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SYNTHESIS OF 3,4-DIHYDRO-2*H*-1,3-BENZOXAZINE-2-THIONES VIA CYCLIZATION OF 2-(1-ISOTHIOCYANATOALKYL)PHENOLS

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Abstract – Convenient sequences for the preparation of 3,4-dihydro-2*H*-1,3-benzoxazine-2-thiones from 2-hydroxybenzaldehyde and 2-hydroxyphenyl ketones or 2-methylphenols have been developed, which both employ cyclization of 2-(1-isothiocyanatoalkyl)phenols generated *in situ* under mild conditions.

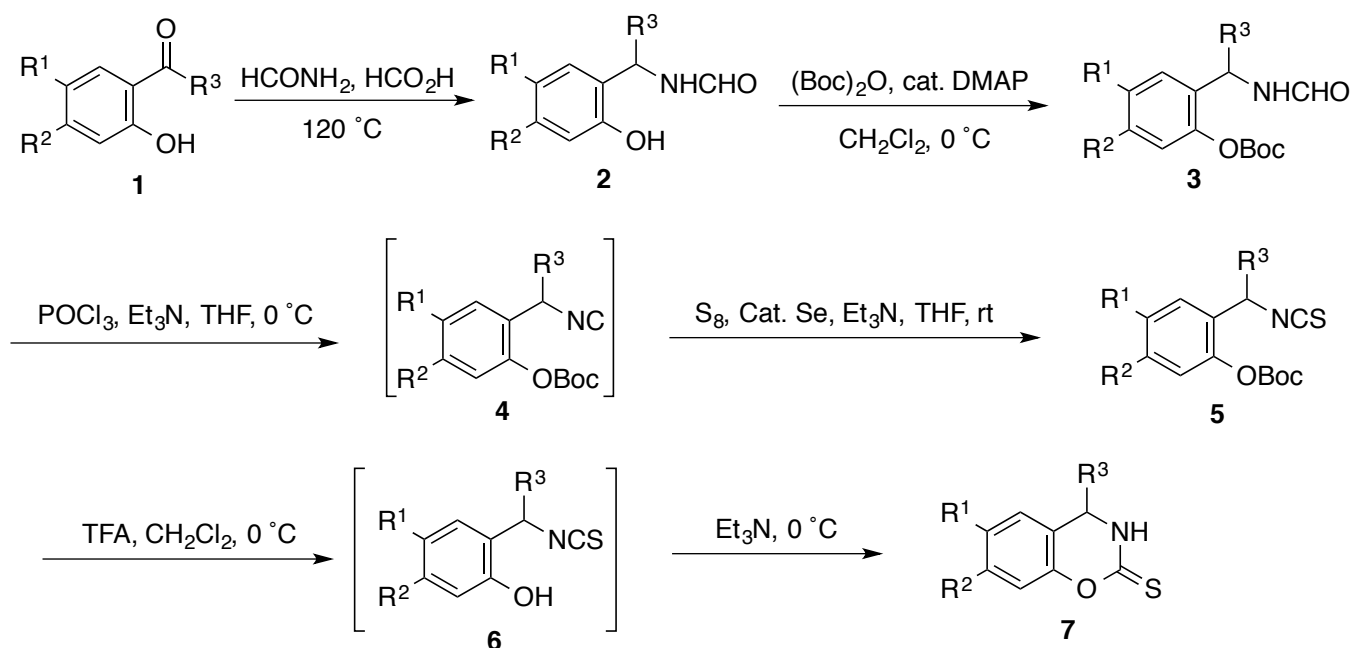
INTRODUCTION

Some 3,4-dihydro-2*H*-1,3-benzoxazine-2-thione derivatives were reported to exhibit antidepressant activity in 1969.¹ In 1977 Arct *et al.* demonstrated that the synthesis of 4-nonsubstituted 3,4-dihydro-2*H*-1,3-benzoxazine-2-thiones can be achieved by reacting *o*-hydroxybenzyltrimethylammonium salts with potassium thiocyanate,² and two years after these 3,4-dihydro-2*H*-1,3-benzoxazine-2-thione derivatives were shown to be potential fungicides.³ However, few methods for the preparation of this class of heterocycles have been reported since then, though only one method has been reported by Yadav *et al.*, which utilizes montmorillonite catalyzed cyclization of salicylaldehyde 4-arylsemicarbazone.⁴ On the other hand, we recently reported a convenient synthesis of 1-acyl-3,4-dihydroquinazoline-2(1*H*)-thiones *via* cyclization of *N*-[2-(isothiocyanatomethyl)phenyl]carboxamides generated *in situ*.⁵ In respect to this method, we envisioned that the achievement of the generation of 2-(1-isothiocyanatoalkyl)phenols would lead to development of new methods for the preparation of 3,4-dihydro-2*H*-1,3-benzoxazine-2-thiones. We now wish to report our investigations which reveal that the isothiocyanatophenols (**6**) can be generated from commercially available 2-hydroxybenzaldehyde and 2-hydroxyphenyl ketones (**1**) utilizing a simply operated sequence and that they cyclized cleanly under mild conditions to give the desired

3,4-dihydro-2*H*-1,3-benzoxazine-2-thiones (**7**). An alternative sequence starting with 2-methylphenols (**8**), *via* cyclization of the corresponding 2-(1-isothiocyanatoalkyl)phenols, is also described.

RESULTS AND DISCUSSION

The synthesis of **7** from **1** was conducted according to the sequence illustrated in Scheme 1. The reaction of **1** with formamide and formic acid at 120 °C afforded the corresponding formylaminophenols (**2**) in reasonable yields. *O*-*tert*-Butoxycarbonylation of **2** with di-*tert*-butyl dicarbonate in dichloromethane could be shortly achieved at 0 °C using a catalytic amount of 4-(dimethylamino)pyridine (DMAP) to provide formylaminocarbonates (**3**) in excellent yields. Conversion of these formamides (**3**) into the corresponding isothiocyanates (**5**), *via* isocyanides (**4**), was carried out by applying the reported procedures.^{6,7} Thus, compounds (**3**) were allowed to react with phosphoryl chloride in THF in the presence of triethylamine at 0 °C to result in the formation of **4**, which, without any purification after usual aqueous workup, were further treated with sulfur in THF in the presence of a catalytic amount of selenium and excess triethylamine at room temperature to afford **5** in good overall yields. These results are summarized in Table 1.



