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Selective syntheses of benzoxazoles and *N*-(2-hydroxyaryl)pyrrolidin-2-ones from the corresponding cyclopropyl amides with PPh_3/CX_4

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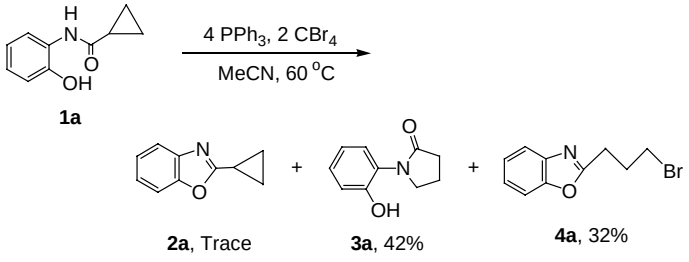
Abstract—Benzoxazoles **2** can be smoothly synthesized by treatment of starting materials of *N*-(2-hydroxyaryl) cyclopropyl amides **1** with PPh_3/CCl_4 in acetonitrile in good yields. When PPh_3/CBr_4/MS 4 Å was used in the reaction system, the corresponding ring-expanding products **3** were obtained in moderate to good yields in acetonitrile at 80 °C. Using DCE as a solvent in this reaction, the corresponding 2-(3-chloropropyl)benzoxazoles **5** were obtained as major products.

1. Introduction

It is well known that triphenylphosphine in the combination with a tetrahalomethane provides reagents that have manifold uses and are finding increasing application in preparative chemistry for halogenation, dehydration, and P–N linking reactions.[1] Of more general importance is tertiary phosphane/tetrachloromethane system, as chlorinating and dehydrating agent for sensitive substrates to the aggressive and readily hydrolyzed acid chlorides such as PCl_5, $P(O)Cl_3$, thionyl chloride and sulfonyl chloride. A great advantage can also be seen in the ability to the demands made by the various donor strengths of the substituents chosen for attachment to the phosphorus atom.[2] However, there are few reports about changing the halogen atom in the reaction by use of tetrahalomethane in the combination with tertiary phosphane system.[1a,3]

Recently, we reported a new preparation method for *N*-substituted pyrrolidin-2-ones from cyclopropyl amides in good yields in the presence of 2.0 equiv of PPh_3 and 1.0 equiv of CBr_4.[4] As it is well known, lactam rings are of important structures in a number of biologically and pharmaceutically active compounds as well as some alkaloids such as cotinine or mannolactam having lactam structures.[5] Among these lactam compounds, pyrrolidinones are often found in natural products and a variety of pharmacologically active compounds, for example, convultamides,[6] enzyme inhibitors[7] and various drugs.[8] Therefore, in order to extend the scope and limitations of this interesting ring-expanding reaction, we next carried out the reaction of *N*-(2-hydroxyphenyl)cyclopropyl amide **1a** in the presence of PPh_3/CBr_4 under the same reaction conditions. As shown in Scheme 1, *N*-(2-hydroxyphenyl)-pyrrolidin-2-one **3a** as a ring-expanding product was



Scheme 1. Reaction of *N*-(2-hydroxyphenyl) cyclopropyl amide **1a** with PPh_3/CBr_4.

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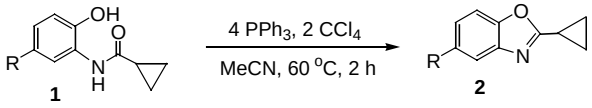
obtained in 42% yield along with a trace of benzoxazole product **2a** and 32% of 2-(3-bromopropyl)benzoxazole **4a**, which was determined as a ring-opening product of **2a** by Br^- (see Supporting information for spectroscopic data).

This result intrigued us to explore the precious reaction conditions to prepare benzoxazole products and *N*-(2-hydroxyaryl)pyrrolidin-2-one derivatives selectively from *N*-(2-hydroxyaryl) cyclopropyl amide **1** since highly selective synthesis beginning from the same starting materials is a formidable challenge in organic synthesis.[9]

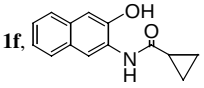
2. Results and discussion

After trial and error, we found that the dehydration reaction proceeded smoothly to give the desired benzoxazole product **2a** in 88% yield as a sole product in acetonitrile at 60 °C with 4.0 equiv of PPh_3 and 2.0 equiv of CCl_4 without ring-expanding product **3a** and ring-opening product **4a** (Table 1, entry 1). Moreover, the above reaction conditions were found to be quite general. Other *N*-(2-hydroxyaryl) cyclopropyl amides **1a–g** bearing a variety of substituted phenyl groups as well as cyclopropanecarboxylic acid (3-hydroxynaphthalen-2-yl) amide **1f** also underwent the dehydration and cyclization to give the corresponding benzoxazoles **2**, as a sole product, in excellent yields under the same reaction conditions within 2 h (Table 1, entries 2–6).

Table 1. Intramolecular dehydration reaction of **1** with PPh_3/CBr_4



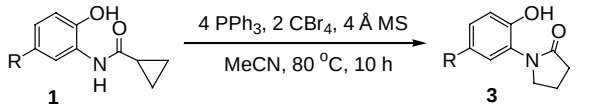
1 2

Entry	R	Yield (%)[a]
		2
1	**1a**, H	**2a**, 88
2	**1b**, Me	**2b**, 96
3	**1c**, OMe	**2c**, 95
4	**1d**, Cl	**2d**, 97
5	**1e**, F	**2e**, 85
6	**1f**, 	**2f**, 96

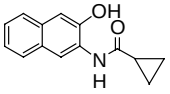
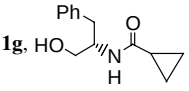
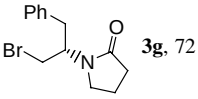
[a] Isolated yields.

