-1,3-benzoxazine (2h, the presumed by-product) ^{1}H NMR ($CDCl_3$): δ 2.25 (s, 3H, Me), 4.42 (s, 2H, CH_2Cl), 5.79 (s, 1H, CHN), 6.82 (d, 1H, $^3J_{HH}$ = 8 Hz, Ar), 7.16 (d, 1H, $^3J_{HH}$ = 8 Hz, Ar), 7.23 (s, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ 20.7 (Me), 43.2 (CH_2Cl), 94.0 (C-2), 98.8 (CCl_3), 114.5 (C-4a), 116.2 (C-8), 125.8 (C-5), 132.0 (C-6), 135.7 (C-7), 152.0 (C-8a), 163.2 (C-4).

4-Phenyl-2-(trichloromethyl)-2*H*-naphtho-1,3-oxazine (4) Yield 66% (method A); yellowish solid; mp 161–162°C; ^{1}H NMR ($CDCl_3$): δ 6.40 (s, 1H, CHN), 7.41 (d, 1H, $^3J_{HH}$ = 8 Hz, Ar), 7.53–7.9 (m, 9H, Ar), 8.44 (d, 1H, $^3J_{HH}$ = 8 Hz, Ar); ^{13}C NMR ($CDCl_3$): δ 94.7 (C-2), 99.3 (CCl_3), 112.0 (C-4a), 121.1 (C-7), 122.8 (C-9), 123.5 (C^{1}_{Ph}), 123.6 (C-6), 126.8 (C-5), 127.8 (C-10), 128.6 ($C^{3,5}_{Ph}$), 129.4 (C^{4}_{Ph}), 129.4 (C^{2}_{Ph}), 130.7 (C-8), 135.9 (C-6a), 136.7 (C-10a), 152.7 (C-10b), 167.8 (C-4). Anal. Calcd for $C_{19}H_{12}Cl_3NO$: C, 60.59; H, 3.21; Cl, 28.24; N, 3.72. Found: C, 60.81; H, 3.31; Cl, 28.18; N, 3.89.

General procedure for the preparation of 2-dichloromethylenebenzoxazines 5a–c and 6

A solution of the benzoxazine **2a–c** or **4** (0.5 mmol) and DBU (0.08 g, 0.5 mmol) in chloroform (2 mL) was allowed to stand at room temperature for 6 days. The solvent was evaporated under reduced pressure. The solid residue was triturated with water, filtered and crystallized from aqueous ethanol (1:1).

2-Dichloromethylene-4-phenyl-2*H*-1,3-benzoxazine (5a) Yield 41%; white solid; mp 125–126°C; ^{1}H NMR ($CDCl_3$): δ 7.05 (m, 2H, Ar), 7.5 (m, 5H, Ar), 7.7 (m, 2H, Ar). Anal. Calcd for $C_{15}H_9Cl_2NO$: C, 62.09; H, 3.13; Cl, 24.44; N, 4.83. Found: C, 62.21; H, 3.28; Cl, 24.27; N, 5.08.

2-Dichloromethylene-6-fluoro-4-phenyl-2*H*-1,3-benzoxazine (5b) Yield 60%; white solid; mp 155–156°C; ^{1}H NMR ($CDCl_3$): δ 7.05 (m, 1H, Ar), 7.15 (m, 2H, Ar), 7.54 (m, 3H, Ar), 7.7 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$): δ 102.1 (CCl_2), 114.0 (d, $^2J_{CF}$ = 25 Hz, C-5), 117.0 (d, $^3J_{CF}$ = 8 Hz, C-4a), 117.3 (d, $^3J_{CF}$ = 7 Hz, C-8), 121.3 (d, $^2J_{CF}$ = 24 Hz, C-7), 128.8 ($C^{2,6}_{Ph}$), 128.9 ($C^{3,5}_{Ph}$), 130.9 (C^{4}_{Ph}), 135.0 (C^{1}_{Ph}), 147.5 (C-2), 151.2 (d, $^4J_{CF}$ = 2 Hz, C-8a), 157.9 (d, $^1J_{CF}$ = 243 Hz, C-6), 160.2 (d, $^4J_{CF}$ = 2 Hz, C-4); ^{19}F NMR ($CDCl_3$): δ –118.3. Anal. Calcd for $C_{15}H_8Cl_2FNO$: C, 58.47; H, 2.62; Cl, 23.01; N, 4.55. Found: C, 58.60; H, 2.88; Cl, 23.00; N, 4.85.