Scheme 1

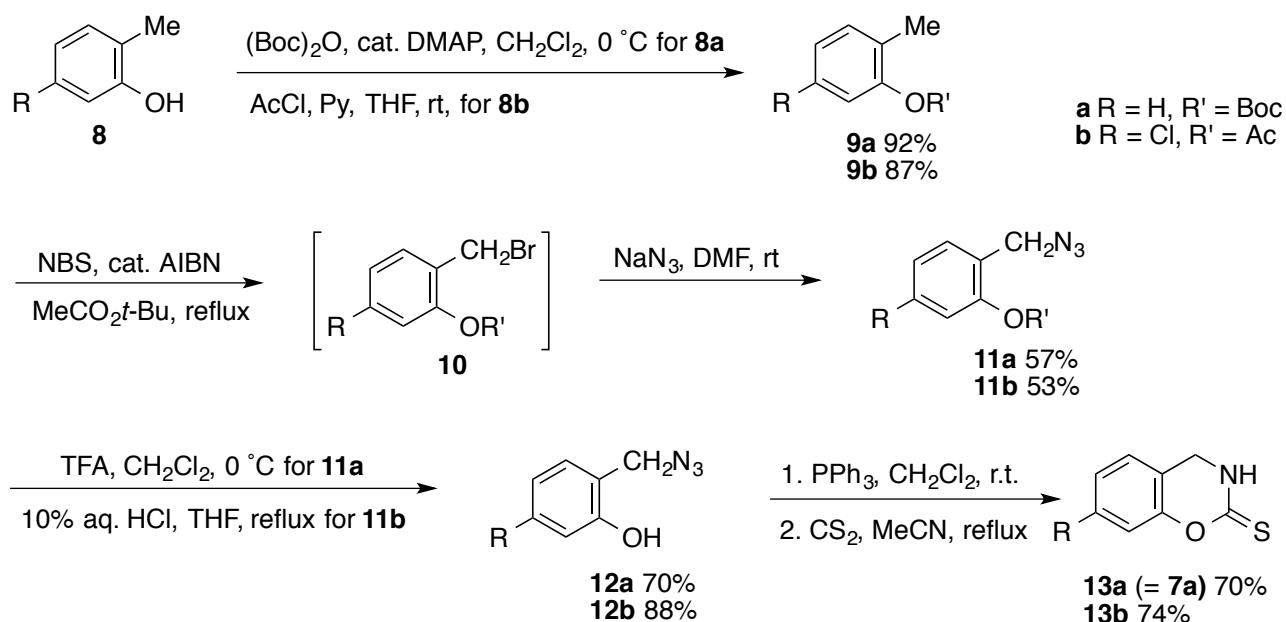
The isothiocyanatocarbonate (**5**), thus obtained, were treated with trifluoroacetic acid in dichloromethane at 0 °C to generate 2-(1-isothiocyanatoalkyl)phenol intermediates (**6**), which on treatment with excess triethylamine at the same temperature underwent clean cyclization by intramolecular attack of the hydroxy oxygen on the isothiocyanato carbon to afford, after aqueous workup followed by purification of

the crude products by column chromatography on silica gel, the desired products (**7**). The yields of the products were fair to good as compiled in Table 1 as well.

Table 1. Preparation of 3,4-dihydro-2*H*-1,3-benzoxazine-2-thiones (**7**)

Entry	1	2	Yield ^a	3	Yield ^a	5	Yield ^{a,b}	7	Yield ^{a,c}
1	1a (R ¹ = R ² = R ³ = H)	2a	64	3a	94	5a	86	7a	81
2	1b (R ¹ = R ² = H, R ³ = Me)	2b	72	3b	87	5b	74	7b	67
3	1c (R ¹ = R ² = H, R ³ = Et)	2c	61	3c	97	5c	79	7c	67
4	1d (R ¹ = R ² = H, R ³ = Ph)	2d	84	3d	89	5d	72	7d	71
5	1e (R ¹ = H, R ² = R ³ = Me)	2e	64	3e	85	5e	85	7e	61
6	1f (R ¹ = R ³ = Me, R ² = H)	2f	63	3f	94	5f	78	7f	70
7	1g (R ¹ = Cl, R ² = H, R ³ = Me)	2g	65	3g	85	5g	87	7g	64
8	1h (R ¹ = MeO, R ² = H, R ³ = Me)	2h	62	3h	85	5h	87	7h	70

^a Yields/% of isolated products. ^b Yields from **3**. ^c Yields from **5**.



Scheme 2

We then decided to carry out exploration of an alternative method using 2-methylphenols as simpler starting materials and *tert*-butoxycarbonyl and acetyl groups as protecting groups. We have found that 3,4-dihydro-2*H*-1,3-benzoxazine-2-thione (**13a** = **7a**) and 7-chloro-3,4-dihydro-2*H*-1,3-benzoxazine-2-thione (**13b**) can be prepared from 2-methylphenol (**8a**) and 5-chloro-2-methylphenol (**8b**), respectively, *via* six-step operationally simple sequences (Schemes 2). Thus, the hydroxy groups of **8a** and **8b** were protected as the *tert*-butyl carbonate (**9a**) on treatment with di-*tert*-butyl dicarbonate in dichloromethane in the presence of a catalytic amount of 4-(dimethylamino)pyridine (DMAP) at 0 °C and as the acetate (**9b**) on treatment with acetyl chloride in THF in the presence of triethylamine at room temperature. Benzylic bromination of compounds (**9**) was then achieved with *N*-bromosuccinimide (NBS) in the

presence of a catalytic amount of azobisisobutyronitrile (AIBN) in refluxing *tert*-butyl acetate. The resulting bromides (**10**) were used without purification in the next reaction with sodium azide in DMF at room temperature to afford benzyl azides (**11**) in reasonable yields from **9**. Treatment of **11a** with trifluoroacetic acid (TFA) in dichloromethane at 0 °C gave 2-(azidomethyl)phenol (**12a**). Hydrolysis of **11b** with 10% hydrochloric acid in refluxing THF gave 2-(azidomethyl)-5-chlorophenol (**12b**). The reaction of compounds (**12**) with triphenylphosphine in dichloromethane at room temperature was followed by treatment with excess carbon disulfide in refluxing acetonitrile to generate the corresponding 2-(isothiocyanatomethyl)phenols, cyclization of which occurred immediately under the reaction conditions to result in the formation of 3,4-dihydro-2*H*-1,3-benzoxazine-2-thiones (**13**) in satisfactory yields. Unfortunately, however, this method is only applicable to the synthesis of 4-nonsubstituted derivatives. Starting from 2-ethylphenol, the transformation of the corresponding azide into isothiocyanate did not proceed cleanly to give the desired product in very low yield.