Interestingly, we found that when CBr_4 was utilized to replace CCl_4 for this reaction, the corresponding ring-expanding product **3a** was formed in 87% yield in acetonitrile after the reaction solution was stirred for 10 h at 80 °C in the presence of molecular sieves 4 Å (100 mg for 0.3 mmol) (Table 2, entry 1). It should be noted that molecular sieves 4 Å was necessary for this reaction because three products were formed in the absence of MS 4 Å (Scheme 1). Next, under these optimized reaction conditions, the ring-expanding reactions of other substrates were also investigated in the presence of PPh_3/CBr_4/MS 4 Å in acetonitrile. The results are summarized in Table 2. The corresponding 1-(2-hydroxyphenyl)pyrrolidin-2-ones **3** were obtained in good yields for a variety of *N*-(2-hydroxyaryl) cyclopropyl amides **1** (Table 2, entries 2–4). However, for substrate **3e** bearing an electron-withdrawing fluoro group on the benzene ring, the reaction became sluggish and some of the starting materials (amide **1e**) can be recovered even if the reaction time was prolonged to 3 days (Table 2, entry 5). Using **1f** as substrate, no reaction occurred (Table 2, entry 6). As for aliphatic cyclopropyl amide **1g**, a L-2-amino-3-phenylpropanol derivative, the corresponding ring-expanding as well as brominated product **3g** was formed in 72% yield under identical conditions (Table 2, entry 7).

Table 2. Ring-expanding reaction of **1** with PPh_3/CBr_4/MS 4 Å in MeCN



1 3

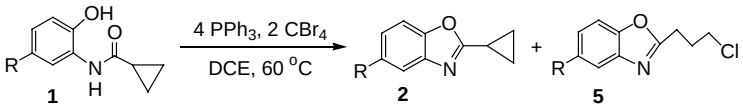
Entry	R	Yield (%)[a]
		3
1	**1a**, H	**3a**, 87
2	**1b**, Me	**3b**, 77
3	**1c**, OMe	**3c**, 50
4	**1d**, Cl	**3d**, 88
5	**1e**, F	**3e**, 51 (26)[b]
6	**1f**, 	NR
7	**1g**, 	 **3g**, 72

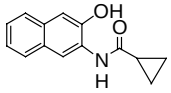
[a] Isolated yields.
[b] The reaction time was prolonged to 3 days, the yield in bracket is the recovered yield of starting materials **1e**.

The structures of benzoxazole products **2** and pyrrolidin-2-ones **3** were determined by NMR spectroscopic data, microanalyses and HRMS (see Supporting information).

The similar reaction was also investigated using 1,2-dichloroethane (DCE) instead of acetonitrile as a solvent. We found that *N*-(2-hydroxyaryl) cyclopropyl amides **1a–1f** could surprisingly undergo dehydration and subsequent chloride displacement to afford the corresponding 2-(3-chloropropyl)benzoxazole products **5a–5f** in moderate to good yields along with 2-cyclopropylbenzoxazoles **2** as minor constituents during a prolonged reaction time (Table 3, entries 1–6). The structure of **5d** was further determined by X-ray diffraction. The ORTEP draw of **5d** is shown in Figure 1.[10] The control experiment showed that after a prolonged reaction time, 2-(3-chloropropyl)benzoxazole product **5a** can be obtained from the corresponding 2-(3-bromopropyl)benzoxazole **4a** in 88% yield when the reaction was carried out in DCE, in addition, no reaction occurred when **2a** was treated with PPh_3 in DCE under identical conditions (Scheme 2). Therefore, we believe that products **5** were formed through the corresponding products **4** when DCE, containing Cl atom, was used as a solvent. Namely, although Cl^-, generated from PPh_3 and DCE,[11] cannot trigger the ring-opening reaction of benzoxazole products **2** bearing a cyclopropyl ring to take place presumably due to its weak nucleophilicity, nucleophilic displacement of bromo atom in compounds **4** by chloro

Table 3. Reaction of **1** with PPh_3/CBr_4 in DCE



Entry	R	Time (days)	Yield (%)[a]	Yield (%)[a]
			2	**5**
1	**1a**, H	3	**2a**, Trace	**5a**, 79
2	**1b**, Me	3	**2b**, Trace	**5b**, 64
3	**1c**, OMe	4	**2c**, Trace	**5c**, 89
4	**1d**, Cl	3	**2d**, Trace	**5d**, 84
5	**1e**, F	5	**2e**, 17	**5e**, 69
6	**1f**, 	5	**2f**, 20	**5f**, 73

[a] Isolated yields.

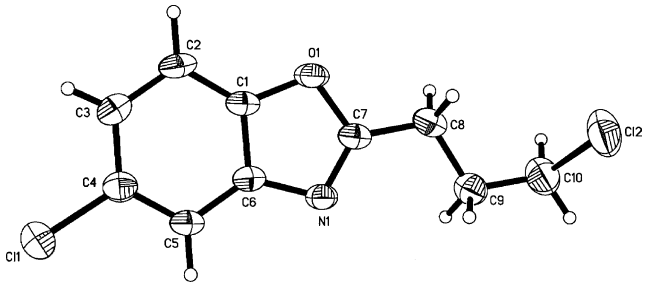
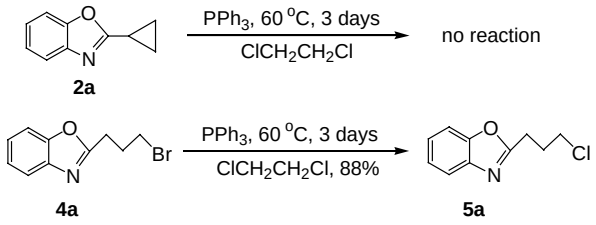


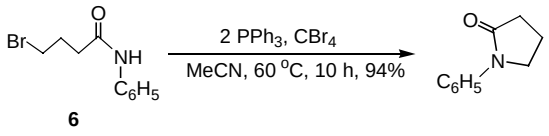
Figure 1. ORTEP drawing of **5d**.



Scheme 2. Control experiment of the formation of **5a**.

atom could occur to give the corresponding chlorinated products **5** at 60 °C.