2-Dichloromethylene-6-methyl-4-phenyl-2*H*-1,3-benzoxazine (5c) Yield 58%; white solid; mp 130–130.5°C; ^{1}H NMR ($CDCl_3$): δ 2.27 (s, 3H, Me), 6.97 (d, 1H, $^3J_{HH}$ = 8.4 Hz, Ar), 7.19 (s, 1H, Ar), 7.26 (d, 1H, $^3J_{HH}$ = 8.4 Hz, Ar), 7.5 (m, 3H, Ar), 7.7 (m, 2H, Ar). Anal. Calcd for $C_{16}H_{11}Cl_2NO$: C, 63.18; H, 3.65; Cl, 23.31; N, 4.60. Found: C, 63.33; H, 3.82; Cl, 23.38; N, 4.66.

2-Dichloromethylene-6-methyl-4-trifluoromethyl-1,3-benzoxazine (5d) A solution of benzoxazine **2d** (0.2 g, 1.1 mmol) and Et_3N (0.17 mL, 1.7 mmol) in dichloromethane (0.5 mL) was stirred at room temperature overnight. The mixture was washed with water (2 × 3 mL) and dried ($MgSO_4$). After evaporation of solvent the residue was extracted with hot hexane: yield 89%; red solid; mp 155–156°C; ^{1}H NMR ($CDCl_3$): δ 2.33 (s, 3H, Me), 6.91 (d, 1H, $^3J_{HH}$ = 8.4 Hz, Ar), 7.24 (m, 1H, Ar), 7.29 (m, 1H, $^3J_{HH}$ = 8.4 Hz, Ar); ^{13}C NMR ($CDCl_3$): δ 20.7 (Me), 111.5 (CCl_2), 115.7 (C-8), 116.2 (C-4a), 119.5 (q, $^1J_{CF}$ = 277 Hz, CF_3), 125.5 (q, $^4J_{CF}$ = 3 Hz, C-5), 132.4 (C-6), 136.8 (C-7), 146.4 (C-2), 148.2 (q, $^2J_{CF}$ = 36 Hz, C-4), 153.1 (C-8a); ^{19}F NMR ($CDCl_3$): δ = –69.17. Anal. Calcd for $C_{11}H_6Cl_2F_3NO$: C, 44.62; H, 2.04; Cl, 23.95; N, 4.73. Found: C, 44.85; H, 2.25; Cl, 23.99; N, 4.89.

4-Phenyl-2-(dichloromethylene)-2*H*-naphtho[2,1-e][1,3]-oxazine (6) Yield 56%; red solid; mp 168°C; ^{1}H NMR ($CDCl_3$): 7.37–7.63 (m, 10H), 8.45 (d, 1H, $^3J_{HH}$ = 8 Hz). Anal. Calcd for $C_{19}H_{11}Cl_2NO$: C, 67.08; H, 3.26; Cl, 20.84; N, 4.12. Found: C, 67.17; H, 3.20; Cl, 20.72; N, 4.09.

General procedure for the preparation of 2-dichloromethylbenzoxazines 7a,b

A solution of benzoxazine **2f,g** (0.43 mmol) and DBU (0.1 g, 0.65 mmol) in dichloromethane (2 mL) was stirred at room temperature for 12 h. The mixture was washed with water and dried ($MgSO_4$). The solvent was evaporated under reduced pressure and the residue was extracted with hot hexane.

2-Dichloromethyl-6-methyl-4-methylene-4*H*-1,3-benzoxazine (7a) Yield 37%; colorless oil; ^{1}H NMR ($CDCl_3$): δ 2.38 (s, 3H, Me), 5.11 (s, 1H, $=CH_a$), 5.30 (s, 1H, $=CH_b$), 6.19 (s, 1H, $CHCl_2$), 7.02 (d, 1H, $^3J_{HH}$ = 8.5 Hz, 8-H), 7.17 (d, 1H, $^3J_{HH}$ = 8.5 Hz, 7-H), 7.33 (s, 1H, 5-H); ^{13}C NMR ($CDCl_3$): δ 21.1 (Me), 66.7 ($CHCl_2$), 103.4 ($=CH_2$), 116.40 (C-8), 117.8 (C-4a), 123.6 (C-5), 131.4 (C-7), 136.1 (C-6), 139.2 (C-4), 146.9 (C-8a), 150.3 (C-2). Anal. Calcd for $C_{11}H_9Cl_2NO$: C, 54.57; H, 3.75; Cl, 29.29; N, 5.79. Found: C, 54.71; H, 3.88; Cl, 29.27; N, 5.91.