In conclusion, the results detailed herein demonstrate that 3,4-dihydro-2*H*-1,3-benzoxazine-2-thiones can be conveniently prepared from commercially available starting materials. These methods may be of value in organic synthesis because of their usefulness in the simple manipulations.

EXPERIMENTAL

All melting points were obtained on a Laboratory Devices MEL-TEMP II melting apparatus and are uncorrected. IR spectra were recorded with a Perkin-Elmer Spectrum65 FTIR spectrophotometer. ¹H NMR and ¹³C NMR spectra were recorded using TMS as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 500 and 125 MHz, respectively. High-resolution MS spectra (DART, positive) were measured by a Thermo Scientific Exactive spectrometer. Elemental analyses were performed with an Elementar Vario EL II instrument. TLC was carried out on Merck Kieselgel 60 PF₂₅₄. Column chromatography was performed using WAKO GEL C-200E. All of the organic solvents used in this study were dried over appropriate drying agents and distilled prior to use.

Starting Materials. All chemicals used in this study were commercially available.

Typical Procedure for the Preparation of Formamides (2).
***N*-[(2-Hydroxyphenyl)methyl]formamide (2a).**⁸ A mixture of 2-hydroxybenzaldehyde (2.4 g, 20 mmol), HCONH₂ (11 g, 0.23 mol), and HCO₂H (7.5 g, 0.16 mol) was heated at 120 °C for 6 h. After cooling to rt, the mixture was diluted with H₂O (100 mL) and extracted with AcOEt (3 × 25 mL). The combined extracts were washed with saturated aqueous NaHCO₃ (4 × 20 mL) and brine (20 mL), dried (Na₂SO₄), and concentrated by evaporation. The residue was purified by column chromatography on SiO₂ (AcOEt/CH₂Cl₂ 1:2) to afford **2a** (1.9 g, 64%); a white solid; mp 87–90 °C (hexane/CH₂Cl₂) (lit.,⁸ mp 92–93 °C); IR (KBr) 3223, 1644, 1607 cm⁻¹; ¹H NMR (CDCl₃) δ 4.40 (d, *J* = 6.3 Hz, 2H), 6.58 (br s, 1H),

6.85 (ddd, $J = 7.4, 6.3, 1.1$ Hz, 1H), 6.95 (dd, $J = 8.0, 1.1$ Hz, 1H), 7.11 (dd, $J = 7.4, 1.7$ Hz, 1H), 7.23 (ddd, $J = 8.0, 6.3, 1.7$ Hz, 1H), 8.15 (s, 1H), 8.74 (s, 1H).

***N*-[1-(2-Hydroxyphenyl)ethyl]formamide (2b)**: a colorless oil; R_f 0.16 (AcOEt/hexane 1:1); IR (neat) 3276, 1657, 1608 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.59 and 1.60 (2d, $J = 7.4$ and 6.9 Hz, respectively, combined 3H), 4.62–4.68 and 5.33–5.39 (2m, combined 1H), 6.28 (br s, 1H), 6.82–6.94 (m, 2H), 7.06–7.22 (m, 2H), 8.07–8.57 (m, 2H). Anal. Calcd for $\text{C}_9\text{H}_{11}\text{NO}_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.18; H, 6.70; N, 8.31.

***N*-[1-(2-Hydroxyphenyl)propyl]formamide (2c)**: a pale-yellow oil; R_f 0.23 (AcOEt/hexane 1:1); IR (neat) 3272, 1660, 1608 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.92 and 0.98 (2t, $J = 7.4$ Hz, each, combined 3H), 1.95–2.01 (m, 2H), 4.97 and 6.05 (2q, $J = 7.4$ Hz each, combined 1H), 6.25 (br s, 1H), 6.83–6.94 (m, 2H), 7.12–7.22 (m, 2H), 8.12–9.00 (m, 2H). Anal. Calcd for $\text{C}_{10}\text{H}_{13}\text{NO}_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 66.95; H, 7.41; N, 7.68.

***N*-[(2-Hydroxyphenyl)(phenyl)methyl]formamide (2d)**: a pale-yellow solid; mp 152–154 $^\circ\text{C}$ (hexane/ CH_2Cl_2); IR (KBr) 3327, 1652, 1635 cm^{-1} ; ^1H NMR (CDCl_3) δ 6.04 and 6.42 (2d, $J = 9.2$ Hz each, combined 1H), 6.75–9.62 (m, 12H). Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{NO}_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.93; H, 5.87; N, 6.07.

***N*-[1-(2-Hydroxy-4-methylphenyl)ethyl]formamide (2e)**: a yellow oil; R_f 0.22 (AcOEt/hexane 1:1); IR (neat) 3300, 1663, 1632 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.51 and 1.57 (2d, $J = 7.4$ Hz each, combined 3H), 2.24 and 2.26 (2s, combined 3H), 4.61 and 5.30 (2 quint, $J = 7.4$ Hz each, combined 1H), 6.45 (br s, 1H), 6.63–7.35 (m, 3H), 8.04–8.79 (m, 2H). Anal. Calcd for $\text{C}_{10}\text{H}_{13}\text{NO}_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 73.93; H, 5.87; N, 6.07.

***N*-[1-(2-Hydroxy-5-methylphenyl)ethyl]formamide (2f)**: a pale-yellow solid; mp 161–163 $^\circ\text{C}$ (hexane/ CH_2Cl_2); IR (KBr) 3291, 1659, 1627 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.57 and 1.60 (2d, $J = 6.9$ Hz each, combined 3H), 2.25 and 2.27 (2s, combined 3H), 4.62–4.66 and 5.30–5.36 (2m, combined 1H), 6.19 (br, 1H), 6.72–8.18 (m, 5H). Anal. Calcd for $\text{C}_{10}\text{H}_{13}\text{NO}_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.02; H, 7.45; N, 7.61.