Based on the above results and previous literature on the reaction of amide with PPh_3/CX_4[12] as well as our studies on the mechanism in the transformation of cyclopropyl amides to *N*-substituted pyrrolidin-2-ones in which we confirmed that the ring-expanding reaction proceeded through 4-bromo-butyramide intermediate **6** as shown in Scheme 3,[4] a plausible reaction mechanism is proposed in Scheme 4. At first, triphenylphosphine reacts with carbon tetrahalide to give the corresponding dihalogentriphenylphosphorane **7**

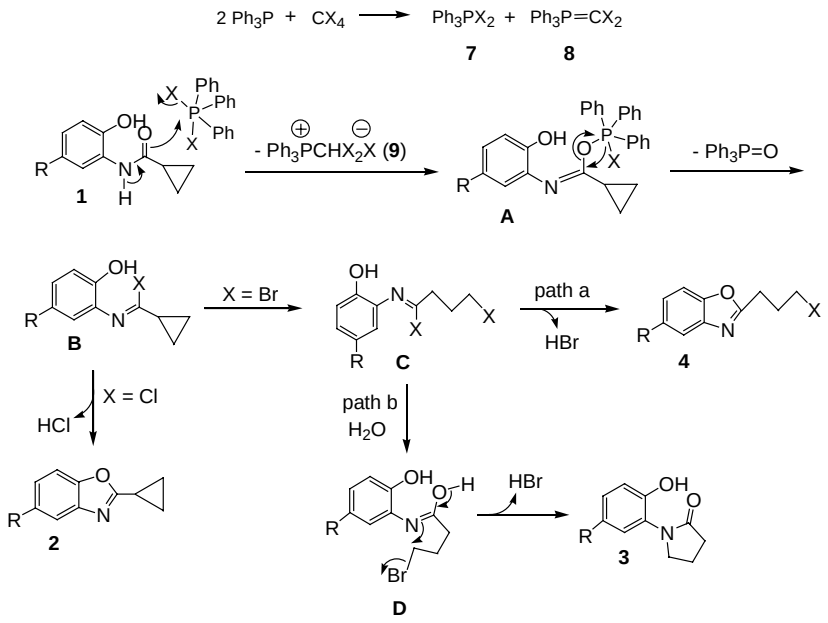


Scheme 3. Ring-closure reaction of 4-bromo-*N*-phenyl-butyramide **6** with PPh_3/CBr_4.

and dihalogenmethylene ylid **8**. Next, the intermediate **A** is formed by the reaction of *N*-(2-hydroxyaryl) cyclopropyl amide **1** with dihalogentriphenylphosphorane **7** to release a dihalogenmethyltriphenylphosphonium salt **9** as white precipitates, which is dissolved after the solution was heated.[1f,g] Thus, the corresponding *N*-substituted formimidoyl halogen **B** is formed along with the generation of triphenylphosphine oxide. When CCl_4 is used in the reaction, intramolecular ring-closure smoothly takes place to give the corresponding benzoxazoles bearing cyclopropyl group **2**. On the other hand, if CBr_4 is subjected into the reaction instead of CCl_4, the subsequent ring-opening process of *N*-substituted formimidoyl halogen **B** takes place, because of the comparatively stronger nucleophilicity of Br^- than Cl^-, to give another formimidoyl halogen **C**, which gives the ring-closure product **4** through intramolecuar substitution of Br atom by the phenolic OH group on the *ortho* position (path a). If the Br atom in formimidoyl halogen **C** is substituted by OH group of ambient H_2O in the reaction system, the corresponding pyrrolidin-2-one **3** can be obtained through intermediate **D** (path b). Though it is difficult to explain the exact role of molecular sieves 4 Å at present stage, experiment results indicate that molecular sieves 4 Å prevent the intramolecuar substitution of Br atom by the phenolic OH group on the *ortho* position and alternatively, intermolecular attack by ambient H_2O in reaction system takes place to give the corresponding pyrrolidin-2-one product **3**.

3. Conclusion

We succeeded in the preparation of intramolecular dehydration product benzoxazoles bearing cyclopropyl group **2** from the *N*-(2-hydroxyaryl) cyclopropyl amide **1** with PPh_3/CCl_4. When CBr_4 was used instead of CCl_4 in the reaction, 1-(2-hydroxyaryl)pyrrolidin-2-ones **3** can be obtained in moderate to good yield in the presence of molecular sieves 4 Å. Using DCE as a solvent for the reaction, the corresponding 2-(3-chloropropyl)benzoxazoles **5** were obtained as major products. Efforts are underway to elucidate the mechanistic details and to extend the scope of this reaction.



Scheme 4. A possible reaction mechanism.

4. Experimental

4.1. General methods

^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Mass spectra were recorded by EI and MALDI methods, and HRMS was measured on Kratos Analytical Concept mass spectrometer (EI), Bruker FT mass spectrometer (ESI), and IonSpec 4.7 T FTMS (MALDI). Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Yinlong GF254 silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure.

4.2. General procedure for the preparation of *N*-(2-hydroxyaryl) cyclopropyl amide

Added dropwise cyclopropanecarbonyl chloride (261 mg, 2.5 mmol, 228 μL) to the mixture of 2-aminophenol (2.5 mmol) and pyridine (3.0 mmol) in ethyl acetate (EtOAc) (20 mL) at room temperature. After stirring for another 2 h, the reaction mixture was washed with 10% HCl (50 mL×2) and dried over anhydrous $MgSO_4$. The corresponding pure *N*-(2-hydroxyaryl) cyclopropyl amide can be obtained through a short column chromatography (SiO_2).

4.3. General procedure for the synthesis of benzoxazole from *N*-(2-hydroxyaryl) cyclopropyl amide

A mixture of *N*-(2-hydroxyaryl) cyclopropyl amide (0.3 mmol), PPh_3 (314 mg, 1.2 mmol) and CCl_4 (92 mg, 58 μL, 0.6 mmol) was dissolved in acetonitrile (3.0 mL). The solvent was evaporated after the reaction system was heated at 60 °C for 2 h. The residue was dissolved in CH_2Cl_2 (50 mL), washed with H_2O (50 mL×2), and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by a silica gel column chromatography to give the corresponding benzoxazole product.

4.4. General procedure for the synthesis of *N*-(2-hydroxyphenyl)pyrrolidin-2-one from *N*-(2-hydroxyaryl) cyclopropyl amide

Molecular sieves 4 Å (100 mg) was put into a glass vessel and the vessel was flame-dried under reduced pressure. Then, *N*-(2-hydroxyaryl) cyclopropyl amide (0.3 mmol), PPh_3 (314 mg, 1.2 mmol) and CBr_4 (200 mg, 0.6 mmol) and acetonitrile (3.0 mL) were added successively. Kept the reaction system at 80 °C for necessary time. After filtration, the solvent was evaporated and the residue was dissolved in CH_2Cl_2 (50 mL), washed with H_2O (50 mL×2), and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by a silica gel column chromatography to give the corresponding pyrrolidin-2-one product.