2-Dichloromethyl-6-methyl-4-(fluoromethylene)-4*H*-1,3-benzoxazine (7b) This compound was purified by column chromatography (silica gel, benzene) and isolated as a mixture (10:1) of *E*/*Z* isomers; yield 70%; colorless oil.

***E*-isomer** ^{1}H NMR (C_6D_6): δ 2.04 (s, 3H, Me), 6.10 (s, 1H, $CHCl_2$), 6.58 (d, 1H, $^2J_{HF}$ = 76.3 Hz, CHF), 6.55 (s, 1H, 5-H), 6.68 (1H) and 6.74 (1H), two doublets, $^3J_{HH}$ = 9 Hz (7-H and 8-H); ^{13}C NMR (C_6D_6): δ 20.5 (Me), 66.8 ($CHCl_2$), 114.4 (d, $^3J_{CF}$ = 3 Hz, C-4a), 116.3 (C-8), 120.8 (d, $^6J_{CF}$ = 1 Hz, C-7), 121.2 (d, $^2J_{CF}$ = 9 Hz, C-4), 130.5 (d, $^4J_{CF}$ = 2.5 Hz, C-5), 135.6 (d, $^5J_{CF}$ = 1 Hz, C-6), 140.4 (d, $^1J_{CF}$ = 269 Hz, =CF), 146.6 (d, $^4J_{CF}$ = 7 Hz) and 150.4 (d, $^4J_{CF}$ = 5 Hz) (C-2 and C-8a); ^{19}F NMR (C_6D_6): δ = –150.6 (d, $^2J_{FH}$ = 76.3 Hz).

***Z*-isomer** ^{1}H NMR (C_6D_6): δ 2.06 (s, 3H, Me), 6.00 (s, 1H, $CHCl_2$), 7.11 (d, 1H, $^2J_{HF}$ = 80 Hz, CHF); ^{13}C NMR (C_6D_6): δ 20.5 (Me), 66.6 ($CHCl_2$), 115.8 (C-8), 131.1 (d, $^4J_{CF}$ = 2 Hz, C-5); ^{19}F NMR (C_6D_6): δ = –142.9 (d, $^2J_{FH}$ = 80 Hz). Analysis for mixture. Calcd for $C_{11}H_8Cl_2FNO$: C, 50.80; H, 3.10; Cl, 27.26; N, 5.39. Found: C, 50.97; H, 3.15; Cl, 27.39; N, 5.50.

***N*-(1,2,2,2-Tetrachloroethyl)trifluoroacetamide (9b)** A solution of acetamide **8b** (10 g, 0.04 mol) and phosphorus pentachloride (8 g, 0.04 mol) in benzene (50 mL) was heated until evolution of hydrogen chloride ceased. After cooling to room temperature, the precipitated solid was separated by filtration and purified by sublimation in vacuo: yield 70%; white solid; mp 49–50°C; ^{1}H NMR ($CDCl_3$): δ 6.45 (d, 1H, $^3J_{HH}$ = 10 Hz, CHN), 7.09 (br s, 1H, NH); ^{19}F NMR ($CDCl_3$): δ –76.3. Anal. Calcd for $C_4H_2Cl_4F_3NO$: C, 17.23; H, 0.72; Cl, 50.85; N, 5.02. Found: C, 17.35; H, 0.79; Cl, 50.99; N, 5.14.

General procedure for the preparation of *N*-substituted amides 10a–h

A solution of chloride **9a–d** (20 mmol), respective phenol (20 mmol) and triethylamine (2.8 mL, 20 mmol) in anhydrous benzene (50 mL) was heated under reflux for 3 h. The precipitated product was separated by filtration, successively washed with benzene and water and crystallized from ethanol (**10a–f,h**). Compound **10g** was purified by column chromatography (silica-gel, hexane-ethyl acetate, 9:1).