***N*-[1-(5-Chloro-2-hydroxyphenyl)ethyl]formamide (2g)**: a pale-yellow solid; mp 169–172 $^\circ\text{C}$ (hexane/ CH_2Cl_2); IR (KBr) 3295, 1667, 1634 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.26 and 1.33 (2d, $J = 6.9$ Hz each, combined 3H), 4.86 and 5.17 (2quint, $J = 6.9$ Hz each, combined 1H), 6.78–9.85 (m, 6H). Anal. Calcd for $\text{C}_9\text{H}_{10}\text{ClNO}_2$: C, 54.15; H, 5.05; N, 7.02. Found: C, 54.03; H, 5.25; N, 6.88.

***N*-[1-(2-Hydroxy-5-methoxyphenyl)ethyl]formamide (2h)**: a yellow solid; mp 134–137 $^\circ\text{C}$ (hexane/ CH_2Cl_2); IR (KBr) 3261, 1637 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.25 and 1.32 (2d, $J = 6.9$ Hz, each, combined 3H), 4.86 and 5.18 (2quint, $J = 6.9$ Hz each, combined 1H), 3.64 and 3.65 (2s, combined 3H),

6.60–9.14 (m, 6H). Anal. Calcd for $C_{10}H_{13}NO_3$: C, 61.53; H, 6.71; N, 7.18. Found: C, 61.47; H, 6.78; N, 7.06.

Typical Procedure for the Preparation of Carbonates (3). **1,1-Dimethylethyl 2-[(Formylamino)methyl]phenyl Carbonate (3a).** To a stirring solution of **2a** (0.35 g, 2.3 mmol), 4-(dimethylamino)pyridine (DMAP) (29 mg, 0.23 mmol) in CH_2Cl_2 (4 mL) at 0 °C was added dropwise $(Boc)_2O$ (0.56 g, 2.6 mmol). After 5 min, the mixture was diluted with AcOEt (30 mL), washed with H_2O (2 × 10 mL) and brine (10 mL), dried (Na_2SO_4), and concentrated by evaporation. The residue was purified by column chromatography on SiO_2 to afford **3a** (0.48 g, 78%); a pale-yellow oil; R_f 0.43 (AcOEt/ CH_2Cl_2 1:2); IR (neat) 3287, 1758, 1666, 1147 cm^{-1} ; 1H NMR ($CDCl_3$) δ 1.56 (s, 9H), 4.37 and 4.45 (2d, $J = 5.7$ Hz each, combined 2H), 5.99 (br, 1H), 7.15 (dd, $J = 8.0, 1.1$ Hz, 1H), 7.24 (ddd, $J = 7.4, 6.3, 1.1$ Hz, 1H), 7.34 (ddd, $J = 8.0, 6.3, 1.7$ Hz, 1H), 7.40 (dd, $J = 7.4, 1.7$ Hz, 1H), 8.18 and 8.20 (2s, combined 1H). Anal. Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.11; H, 7.05; N, 5.57.

1,1-Dimethylethyl 2-[1-(Formylamino)ethyl]phenyl Carbonate (3b): a pale-yellow oil; R_f 0.45 (AcOEt/hexane 2:1); IR (neat) 3285, 1759, 1667, 1148 cm^{-1} ; 1H NMR ($CDCl_3$) δ 1.50 and 1.53 (2d, $J = 6.9$ and 7.4 Hz, respectively, combined 3H), 1.56 (s, 9H), 4.88 and 5.37 (quint, $J = 7.4$ and 6.9 Hz, respectively, combined 1H), 5.90 and 5.98 (2br s, combined 1H), 7.16–7.25 (m, 2H), 7.31–7.36 (m, 2H), 8.13–8.17 (m, 1H). Anal. Calcd for $C_{14}H_{19}NO_4$: C, 63.38; H, 7.22; N, 5.28. Found: C, 63.28; H, 7.44; N, 5.28.

1,1-Dimethylethyl 2-[1-(Formylamino)propyl]phenyl Carbonate (3c): a pale-yellow oil; R_f 0.45 (AcOEt/ CH_2Cl_2 1:3); IR (neat) 3284, 1759, 1662, 1148 cm^{-1} ; 1H NMR ($CDCl_3$) δ 0.88 and 0.95 (2t, $J = 7.4$ Hz each, combined 3H), 1.56 (s, 9H), 1.74–1.92 (m, 2H), 4.54 and 5.14 (2q, $J = 7.4$ Hz each, combined 1H), 5.95 and 6.05 (2br s, combined 1H), 7.16–7.25 (m, 2H), 7.30–7.35 (m, 2H), 8.11–8.36 (m, 1H). Anal. Calcd for $C_{15}H_{21}NO_4$: C, 64.50; H, 7.58; N, 5.01. Found: C, 64.50; H, 7.70; N, 4.91.

1,1-Dimethylethyl 2-[(Formylamino)(phenyl)methyl]phenyl Carbonate (3d): a pale-yellow solid; mp 143–145 °C (hexane/ CH_2Cl_2); IR (KBr) 3320, 1761, 1660, 1146 cm^{-1} ; 1H NMR ($CDCl_3$) δ 1.36 and 1.37 (2s, combined 9H), 5.93 and 6.51 (2d, $J = 8.6$ Hz each, combined 1H), 6.33 and 6.45 (br, combined 1H), 7.18–7.39 (m, 9H), 8.22–8.33 (m, 1H). Anal. Calcd for $C_{19}H_{21}NO_4$: C, 69.71; H, 6.47; N, 4.28. Found: C, 69.64; H, 4.63; N, 3.98.

1,1-Dimethylethyl 2-[1-(Formylamino)ethyl]-5-methylphenyl Carbonate (3e): a colorless oil; R_f 0.40 (AcOEt/hexane 1:1); IR (neat) 3273, 1759, 1664, 1241 cm^{-1} ; 1H NMR ($CDCl_3$) δ 1.49 and 1.51 (2d, $J = 6.9$ Hz each, combined 3H), 1.56 (s, 9H), 2.345 and 2.352 (2s, combined 3H), 4.83 and 5.31 (quint, $J = 6.9$ Hz each, combined 1H), 6.97–8.16 (m, 5H). Anal. Calcd for $C_{15}H_{21}NO_4$: C, 64.50; H, 7.58; N, 5.01. Found: C, 64.46; H, 7.60; N, 4.81.