4.5. General procedure for the synthesis of 2-(3-chloropropyl)benzoxazole from *N*-(2-hydroxyaryl) cyclopropyl amide

A mixture of *N*-(2-hydroxyaryl) cyclopropyl amide (0.3 mmol), PPh_3 (314 mg, 1.2 mmol) and CBr_4 (200 mg, 0.6 mmol) was dissolved in DCE (3.0 mL). Then the reaction system was heated to 60 °C. The solvent was evaporated after the necessary reaction time, which can be monitored by ^{1}H NMR spectroscopy. The residue was dissolved in CH_2Cl_2 (50 mL), washed with H_2O (50 mL×2), and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by a silica gel column chromatography to give the corresponding 2-(3-chloropropyl)benzoxazole product.

4.5.1. Cyclopropanecarboxylic acid (2-hydroxyphenyl)-amide (1a). This compound was obtained as a white solid, yield: 92%, mp 125–126 °C. IR (CH_2Cl_2): ν 1098, 1136,

1178, 1200, 1247, 1311, 1384, 1455, 1498, 1533, 1601, 1656, 1753, 3285 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 0.91–0.95 (m, 2H, CH_2), 1.12–1.15 (m, 2H, CH_2), 1.62–1.70 (m, 1H, CH), 6.83–6.88 (m, 1H, Ar), 6.99–7.02 (m, 2H, Ar), 7.26–7.27 (m, 1H, Ar), 7.84 (br, 1H, NH), 9.01 (br, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 8.8, 15.3, 119.8, 120.3, 122.0, 125.8, 127.0, 148.7, 174.2; MS (EI) *m/z*: 177 (M^+, 51), 159 (4), 133 (1), 120 (1), 109 (100), 80 (14), 69 (93), 41 (54). Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.25; N, 7.90%. Found: C, 67.51; H, 6.25; N, 7.83%.

4.5.2. Cyclopropanecarboxylic acid (2-hydroxy-5-methylphenyl)amide (1b). This compound was obtained as a white solid, yield: 86%, mp 110–112 °C. IR (CH_2Cl_2): ν 1215, 1242, 1273, 1316, 1383, 1439, 1505, 1537, 1602, 1653, 3284 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 0.86–0.92 (m, 2H, CH_2), 1.08–1.13 (m, 2H, CH_2), 1.60–1.65 (m, 1H, CH), 2.22 (s, 3H, CH_3), 6.85 (s, 1H, Ar), 6.88 (s, 2H, Ar), 8.00 (br, 1H, NH), 8.87 (br, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 8.6, 15.2, 20.3, 119.3, 122.4, 125.4, 127.5, 129.8, 146.1, 174.1; MS (EI) *m/z*: 191 (M^+, 40), 172 (1), 160 (3), 132 (1), 123 (100), 106 (3), 69 (26), 41 (18). Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32%. Found: C, 68.89; H, 6.79; N, 7.07%.

4.5.3. Cyclopropanecarboxylic acid (2-hydroxy-5-methoxyphenyl)amide (1c). This compound was obtained as a white solid, yield: 87%, mp 124–126 °C. IR (CH_2Cl_2): ν 1039, 1102, 1151, 1198, 1219, 1273, 1307, 1376, 1431, 1453, 1508, 1540, 1600, 1650, 3182 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 0.86–0.89 (m, 2H, CH_2), 1.08–1.13 (m, 2H, CH_2), 1.60–1.65 (m, 1H, CH), 3.69 (s, 3H, OCH_3), 6.64 (d, J=7.2 Hz, 1H, Ar), 6.79 (s, 1H, Ar), 6.88 (d, J=7.2 Hz, 1H, Ar), 8.28 (br, 1H, NH), 8.46 (br, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 8.6, 15.2, 55.7, 107.3, 112.0, 119.4, 126.4, 141, 8, 153.3, 174.1; MS (EI) *m/z*: 207 (M^+, 19), 185 (10), 174 (4), 149 (6), 139 (100), 124 (6), 110 (9), 69 (58), 41 (64). Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; N, 6.76%. Found: C, 63.47; H, 6.25; N, 6.59%.

4.5.4. Cyclopropanecarboxylic acid (5-chloro-2-hydroxyphenyl)amide (1d). This compound was obtained as a white solid, yield: 85%, mp 178–180 °C. IR (CH_2Cl_2): ν 1204, 1268, 1371, 1426, 1542, 1589, 1655, 3016 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 0.94–1.00 (m, 2H, CH_2), 1.14–1.19 (m, 2H, CH_2), 1.59–1.65 (m, 1H, CH), 6.91–6.95 (m, 1H, Ar), 7.06–7.09 (m, 2H, Ar), 7.65 (br, 1H, NH), 8.83 (s, 1H, OH); ^{13}C NMR (75 MHz, CD_3COCD_3): δ 7.0, 14.0, 116.8, 120.2, 123.0, 123.5, 127.7, 145.6, 172.8; MS (EI) *m/z*: 213 (16), 211 (M^+, 50), 193 (5), 167 (1), 154 (1), 145 (15), 143 (44), 114 (11), 99 (2), 69 (100), 41 (37). Anal. Calcd for $C_{10}H_{10}ClNO_2$: C, 56.75; H, 4.76; N, 6.62%. Found: C, 57.11; H, 4.72; N, 6.62%.

4.5.5. Cyclopropanecarboxylic acid (5-fluoro-2-hydroxyphenyl)amide (1e). This compound was obtained as a white solid, yield: 76%, mp 165–167 °C. IR (CH_2Cl_2): ν 1134, 1190, 1212, 1261, 1311, 1443, 1534, 1620, 1655 cm^{-1}; ^1H NMR (300 MHz, CD_3COCD_3): δ 0.80–0.88 (m, 2H, CH_2), 0.90–1.03 (m, 2H, CH_2), 1.98–2.03 (m, 1H, CH), 3.34 (br, 2H, OH, NH), 6.66–6.73 (m, 1H, Ar), 6.84–6.89 (m, 1H, Ar), 7.65–7.69 (m, 1H, Ar); ^{13}C NMR (75 MHz, CD_3SOCD_3): δ 7.5, 14.2, 108.1 (d, J_{C-F}=27.2 Hz), 109.4 (d, J_{C-F}=23.1 Hz), 115.3 (d, J_{C-F}=9.0 Hz), 127.4 (d, J_{C-F}=11.3 Hz), 143.3, 154.8 (d, J_{C-F}=230.8 Hz), 172.4; MS (EI) *m/z*: 195 (M^+, 14), 177 (2), 154 (1), 127 (19), 109 (1), 98 (5), 69 (100), 41 (43); HRMS (EI) Calcd for $(C_{10}H_{10}FNO_2)^+$: 195.0696, found: 195.0699.