***N*-(2,2,2-Trichloro-1-phenoxyethyl)benzamide (10a)** Yield 80%; mp 175–176°C, lit. mp 175–176°C [31].

***N*-[2,2,2-Trichloro-1-(4-fluorophenoxy)ethyl]benzamide (10b)** Yield 77%; white solid; mp 137–138°C; ^{1}H NMR ($CDCl_3$): δ 6.55 (d, 1H, $^3J_{HH}$ = 9.9 Hz, CHN), 6.95 (d, 1H, $^3J_{HH}$ = 9.9 Hz, NH), 7.01 (t, 2H, $^3J_{HH}$ = $^3J_{HF}$ = 7.8 Hz, Ar), 7.12 (m, 2H, Ar), 7.49 (t, 2H, $^3J_{HH}$ = 7.5 Hz, Ar), 7.59 (t, 1H, $^3J_{HH}$ = 7.5 Hz, Ar), 7.82 (d, 2H, $^3J_{HH}$ = 7.5 Hz, Ar); ^{19}F NMR ($CDCl_3$): δ = –119.9. Anal. Calcd for $C_{15}H_{11}Cl_3FNO_2$: C, 49.68; H, 3.06; Cl, 29.33; N, 3.86. Found: C, 49.90; H, 3.21; Cl, 29.41; N, 3.94.

***N*-[2,2,2-Trichloro-1-(4-methylphenoxy)ethyl]benzamide (10c)** Yield 75%; white solid; mp 116–117°C; ^{1}H NMR ($CDCl_3$): δ 2.29 (s, 3H, Me), 6.59 (d, 1H, $^3J_{HH}$ = 9.9 Hz, CHN), 6.91 (d, 1H, $^3J_{HH}$ = 9.9 Hz, NH), 7.04 (d, 2H, $^3J_{HH}$ = 8.7 Hz, Ar), 7.12 (d, 2H, $^3J_{HH}$ = 8.7 Hz, Ar), 7.48 (t, 2H, $^3J_{HH}$ = 7.5 Hz, Ar), 7.58 (t, 1H, $^3J_{HH}$ = 7.5 Hz, Ar), 7.81 (d, 2H, $^3J_{HH}$ = 7.5 Hz, Ar). Anal. Calcd for $C_{16}H_{14}Cl_3NO_2$: C, 53.58; H, 3.93; Cl, 29.65; N, 3.91. Found: C, 53.71; H, 4.10; Cl, 29.50; N, 4.05.

***N*-[2,2,2-Trichloro-1-(4-methylphenoxy)ethyl]trifluoroacetamide (10d)** Yield 50%; colorless oil; ^{1}H NMR ($CDCl_3$): δ 2.32 (s, 3H, Me), 6.30 (d, 1H, $^3J_{HH}$ = 10 Hz, CHN), 6.94 (d, 2H, $^3J_{HH}$ = 8.5 Hz, Ar), 7.02 (d, 1H, $^3J_{HH}$ = 10 Hz, NH), 7.12 (d, 2H, $^3J_{HH}$ = 8.5 Hz, Ar); ^{13}C NMR

($CDCl_3$): δ 20.6 (Me), 85.2 (CHN), 97.8 (CCl_3), 116.3 ($C^{2,6}{}_{Ar}$), 130.6 ($C^{3,5}{}_{Ar}$), 133.8 ($C^{4}{}_{Ar}$), 153.3 (C=O), 157.0 (q, $^1J_{CF}$ = 39 Hz, $C^{1}{}_{Ar}$); ^{19}F-{H} NMR ($CDCl_3$): δ –76.4. Anal. Calcd for $C_{11}H_9Cl_3F_3NO_2$: C, 37.69; H, 2.59; Cl, 30.34; N, 4.00. Found: C, 37.86; H, 2.68; Cl, 30.57; N, 4.15.