1,1-Dimethylethyl 2-[1-(Formylamino)ethyl]-4-methylphenyl Carbonate (3f): a pale-yellow oil; R_f 0.36 (AcOEt/hexane 1:1); IR (neat) 3281, 1756, 1664 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 1.47 and 1.49 (2d, $J = 6.9$ Hz each, combined 3H), 1.54 and 1.55 (2s, combined 9H), 2.05 and 2.33 (2s, combined 3H), 4.82 and 5.31 (2quint, $J = 6.9$ Hz each, combined 1H), 6.05 (br, 1H), 7.02–8.15 (m, 4H). Anal. Calcd for $\text{C}_{15}\text{H}_{21}\text{NO}_4$: C, 64.50; H, 7.58; N, 5.01. Found: C, 64.31; H, 7.70; N, 4.90.

1,1-Dimethylethyl 4-Chloro-2-[1-(formylamino)ethyl]phenyl Carbonate (3g): a yellow oil; R_f 0.48 (AcOEt/hexane 1:1); IR (neat) 3279, 1760, 1663 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 1.48 and 1.52 (2d, $J = 6.9$ Hz each, 3H), 1.56 (s, 9H), 4.84 and 5.33 (2quint, $J = 6.9$ Hz each, combined 1H), 5.94 (br, 1H), 7.11–8.16 (m, 4H). Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{ClNO}_4$: C, 56.10; H, 6.05; N, 4.67. Found: C, 56.07; H, 6.06; N, 4.61.

1,1-Dimethylethyl 2-[1-(Formylamino)ethyl]-4-methoxyphenyl Carbonate (3h): a beige oil; R_f 0.27 (AcOEt/hexane 2:1); IR (neat) 3280, 1757, 1663 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 1.48 and 1.51 (2d, $J = 6.9$ Hz each, combined 3H), 1.55 (s, 9H), 3.80 (s, 3H), 4.81 and 5.23 (2quint, $J = 6.9$ Hz each, combined 1H), 5.98 (br s, 1H), 6.80–8.16 (m, 4H). Anal. Calcd for $\text{C}_{15}\text{H}_{21}\text{NO}_5$: C, 61.00; H, 7.17; N, 4.74. Found: C, 60.94; H, 7.28; N, 4.60.

General Procedure for the Preparation of Isothiocyanates (5). Compounds (3) (1.0 mmol) were treated with POCl_3 (0.22 g, 1.5 mmol) in the presence of Et_3N (0.71 g, 7.0 mmol) under conditions reported previously.⁶ After aqueous workup, the crude isocyanides 4 were, without any purification, subjected to the treatment with S_8 (32 mg, 1.0 mmol) in the presence of a catalytic amount of Se (4.7 mg, 0.060 mmol) and excess Et_3N (0.35 mL) at rt.⁷ The crude products were purified by column chromatography on SiO_2 to give 5.

1,1-Dimethylethyl 2-(Isothiocyanatomethyl)phenyl Carbonate (5a): a pale-yellow oil; R_f 0.12 (CH_2Cl_2 /hexane 1:2); IR (neat) 2173, 2094, 1760 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 1.57 (s, 9H), 4.74 (s, 2H), 7.22 (d, $J = 8.0$ Hz, 1H), 7.29 (t, $J = 7.4$ Hz, 1H), 7.38 (dd, $J = 8.0, 7.4$ Hz, 1H), 7.44 (d, $J = 7.4$ Hz, 1H). Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_3\text{S}$: C, 58.85; H, 5.70; N, 5.28. Found: C, 58.53; H, 5.81; N, 5.24.

1,1-Dimethylethyl 2-(1-Isothiocyanatoethyl)phenyl Carbonate (5b): a yellow oil; R_f 0.32 (AcOEt/hexane 1:10); IR (neat) 2124, 2093, 1760 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 1.56 (s, 9H), 1.65 (d, $J = 6.8$ Hz, 3H), 5.18 (q, $J = 6.8$ Hz, 1H), 7.18 (d, $J = 7.8$ Hz, 1H), 7.30 (dd, $J = 7.8, 7.4$ Hz, 1H), 7.35 (dd, $J = 7.8, 7.4$ Hz, 1H), 7.50 (d, $J = 7.8$ Hz, 1H). Anal. Calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_3\text{S}$: C, 60.19; H, 6.13; N, 5.01. Found: C, 60.06; H, 6.44; N, 4.85.

1,1-Dimethylethyl 2-(1-Isothiocyanatopropyl)phenyl Carbonate (5c): a yellow oil; R_f 0.28 (AcOEt/hexane 1:10); IR (neat) 2084, 1760 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 1.04 (t, $J = 7.4$ Hz, 3H), 1.56 (s, 9H), 1.93 (qd, $J = 7.4, 6.3$ Hz, 2H), 4.99 (t, $J = 6.3$ Hz, 1H), 7.17 (d, $J = 7.4$ Hz, 1H), 7.29 (t, $J = 7.4$ Hz, 1H), 7.35 (t, $J = 7.4$ Hz, 1H), 7.46 (d, $J = 7.4$ Hz, 1H). Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_3\text{S}$: C, 61.41; H, 6.53; N, 4.77. Found: C, 61.30; H, 6.67; N, 4.71.

1,1-Dimethylethyl 2-[(Isothiocyanato)(phenyl)methyl]phenyl Carbonate (5d): a yellow oil; R_f 0.37 ($\text{CH}_2\text{Cl}_2/\text{hexane}$ 1:2); IR (neat) 2068, 1760 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.47 (s, 9H), 6.28 (s, 1H), 7.20 (d, $J = 8.0$ Hz, 1H), 7.26–7.39 (m, 7H), 7.46 (dd, $J = 7.4, 1.7$ Hz, 1H). Anal. Calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_3\text{S}$: C, 66.84; H, 5.61; N, 4.10. Found: C, 66.72; H, 5.63; N, 4.02.

1,1-Dimethylethyl 2-(1-Isothiocyanatoethyl)-5-methylphenyl Carbonate (5e): a beige oil; R_f 0.29 ($\text{CH}_2\text{Cl}_2/\text{hexane}$ 1:3); IR (neat) 2132, 2086, 1759 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.56 (s, 9H), 1.63 (d, $J = 6.3$ Hz, 3H), 2.36 (s, 3H), 5.12 (q, $J = 6.3$ Hz, 1H), 6.98 (s, 1H), 7.10 (d, $J = 8.0$ Hz, 1H), 7.36 (d, $J = 8.0$ Hz, 1H). Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_3\text{S}$: C, 61.41; H, 6.53; N, 4.77. Found: C, 61.34; H, 6.51; N, 4.69.