4.5.6. Cyclopropanecarboxylic acid (3-hydroxynaphthalen-2-yl)amide (1f). This compound was obtained as a white solid, yield: 66%, mp 180–182 °C. IR (CH_2Cl_2): ν 1234, 1304, 1434, 1505, 1536, 1626, 3257 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 0.98–1.04 (m, 2H, CH_2), 1.20–1.28 (m, 2H, CH_2), 1.79–1.86 (m, 1H, CH), 7.26 (d, J=8.7 Hz, 1H, Ar), 7.39 (dt, J=1.2, 3.6 Hz, 1H, Ar), 7.53 (dt, J=1.5, 6.9 Hz, 1H, Ar), 7.69 (d, J=1.2 Hz, 1H, Ar), 7.80 (t, J=9.0 Hz, 2H, Ar), 7.94 (br, 1H, NH), 8.78 (br, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 9.0, 15.3, 117.1, 119.1, 121.6, 123.7, 126.9, 128.16, 128.2, 128.7, 129.0, 148.1, 174.5; MS (EI) *m/z*: 227 (M^+, 25), 209 (3), 180 (1), 159 (100), 149 (2), 130 (19), 103 (10), 69 (43), 41 (42); HRMS (ESI) Calcd for $(C_{14}H_{13}NO_2+Na)^+$: 250.0838, found: 250.0841.

4.5.7. Cyclopropanecarboxylic acid (1-benzyl-2-hydroxyethyl)amide (1g). This compound was obtained as a white solid, yield: 91%, mp 113–115 °C. IR (CH_2Cl_2): ν 1036, 1250, 1455, 1497, 1542, 1645, 3290, 3649 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 0.70–0.76 (m, 2H, CH_2), 0.93–0.97 (m, 2H, CH_2), 1.26–1.36 (m, 1H, CH), 2.88 (d, J=6.9 Hz, 2H, CH_2), 3.34 (br, 1H, OH), 3.57–3.71 (m, 2H, CH_2), 4.11–4.19 (m, 1H, CH), 6.10 (br, 1H, NH), 7.21–7.33 (m, 5H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 7.3, 7.4, 14.7, 37.0, 53.0, 63.9, 126.6, 128.6, 129.2, 137.7, 174.4; MS (EI) *m/z*: 219 (M^+, 1), 188 (3), 168 (1), 128 (39), 91 (32), 69 (100), 41 (41). Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39%. Found: C, 71.08; H, 7.65; N, 6.32%.

4.5.8. 2-Cyclopropylbenzooxazole (2a). This compound was obtained as a pale oil,[13] yield: 42 mg, 88%. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.13–1.21 (m, 2H, CH_2), 1.25–1.30 (m, 2H, CH_2), 2.16–2.25 (m, 1H, CH), 7.21–7.30 (m, 2H, Ar), 7.41–7.43 (m, 1H, Ar), 7.59–7.62 (m, 1H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 9.1, 9.2, 109.9, 118.9, 123.9, 124.0, 141.5, 150.3, 168.5.

4.5.9. 2-Cyclopropyl-5-methylbenzooxazole (2b). This compound was obtained as a pale oil, yield: 50 mg, 96%. IR (CH_2Cl_2): ν 1029, 1044, 1083, 1158, 1180, 1260, 1456, 1483, 1576, 1615, 2856, 2924, 3015 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.10–1.19 (m, 2H, CH_2), 1.22–1.28 (m, 2H, CH_2), 2.13–2.22 (m, 1H, CH), 2.43 (s, 3H, CH_3), 7.04 (dd, J=8.4, 1.5 Hz, 1H, Ar), 7.28 (d, J=8.4 Hz, 1H, Ar), 7.38 (d, J=1.5 Hz, 1H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 9.0, 9.3, 21.4, 109.3, 118.9, 124.8, 133.7, 141.7, 148.6, 168.6; MS (EI) *m/z*: 173 (M^+, 100), 158 (8), 154 (1), 147 (43), 144 (11), 130 (5), 117 (3), 106 (5), 78 (14); HRMS (MALDI) Calcd for $(C_{11}H_{11}NO+H)^+$: 174.0913, found: 174.0906.

4.5.10. 2-Cyclopropyl-5-methoxybenzooxazole (2c). This compound was obtained as a pale oil, yield: 54 mg, 95%. IR (CH_2Cl_2): ν 1028, 1153, 1174, 1195, 1288, 1441, 1483, 1574, 1615, 2834, 2939, 3011 cm^{-1}; ^1H NMR (300 MHz,

$CDCl_3$, TMS): δ 1.11–1.16 (m, 2H, CH_2), 1.22–1.27 (m, 2H, CH_2), 2.12–2.20 (m, 1H, CH), 3.82 (s, 3H, OCH_3), 6.83 (dd, J=2.7, 8.7 Hz, 1H, Ar), 7.10 (d, J=2.7 Hz, 1H, Ar), 7.29 (d, J=8.7 Hz, 1H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 9.0, 9.2, 55.7, 102.3, 109.9, 111.9, 142.3, 144.9, 156.9, 169.3; MS (EI) *m/z*: 189 (M^+, 100), 174 (57), 163 (26), 146 (6), 107 (57), 79 (75), 63 (13), 51 (43); HRMS (MALDI) Calcd for $(C_{11}H_{11}NO_2+H)^+$: 190.0863, found: 190.0868.

4.5.11. 5-Chloro-2-cyclopropylbenzooxazole (2d). This compound was obtained as a white solid, yield: 56 mg, 97%, mp 70–72 °C. IR (CH_2Cl_2): ν 1028, 1047, 1291, 1343, 1456, 1571, 1607, 2924, 3049, 3094 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.15–1.22 (m, 2H, CH_2), 1.23–1.30 (m, 2H, CH_2), 2.14–2.32 (m, 1H, CH), 7.20 (dd, J=1.8, 8.7 Hz, 1H, Ar), 7.32 (d, J=8.7 Hz, 1H, Ar), 7.56 (d, J=1.8 Hz, 1H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 9.3, 9.4, 110.6, 118.9, 124.1, 129.4, 142.7, 148.9, 170.0; MS (EI) *m/z*: 195 (31), 193 (M^+, 100), 178 (8), 169 (18), 167 (63), 130 (14), 112 (4), 102 (12), 63 (53), 41 (19). Anal. Calcd for $C_{10}H_8ClNO$: C, 62.03; H, 4.16; N, 7.23%. Found: C, 62.09; H, 4.27; N, 7.15%.