***N*-[2,2,2-Trichloro-1-(3,4-dimethylphenoxy)ethyl]benzamide (10e)** Yield 79%, white solid, mp 155°C. ^{1}H NMR ($CDCl_3$): δ = 2.18 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 6.59 (d, 1H, $^3J_{HH}$ = 9 Hz, CHN), 6.8–6.94 (m, 3H, Ar), 7.06 (d, 1H, $^3J_{HH}$ = 9 Hz, NH), 7.47 (t, 2H, $^3J_{HH}$ = 7.8 Hz, Ar), 7.56 (m, 1H, $^3J_{HH}$ = 7.8 Hz, Ar), 7.81 (d, 2H, $^3J_{HH}$ = 7.8 Hz, Ar). Anal. Calcd for $C_{17}H_{16}Cl_3NO_2$: C, 54.79; H, 4.33; Cl, 28.54; N, 3.76. Found: C, 54.89; H, 4.56; Cl, 28.20; N, 3.85.

***N*-[2,2,2-Trichloro-1-(4-methylphenoxy)ethyl]acetamide (10f)** Yield 60%; white solid; mp 107–108°C; ^{1}H NMR ($CDCl_3$): δ 2.11 (s, 3H, Me), 2.31 (s, 3H, Me), 6.37 (d, 1H, $^3J_{HH}$ = 10 Hz, CHN), 6.44 (d, 1H, $^3J_{HH}$ = 10 Hz, NH), 6.97 (d, 2H, $^3J_{HH}$ = 8 Hz, Ar), 7.12 (d, 2H, $^3J_{HH}$ = 8 Hz, Ar); ^{13}C NMR ($CDCl_3$): δ 20.6 (MeAr), 23.3 (MeC=O), 84.5 (CHN), 99.1 (CCl_3), 116.1 ($C^{2,6}{}_{Ar}$), 130.3 ($C^{3,5}{}_{Ar}$), 132.6 ($C^{4}{}_{Ar}$), 153.8 ($C^{1}{}_{Ar}$), 170.0 (C=O). Anal. Calcd for $C_{11}H_{12}Cl_3NO_2$: C, 44.55; H, 4.08; Cl, 35.86; N, 4.72. Found: C, 44.73; H, 4.20; Cl, 35.97; N, 4.81.

***N*-[2,2,2-Trichloro-1-(4-methylphenoxy)ethyl]fluoroacetamide (10g)** Yield 80%; white solid; mp 46–48°C; ^{1}H NMR ($CDCl_3$): δ 2.30 (s, 3H, Me), 4.91 (dd,1H, $^2J_{HF}$ = 47 Hz, $^2J_{HH}$ = 15 Hz, CH_AF), 4.84 (dd, 1H, $^2J_{HF}$ = 47 Hz, $^2J_{HH}$ = 15 Hz, CH_BF), 6.39 (d, 1H, $^3J_{HH}$ = 10 Hz, CHN), 6.97 (d, 2H, $^3J_{HH}$ = 8 Hz, Ar), 7.12 (m, 3H, Ar, NH); ^{13}C NMR ($CDCl_3$): δ 20.6 (Me), 79.7 (d, $^1J_{CF}$ = 187 Hz, CH_2F), 84.1 (CHN), 98.6 (CCl_3), 116.2 ($C^{2,6}{}_{Ar}$), 130.4 ($C^{3,5}{}_{Ar}$), 133.1 ($C^{4}{}_{Ar}$), 153.6 ($C^{1}{}_{Ar}$), 167.8 (d, $^2J_{CF}$ = 19 Hz, C=O); ^{19}F-{H} NMR ($CDCl_3$): δ –226.5. Anal. Calcd for $C_{11}H_{11}Cl_3FNO_2$: C, 42.00; H, 3.52; Cl, 33.81; N, 4.45. Found: C, 42.19; H, 3.75; Cl, 33.95; N, 4.50.

***N*-[2,2,2-Trichloro-1-(1-naphthyloxy)ethyl]benzamide (10h)** Yield 50%; light red solid; mp 177–178°C; ^{1}H NMR ($CDCl_3$): δ 6.87 (d, 1H, $^3J_{HH}$ = 10 Hz, CHN), 7.02 (d, 1H, $^3J_{HH}$ = 10 Hz, NH), 7.23 (d, 1H, $^3J_{HH}$ = 7.2 Hz, Ar), 7.36–7.59 (m, 7H, Ar), 7.82 (m, 3H, Ar), 8.33 (m, 1H, Ar). Anal. Calcd for $C_{19}H_{14}Cl_3NO_2$: C, 57.82; H, 3.58; Cl, 26.95; N, 3.55. Found: C, 57.75; H, 3.41; Cl, 26.90; N, 3.73.

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