1,1-Dimethylethyl 2-(1-Isothiocyanatoethyl)-4-methylphenyl Carbonate (5f): a yellow oil; R_f 0.36 ($\text{CH}_2\text{Cl}_2/\text{hexane}$ 1:3); IR (neat) 2088, 1759 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.55 (s, 9H), 1.63 (d, $J = 6.3$ Hz, 3H), 2.37 (s, 3H), 5.14 (q, $J = 6.3$ Hz, 1H), 7.04 (d, $J = 8.6$ Hz, 1H), 7.13 (dd, $J = 8.6, 2.3$ Hz, 1H), 7.26 (d, $J = 2.3$ Hz, 1H). Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_3\text{S}$: C, 61.41; H, 6.53; N, 4.77. Found: C, 61.29; H, 6.68; N, 4.60.

4-Chloro-2-(1-isothiocyanatoethyl)phenyl 1,1-Dimethylethyl Carbonate (5g): a reddish-yellow oil; R_f 0.40 ($\text{CH}_2\text{Cl}_2/\text{hexane}$ 1:3); IR (neat) 2083, 1762 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.56 (s, 9H), 1.64 (d, $J = 6.9$ Hz, 3H), 5.15 (q, $J = 6.9$ Hz, 1H), 7.14 (d, $J = 8.6$ Hz, 1H), 7.31 (dd, $J = 8.6, 2.3$ Hz, 1H), 7.46 (d, $J = 2.3$ Hz, 1H). Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{ClNO}_3\text{S}$: C, 53.59; H, 5.14; N, 4.46. Found: C, 53.53; H, 5.18; N, 4.31.

1,1-Dimethylethyl 2-(1-Isothiocyanatoethyl)-4-methoxyphenyl Carbonate (5h): a yellow oil; R_f 0.23 ($\text{CH}_2\text{Cl}_2/\text{hexane}$ 1:2); IR (neat) 2084, 1757, 1610 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.55 (s, 9H), 1.63 (d, $J = 6.9$ Hz, 3H), 3.83 (s, 3H), 5.12 (q, $J = 6.9$ Hz, 1H), 6.85 (dd, $J = 9.2, 2.9$ Hz, 1H), 6.98 (d, $J = 2.9$ Hz, 1H), 7.07 (d, $J = 9.2$ Hz, 1H). Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_4\text{S}$: C, 58.23; H, 6.19; N, 4.53. Found: C, 58.10; H, 6.18; N, 4.29.

Typical Procedure for the Preparation of 3,4-Dihydro-2H-1,3-benzoxazine-2-thiones (7).

3,4-Dihydro-2H-1,3-benzoxazine-2-thione (7a). To a stirred solution of **5a** (0.28 g, 1.1 mmol) in CH_2Cl_2 (3 mL) at 0 °C was added $\text{CF}_3\text{CO}_2\text{H}$ (0.5 mL). After 1 h, Et_3N (1.2 mL) was added and the mixture was poured into cold water (30 mL). The mixture was extracted with CH_2Cl_2 (3 × 10 mL) and the combined extracts were washed with 1% aqueous HCl (2 × 10 mL) and brine (10 mL), dried (Na_2SO_4), and concentrated by evaporation. The residue was purified by column chromatography on SiO_2 (CH_2Cl_2) to afford **7a** (0.17 g, 97%); colorless needles; mp 163–165 °C ($\text{hexane}/\text{CH}_2\text{Cl}_2$); IR (KBr) 3185, 1627, 1197 cm^{-1} ; ^1H NMR ($\text{DMSO}-d_6$) δ 4.41 (s, 2H), 7.08 (d, $J = 7.4$ Hz, 1H), 7.17 (t, $J = 7.4$ Hz, 1H), 7.24 (d, $J = 7.4$ Hz, 1H), 7.31 (t, $J = 7.4$ Hz, 1H), 10.29 (br s, 1H); ^{13}C NMR ($\text{DMSO}-d_6$) δ 41.46, 115.43, 117.02, 125.14, 126.57, 128.99, 148.28, 181.88. HR-MS. Calcd for $\text{C}_8\text{H}_8\text{NOS}$ (M+H): 166.0326. Found: m/z 166.0325. Anal. Calcd for $\text{C}_8\text{H}_7\text{NOS}$: C, 58.16; H, 4.27; N, 8.48. Found: C, 58.06; H, 4.38; N, 8.50.

4-Methyl-3,4-dihydro-2H-1,3-benzoxazine-2-thione (7b): colorless needles; mp 107–108 °C (hexane/CH₂Cl₂); IR (KBr) 3161, 1626, 1183 cm⁻¹; ¹H NMR (CDCl₃) δ 1.60 (d, *J* = 6.9 Hz, 3H), 4.73 (qd, *J* = 6.9, 2.3 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 1H), 8.83 (br s, 1H); ¹³C NMR (DMSO-*d*₆) δ 24.04, 49.08, 116.42, 120.94, 125.33, 125.57, 129.31, 147.85, 182.72. HR-MS. Calcd for C₉H₁₀NOS (M+H): 180.0483. Found: *m/z* 180.0474. Anal. Calcd for C₉H₉NOS: C, 60.31; H, 5.06; N, 7.81; S, 17.89. Found: C, 60.04; H, 4.90; N, 7.72; S, 17.69.

4-Ethyl-3,4-dihydro-2H-1,3-benzoxazine-2-thione (7c): colorless needles; mp 135–136 °C (hexane/CH₂Cl₂); IR (KBr) 3169, 1623, 1194 cm⁻¹; ¹H NMR (CDCl₃) δ 0.92 (t, *J* = 7.4 Hz, 3H), 1.83–2.00 (m, 2H), 4.64 (td, *J* = 7.4, 2.3 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 1H), 9.11 (br s, 1H); ¹³C NMR (DMSO-*d*₆) δ 8.04, 30.91, 54.24, 116.25, 119.21, 125.53, 125.69, 129.17, 148.54, 183.25. HR-MS. Calcd for C₁₀H₁₂NOS (M+H): 194.0639. Found: *m/z* 194.0635. Anal. Calcd for C₁₀H₁₁NOS: C, 62.15; H, 5.74; N, 7.25. Found: C, 62.03; H, 5.79; N, 7.19.