4.5.12. 2-Cyclopropyl-5-fluorobenzooxazole (2e). This compound was obtained as a white solid, yield: 45 mg, 85%, mp 63–65 °C. IR (CH_2Cl_2): ν 1031, 1103, 1136, 1151, 1174, 1265, 1293, 1339, 1350, 1441, 1466, 1481, 1570, 1615, 2851, 2922, 3012, 3034 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.15–1.22 (m, 2H, CH_2), 1.23–1.30 (m, 2H, CH_2), 2.15–2.24 (m, 1H, CH), 6.93–7.00 (m, 1H, Ar), 7.26–7.36 (m, 2H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 9.3, 9.4, 105.5 (d, J_{C-F}=25.7 Hz), 110.1 (d, J_{C-F}=9.8 Hz), 111.3 (d, J_{C-F}=25.7 Hz), 142.4 (d, J_{C-F}=13.2 Hz), 146.7, 159.9 (d, J_{C-F}=238.1 Hz), 170.5; MS (EI) *m/z*: 177 (M^+, 100), 162 (9), 151 (67), 122 (5), 109 (7), 82 (26), 63 (14), 41 (16); HRMS (EI) Calcd for $C_{10}H_8FNO$: 177.0590, found: 177.0576.

4.5.13. 2-Cyclopropylnaphtho[2,3-*d*]oxazole (2f). This compound was obtained as a pale yellow oil, yield: 60 mg, 96%. IR (CH_2Cl_2): ν 1005, 1027, 1099, 1161, 1198, 1236, 1261, 1274, 1372, 1569, 1591, 1641, 2924, 3013, 3064 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.15–1.21 (m, 2H, CH_2), 1.25–1.34 (m, 2H, CH_2), 1.29–2.35 (m, 1H, CH), 7.47–7.64 (m, 3H, Ar), 7.69 (d, J=8.7 Hz, 1H, Ar), 7.92 (d, J=8.4 Hz, 1H, Ar), 8.45 (dd, J=8.1, 0.3 Hz, 1H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 9.0, 9.5, 110.5, 121.9, 124.7, 124.9, 126.0, 126.6, 128.4, 130.9, 136.6, 147.4, 167.5; MS (EI) *m/z*: 209 (M^+, 100), 192 (3), 180 (19), 153 (6), 140 (6), 128 (5), 114 (22), 88 (10), 63 (10); HRMS (ESI) Calcd for $(C_{14}H_{12}NO+Na)^+$: 210.0913, found: 210.0915.

4.5.14. 1-(2-Hydroxyphenyl)pyrrolidin-2-one (3a). This compound was obtained as a white solid,[14] yield: 44 mg, 87%, mp 136–138 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 2.28 (tt, J=8.1, 7.2 Hz, 2H, CH_2), 2.68 (t, J=8.1 Hz, 2H, CH_2), 3.96 (t, J=7.2 Hz, 2H, CH_2), 6.92 (dt, J=0.6, 7.5 Hz, 1H, Ar), 7.06 (dd, J=0.6, 8.4 Hz, 2H, Ar), 7.18 (dt, J=0.9, 7.8 Hz, 1H, Ar), 8.58 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 19.5, 32.2, 50.9, 109.7, 120.5, 120.7, 121.2, 127.7, 150.1, 176.2.

4.5.15. 1-(2-Hydroxy-5-methylphenyl)pyrrolidin-2-one (3b). This compound was obtained as a white solid, yield: 44 mg, 77%, mp 177–179 °C. IR (CH_2Cl_2): ν 1106, 1135, 1186, 1261, 1308, 1420, 1439, 1461, 1510, 1601, 1656, 2851, 2922 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 2.24 (tt, J=8.1, 6.6 Hz, 2H, CH_2), 2.27 (s, 3H, CH_3), 2.64 (t, J=8.1 Hz, 2H, CH_2), 3.93 (t, J=6.6 Hz, 2H, CH_2), 6.85 (d, J=0.6 Hz, 1H, Ar), 6.92–6.99 (m, 2H, Ar), 8.32 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 19.4, 20.5, 32.1, 50.7, 120.3, 121.6, 127.2, 128.2, 129.8, 147.7, 176.0; MS (EI) *m/z*: 191 (M^+, 69), 174 (2), 162 (3), 148 (4), 136 (100), 120 (2), 109 (37), 91 (12), 77 (16). Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32%. Found: C, 68.83; H, 6.64; N, 7.07%.

4.5.16. 1-(2-Hydroxy-5-methoxyphenyl)pyrrolidin-2-one (3c). This compound was obtained as a white solid, yield: 31 mg, 50%, mp 83–85 °C. IR (CH_2Cl_2): ν 1038, 1176, 1212, 1261, 1416, 1461, 1509, 1612, 1662, 2959, 3919 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 2.29 (tt, J=8.1, 6.6 Hz, 2H, CH_2), 2.69 (t, J=8.1 Hz, 2H, CH_2), 3.77 (s, 3H, OCH_3), 3.95 (t, J=6.6 Hz, 2H, CH_2), 6.61 (d, J=3.0 Hz, 1H, Ar), 6.76 (dd, J=9.0, 3.0 Hz, 1H, Ar), 7.00 (d, J=9.0 Hz, 1H, Ar), 7.97 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 19.4, 32.2, 50.8, 55.8, 107.4, 112.45, 121.2, 128.2, 143.9, 153.4, 176.0; MS (EI) *m/z*: 207 (M^+, 100), 192 (9), 179 (3), 164 (10), 152 (78), 136 (11), 125 (14), 69 (9); HRMS (EI) Calcd for $(C_{11}H_{13}NO_3)^+$: 207.0895, found: 207.0908.