4-Phenyl-3,4-dihydro-2H-1,3-benzoxazine-2-thione (7d): a white solid; mp 191–193 °C (hexane/CH₂Cl₂); IR (KBr) 3183, 1620, 1195 cm⁻¹; ¹H NMR (DMSO-*d*₆) δ 5.72 (s, 1H), 7.15–7.19 (m, 3H), 7.28 (d, *J* = 7.4 Hz, 2H), 7.30–7.35 (m, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 10.86 (s, 1H); ¹³C NMR (DMSO-*d*₆) δ 55.65, 115.74, 120.95, 125.52, 126.62, 127.92, 128.20, 129.01, 129.40, 142.35, 147.58, 181.28. HR-MS. Calcd for C₁₄H₁₂NOS (M+H): 242.0639. Found: *m/z* 242.0632. Anal. Calcd for C₁₄H₁₁NOS: C, 69.68; H, 4.59; N, 5.80. Found: C, 69.68; H, 4.72; N, 5.59.

4,7-Dimethyl-3,4-dihydro-2H-1,3-benzoxazine-2-thione (7e): a white solid; mp 144–146 °C (hexane/CH₂Cl₂); IR (KBr) 3182, 1636, 1168 cm⁻¹; ¹H NMR (CDCl₃) δ 1.56 (d, *J* = 6.3 Hz, 3H), 2.35 (s, 3H), 4.67 (q, *J* = 6.3 Hz, 1H), 6.94 (s, 1H), 7.00 (s, 2H), 8.18 (br s, 1H); ¹³C NMR (DMSO-*d*₆) δ 20.99, 24.08, 49.00, 116.70, 121.64, 125.00, 126.47, 139.78, 147.71, 183.02. HR-MS. Calcd for C₁₀H₁₂NOS (M+H): 194.0639. Found: *m/z* 194.0634. Anal. Calcd for C₁₀H₁₁NOS: C, 62.15; H, 5.74; N, 7.25. Found: C, 62.09; H, 5.83; N, 7.23.

4,6-Dimethyl-3,4-dihydro-2H-1,3-benzoxazine-2-thione (7f): a white solid; mp 161–163 °C (hexane/CH₂Cl₂); IR (KBr) 3194, 1625, 1186 cm⁻¹; ¹H NMR (CDCl₃) δ 1.58 (d, *J* = 6.9 Hz, 3H), 2.33 (s, 3H), 4.68 (q, *J* = 6.9 Hz, 1H), 6.91 (s, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 8.73 (br, 1H); ¹³C NMR (DMSO-*d*₆) δ 20.81, 24.20, 49.09, 116.11, 120.64, 125.57, 129.77, 135.36, 145.88, 182.75. HR-MS. Calcd for C₁₀H₁₂NOS (M+H): 194.0639. Found: *m/z* 194.0632. Anal. Calcd for C₁₀H₁₁NOS: C, 62.15; H, 5.74; N, 7.25. Found: C, 62.08; H, 5.80; N, 7.20.

6-Chloro-4-methyl-3,4-dihydro-2H-1,3-benzoxazine-2-thione (7g): a white solid; mp 188–191 °C (hexane/CH₂Cl₂); IR (KBr) 3200, 1618, 1199 cm⁻¹; ¹H NMR (CDCl₃) δ 1.60 (d, *J* = 6.9 Hz, 3H), 4.68 (q,

$J = 6.9$ Hz, 1H), 7.09 (d, $J = 8.6$ Hz, 1H), 7.12 (d, $J = 2.3$ Hz, 1H), 7.29 (dd, $J = 8.6, 2.3$ Hz, 1H), 7.96 (br s, 1H); ^{13}C NMR (DMSO- d_6) δ 23.52, 47.94, 117.48, 124.19, 125.96 (2 overlapped Cs), 128.96, 146.36, 180.61. HR-MS. Calcd for $\text{C}_9\text{H}_9\text{ClNOS}$ (M+H): 214.0093. Found: m/z 214.0090. Anal. Calcd for $\text{C}_9\text{H}_{10}\text{NOS}$: C, 57.40; H, 5.30; N, 6.69. Found: C, 57.31; H, 5.50; N, 6.50.

4-Methyl-6-methoxy-3,4-dihydro-2H-1,3-benzoxazine-2-thione (7h): a white solid; mp 166–168 °C (hexane/ CH_2Cl_2); IR (KBr) 3192, 1631, 1197 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.58 (d, $J = 6.3$ Hz, 3H), 3.80 (s, 3H), 4.67 (q, $J = 6.3$ Hz, 1H), 6.61 (d, $J = 2.3$ Hz, 1H), 6.83 (dd, $J = 8.6, 2.3$ Hz, 1H), 7.08 (d, $J = 8.6$ Hz, 1H), 7.75 (br s, 1H); ^{13}C NMR (DMSO- d_6) δ 23.71, 48.27, 55.58, 110.60, 114.52, 116.49, 122.94, 141.57, 156.38, 181.10. HR-MS. Calcd for $\text{C}_{10}\text{H}_{12}\text{NO}_2\text{S}$ (M+H): 210.0588. Found: m/z 210.0579. Anal. Calcd for $\text{C}_{10}\text{H}_{11}\text{NO}_2\text{S}$: C, 57.39; H, 5.30; N, 6.69. Found: C, 57.15; H, 5.36; N, 6.40.

1,1-Dimethylethyl 2-Methylphenyl Carbonate (9a).⁹ To a stirred solution of 2-methylphenol (**8a**) (0.54 g, 5.0 mmol) in CH_2Cl_2 (7 mL) containing DMAP (61 mg, 0.5 mmol) at 0 °C was added $(\text{Boc})_2\text{O}$ (1.2 g, 5.5 mmol) dropwise. After 10 min, the mixture was diluted with AcOEt (50 mL) and washed with H_2O (2 \times 15 mL) and brine (10 mL). The organic layer was dried (Na_2SO_4) and concentrated by evaporation. The residue was purified by column chromatography on SiO_2 to give **9a** (0.96 g, 92%); a colorless liquid; R_f 0.66 (AcOEt/hexane 1:10). IR and ^1H NMR data of this compound was identical to those reported previously.^{9b}

5-Chloro-2-methylphenyl Acetate (9b).¹⁰ To a stirred solution of 5-chloro-2-methylphenol (**8b**) (1.0 g, 7.0 mmol) and pyridine (0.55 g, 7.0 mmol) in THF (10 mL) at 0 °C was added AcCl (0.55 g, 7.0 mL) dropwise. The mixture was warmed to rt and stirring was continued overnight. Water (30 mL) was added and the mixture was extracted with AcOEt (3 \times 20 mL). The combined extracts were washed with water (3 \times 15 mL) and brine (15 mL), dried (Na_2SO_4), and concentrated by evaporation. The residue was purified by column chromatography on silica gel to afford **9b** (1.1 g, 87%); a colorless liquid; R_f 0.57 (AcOEt/hexane 1:5); IR (neat) 1773, 1604 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.14 (s, 3H), 2.32 (s, 3H), 7.04 (s, 1H), 7.12 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.16 (d, $J = 8.0$ Hz, 1H).

Typical Procedure for the Preparation of Benzyl Azides (11). 2-(Azidomethyl)phenyl 1,1-Dimethylethyl Carbonate (11a). A solution of **9a** (0.95 g, 4.6 mmol), NBS (0.81 g, 4.6 mmol) in *t*-BuOAc (14 mL) containing AIBN (45 mg, 0.27 mmol) was heated at reflux temperature for 2.5 h. After cooling to rt, saturated aqueous NaHCO_3 (30 mL) was added and the mixture was extracted with AcOEt (3 \times 20 mL). The combined extracts were washed with brine (15 mL), dried (Na_2SO_4), and concentrated by evaporation. The residue was dissolved in DMF (15 mL) and NaN_3 (0.30 g, 4.6 mmol) was added under stirring. After 2 h, H_2O (30 mL) was added and the mixture was extracted with AcOEt (3 \times 20 mL). The combined extracts were washed with H_2O (3 \times 10 mL) and brine (15 mL), dried (Na_2SO_4), and

concentrated by evaporation. The residue was purified by column chromatography on SiO₂ to afford **11a** (0.65 g, 57% from **9a**); a colorless liquid; *R_f* 0.17 (AcOEt/hexane 1:20); IR (neat) 2100, 1759 cm⁻¹; ¹H NMR (CDCl₃) δ 1.56 (s, 9H), 4.36 (s, 2H), 7.14 (ddd, *J* = 8.0, 7.4, 1.7 Hz, 1H), 7.26 (td, *J* = 7.4, 1.1 Hz, 1H), 7.36 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.32 (d, *J* = 7.4 Hz, 1H). Anal. Calcd for C₁₂H₁₅N₃O₃: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.70; H, 6.16; N, 16.87.

2-(Azidomethyl)-5-chlorophenyl Acetate (11b): a colorless liquid; *R_f* 0.29 (AcOEt/hexane 1:20); IR (neat) 2104, 1771, 1604 cm⁻¹; ¹H NMR (CDCl₃) δ 2.34 (s, 3H), 4.26 (s, 2H), 7.19 (d, *J* = 1.7 Hz, 1H), 7.25 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H). Anal. Calcd for C₉H₈ClN₃O₂: C, 47.91; H, 3.57; N, 18.62. Found: C, 47.89; H, 3.68; N, 18.40.

2-(Azidomethyl)phenol (12a).¹¹ To a stirred solution of **11a** (0.42 g, 1.7 mmol) in CH₂Cl₂ (5 mL) at 0 °C was added TFA (1 mL). After 30 min, H₂O (20 mL) was added and the mixture was extracted with AcOEt (3 × 15 mL). The combined extracts were washed with H₂O (2 × 10 mL) and brine (15 mL), dried (Na₂SO₄), and concentrated by evaporation. The residue was purified by column chromatography on SiO₂ to afford **12a** (0.17 mg, 70%); a pale-yellow liquid; *R_f* 0.21 (AcOEt/hexane 1:10). IR and ¹H NMR data of this compound was identical to those reported previously.^{11b}

2-(Azidomethyl)-5-chlorophenol (12b). A solution of **11b** (0.47 g, 2.1 mmol) in THF (7 mL) containing 10% aqueous HCl (1.8 mL) was heated at reflux temperature for 4.5 h. After cooling to room temperature, the mixture was worked up and purified in a manner similar to that described for the preparation of **12a** to give **12b** (0.34 g, 88%); a white solid; mp 80–83 °C (hexane/CH₂Cl₂); IR (neat) 3269, 2140, 1604 cm⁻¹; ¹H NMR (CDCl₃) δ 4.39 (s, 2H), 5.67 (s, 1H), 6.89 (d, *J* = 2.3 Hz, 1H), 6.92 (dd, *J* = 8.0, 2.3 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 1H). Anal. Calcd for C₇H₆ClN₃O: C, 45.79; H, 3.29; N, 22.89. Found: C, 45.80; H, 3.39; N, 22.90.

Typical Procedure for the Preparation of 3,4-Dihydro-2H-1,3-benzoxazine-2-thiones (13).

3,4-Dihydro-2H-1,3-benzoxazine-2-thione (13a = 7a). A solution of **12a** (80 mg, 0.53 mmol) and PPh₃ (0.14 g, 0.53 mmol) in CH₂Cl₂ (5 mL) was stirred for 4 h at rt. The solvent was removed by evaporation and the residue was dissolved in MeCN (3 mL). To this solution was added CS₂ (0.5 mL) and the resulting solution was heated at reflux temperature for 30 min. After cooling to rt, the mixture was concentrated by evaporation and the residue was purified by column chromatography on SiO₂ (CH₂Cl₂) to give **13a** (= **7a**) (61 mg, 70%).

7-Chloro-3,4-dihydro-2H-1,3-benzoxazine-2-thione (13b): a white solid; mp 195–197 °C (hexane/CH₂Cl₂); IR (KBr) 3204, 1624, 1192 cm⁻¹; ¹H NMR (DMSO-*d*₆) δ 4.40 (s, 2H), 7.24–7.30 (m, 3H), 10.38 (br s, 1H); ¹³C NMR (DMSO-*d*₆) δ 41.25, 115.58, 116.20, 125.04, 128.08, 132.72, 148.76, 181.27. HR-MS. Calcd for C₈H₇ClNOS (M+H): 199.9937. Found: *m/z* 199.9932. Anal. Calcd for C₈H₆ClNOS: C, 48.13; H, 3.03; N, 7.02. Found: C, 48.01; H, 3.01; N, 6.90.

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