4.5.17. 1-(5-Chloro-2-hydroxy-phenyl)pyrrolidin-2-one (3d). This compound was obtained as a white solid, yield: 56 mg, 88%, mp 213–215 °C. IR (CH_2Cl_2): ν 1024, 1117, 1191, 1282, 1302, 1418, 1464, 1504, 1657, 2852, 2924 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 2.31 (tt, J=7.8, 6.9 Hz, 2H, CH_2), 2.71 (t, J=7.8 Hz, 2H, CH_2), 3.95 (t, J=6.9 Hz, 2H, CH_2), 6.99 (d, J=8.4 Hz, 1H, Ar), 7.04 (d, J=2.4 Hz, 1H, Ar), 7.14 (d, J=2.4, 8.4 Hz, 1H, Ar), 8.57 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 19.5, 32.2, 50.9, 121.0, 121.9, 125.1, 127.5, 148.8, 176.5; MS (EI) *m/z*: 213 (18), 211 (M^+, 64), 194 (2), 183 (4), 169 (2), 156 (100), 148 (3), 129 (23), 93 (16). Anal. Calcd for $C_{10}H_{10}ClNO_2$: C, 56.75; H, 4.76; N, 6.62%. Found: C, 56.62; H, 4.52; N, 6.41%.

4.5.18. 1-(5-Fluoro-2-hydroxyphenyl)pyrrolidin-2-one (3e). This compound was obtained as a white solid, yield: 30 mg, 51%, mp 158–160 °C. IR (CH_2Cl_2): ν 1178, 1270, 1419, 1445, 1519, 1622, 1663, 2962, 3103 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 2.30 (tt, J=7.8, 6.9 Hz, 2H, CH_2), 2.69 (t, J=7.8 Hz, 2H, CH_2), 3.93 (t, J=6.9 Hz, 2H, CH_2), 6.76–6.80 (m, 1H, Ar), 6.86–6.92 (m, 1H, Ar), 6.98–7.03 (m, 1H, Ar), 8.29 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 19.4, 32.2, 50.8, 107.9 (J_{C-F}=25.8 Hz), 114.1 (J_{C-F}=22.3 Hz), 121.4 (J_{C-F}=9.2 Hz), 128.2, 146.1, 156.4 (J_{C-F}=237.6 Hz), 176.4; MS (EI) *m/z*: 195 (M^+, 57), 174 (12), 149 (28), 140 (100), 129 (25), 113 (51), 91 (60), 57 (52); HRMS (EI) Calcd for $(C_{10}H_{10}FNO_2)^+$: 195.0696, found: 195.0692.

4.5.19. 1-(1-Benzyl-2-hydroxyethyl)pyrrolidin-2-one (3g). This compound was obtained as a pale red oil, yield: 61 mg, 72%. IR (CH_2Cl_2): ν 1290, 1462, 1495, 1658, 1729,

2854, 2922 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.89–1.99 (m, 2H, CH_2), 2.29–2.38 (m, 2H, CH_2), 2.98 (d, $J=7.8$ Hz, 2H, CH_2), 3.32 (t, $J=6.9$ Hz, 2H, CH_2), 3.57 (d, $J=7.5$ Hz, 2H, CH_2), 4.47 (tt, $J=7.8$, 7.5 Hz, 1H, CH), 7.20–7.32 (m, 5H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 18.4, 31.2, 33.3, 36.8, 44.7, 54.3, 126.7, 128.5, 128.7, 136.9, 175.3; MS (MALDI) *m/z*: 284 [$(M+3)^+$, 100], 282 [$(M+1)^+$, 100]; HRMS (MALDI) Calcd for $(C_{13}H_{16}BrNO+H)^+$: 282.0488, found: 282.0494.

4.5.20. 2-(3-Bromopropyl)benzooxazole (4a). This compound was obtained as a pale oil, yield: 23 mg, 32%. IR (CH_2Cl_2): ν 1003, 1104, 1155, 1167, 1243, 1455, 1572, 1615, 2853, 2924, 2956 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.46 (tt, $J=7.2$, 6.3 Hz, 2H, CH_2), 3.14 (t, $J=7.2$ Hz, 2H, CH_2), 3.58 (t, $J=6.3$ Hz, 2H, CH_2), 7.30–7.34 (m, 2H, Ar), 7.48–7.51 (m, 1H, Ar), 7.66–7.69 (m, 1H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 26.9, 29.3, 32.3, 110.3, 119.6, 124.2, 124.7, 141.1, 150.7, 165.5; MS (EI) *m/z*: 241 (6), 239 (M^+, 6), 183 (19), 149 (30), 133 (100), 104 (14), 77 (19), 41 (26). Anal. Calcd for $C_{10}H_{10}NOBr$: C, 50.02; H, 4.20; N, 5.83%. Found: C, 50.14; H, 4.38; N, 5.73%.

4.5.21. 2-(3-Chloropropyl)benzooxazole (5a). This compound was obtained as a pale oil, yield: 46 mg, 79%. IR (CH_2Cl_2): ν 1003, 1104, 1143, 1169, 1242, 1277, 1298, 1456, 1573, 1615, 2926, 2961 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.37 (tt, $J=7.2$, 6.6 Hz, 2H, CH_2), 3.13 (t, $J=7.2$ Hz, 2H, CH_2), 3.71 (t, $J=6.6$ Hz, 2H, CH_2), 7.27–7.33 (m, 2H, Ar), 7.46–7.50 (m, 1H, Ar), 7.66–7.69 (m, 1H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 25.6, 29.2, 43.7, 110.26, 119.5, 124.1, 124.6, 141.1, 150.7, 165.6; MS (EI) *m/z*: 197 (5), 195 (M^+, 11), 183 (16), 160 (6), 133 (100), 109 (28), 97 (13), 57 (17); HRMS (EI) Calcd for $(C_{10}H_{10}NOCl)^+$: 195.0451, found: 195.0447.

4.5.22. 2-(3-Chloropropyl)-5-methylbenzooxazole (5b). This compound was obtained as a pale oil, yield: 40 mg, 64%. IR (CH_2Cl_2): ν 1119, 1146, 1177, 1261, 1297, 1430, 1444, 1482, 1574, 2924, 2960 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.36 (tt, $J=7.2$, 6.6 Hz, 2H, CH_2), 2.45 (s, 3H, CH_3), 3.10 (t, $J=7.2$ Hz, 2H, CH_2), 3.69 (t, $J=6.6$ Hz, 2H, CH_2), 7.11 (dd, $J=8.4$, 0.9 Hz, 1H, Ar), 7.35 (d, $J=8.4$ Hz, 1H, Ar), 7.45 (d, $J=0.9$ Hz, 1H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 21.4, 25.7, 29.2, 43.7, 109.6, 119.5, 125.6, 133.9, 141.3, 148.9, 165.7; MS (EI) *m/z*: 211 (5), 209 (M^+, 11), 183 (2), 174 (6), 160 (12), 147 (100), 106 (14), 78 (26); HRMS (EI) Calcd for $(C_{11}H_{12}NOCl)^+$: 209.0607, found: 209.0621.

4.5.23. 2-(3-Chloropropyl)-5-methoxybenzooxazole (5c). This compound was obtained as a colorless oil, yield: 56 mg, 89%. IR (CH_2Cl_2): ν 1027, 1152, 1196, 1284, 1341, 1441, 1483, 1574, 1615, 2835, 2959, 2999 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.35 (tt, $J=7.2$, 6.0 Hz, 2H, CH_2), 3.09 (t, $J=7.2$ Hz, 2H, CH_2), 3.70 (t, $J=6.0$ Hz, 2H, CH_2), 3.84 (s, 3H, OCH_3), 6.89 (dd, $J=8.7$, 2.7 Hz, 1H, Ar), 7.16 (d, $J=2.7$ Hz, 1H, Ar), 7.35 (d, $J=8.7$ Hz, 1H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 25.7, 29.2, 43.7, 55.8, 102.7, 110.3, 112.9, 141.9, 145.3, 157.0, 166.4; MS (EI) *m/z*: 227 (11), 225 (M^+, 40), 189 (7), 176 (31), 163 (100), 148 (14), 107 (19), 79 (25); HRMS (EI) Calcd for $(C_{11}H_{12}NO_2Cl)^+$: 225.0557, found: 225.0545.

4.5.24. 5-Chloro-2-(3-chloropropyl)benzooxazole (5d). This compound was obtained as a white solid, yield: 58 mg, 84%, mp 47–49 °C. IR (CH_2Cl_2): ν 1055, 1145, 1161, 1257, 1428, 1452, 1568, 1609, 2962 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.37 (tt, $J=7.2$, 6.0 Hz, 2H, CH_2), 3.14 (t, $J=7.2$ Hz, 2H, CH_2), 3.71 (t, $J=6.0$ Hz, 2H, CH_2), 7.29 (dd, $J=8.7$, 2.4 Hz, 1H, Ar), 7.41 (d, $J=8.7$ Hz, 1H, Ar), 7.65 (d, $J=2.4$ Hz, 1H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 25.7, 29.1, 43.7, 111.1, 119.7, 125.0, 129.7, 142.3, 149.4, 167.2; MS (EI) *m/z*: 233 (1), 231 (7), 229 (11, M^+), 194 (7), 180 (9), 167 (100), 138 (6), 127 (5), 102 (10), 63 (26); HRMS (EI) Calcd for $(C_{10}H_9NOCl_2)^+$: 229.0061, found: 229.0077.

4.5.25. 2-(3-Chloropropyl)-5-fluorobenzooxazole (5e). This compound was obtained as a pale oil, yield: 44 mg, 69%. IR (CH_2Cl_2): ν 1131, 1167, 1249, 1276, 1299, 1440, 1478, 1572, 2926, 2961 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.37 (tt, $J=7.2$, 6.0 Hz, 2H, CH_2), 3.13 (t, $J=7.2$ Hz, 2H, CH_2), 3.71 (t, $J=6.0$ Hz, 2H, CH_2), 7.01–7.08 (m, 1H, Ar), 7.34–7.44 (m, 2H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 25.8, 29.1, 43.7, 106.1 (d, $J_{C-F}=25.7$ Hz), 110.6 (d, $J_{C-F}=9.7$ Hz), 112.2 (d, $J_{C-F}=25.7$ Hz), 142.1, 147.1, 159.9 (d, $J_{C-F}=238.7$ Hz), 167.6; MS (EI) *m/z*: 215 (4), 213 (9, M^+), 178 (5), 164 (8), 151 (100), 122 (7), 111 (5), 95 (5), 82 (9); HRMS (EI) Calcd for $(C_{10}H_9ClFNO)^+$: 213.0357, found: 213.0343.

4.5.26. 2-(3-Chloropropyl)naphtho[2,3-*d*]oxazole (5f). This compound was obtained as a pale oil, yield: 54 mg, 73%. IR (CH_2Cl_2): ν 1005, 1226, 1274, 1300, 1373, 1445, 1567, 1589, 2924, 2959 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.42 (tt, $J=7.2$, 6.6 Hz, 2H, CH_2), 3.22 (t, $J=7.2$ Hz, 2H, CH_2), 3.74 (t, $J=6.6$ Hz, 2H, CH_2), 7.49–7.55 (m, 1H, Ar), 7.62–7.67 (m, 2H, Ar), 7.76 (d, $J=9.0$ Hz, 1H, Ar), 7.95 (d, $J=8.1$ Hz, 1H, Ar), 8.46 (d, $J=8.1$ Hz, 1H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 26.0, 29.7, 43.9, 110.7, 121.9, 125.2, 125.5, 126.3, 126.9, 128.5, 131.0, 136.4, 147.9, 164.7; MS (EI) *m/z*: 247 (11), 245 (M^+, 32), 209 (47), 196 (6), 183 (100), 154 (8), 140 (4), 127 (11), 114 (20); HRMS (EI) Calcd for $(C_{14}H_{12}ClNO)^+$: 245.0607, found: 245.0596.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2005.11.077. The X-ray crystal data of **5d** is included in Supporting information. This material is available free of charge via the Internet.

References and notes

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10. The crystal data of **5d** has been deposited in CCDC with number 283183. Empirical formula: $C_{10}H_9NOCl_2$; formula weight: 230.08; crystal size: $0.508\times0.472\times0.080$; crystal color, habit: colorless, prismatic; crystal system: monoclinic; lattice type: primitive; lattice parameters: $a=5.4568(8)$ Å, $b=25.949(4)$ Å, $c=7.5903(11)$ Å, $\alpha=90°$, $\beta=25.949(4)°$, $\gamma=90°$, $V=1048.2(3)$ Å^3; space group: $P2(1)/c$; $Z=4$; $D_{calcd}=1.458$ g/cm^3; $F_{000}=472$; $R1=0.0511$, $wR2=0.1176$. Diffractometer: Rigaku AFC7R.
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