

Synthesis of 1(3*H*)-Imino-2-benzothiophene and 1-Imino-1*H*-2-benzothiopyran Derivatives by Reactions of Secondary *o*-(Vinyl)thiobenzamide Derivatives with Iodine

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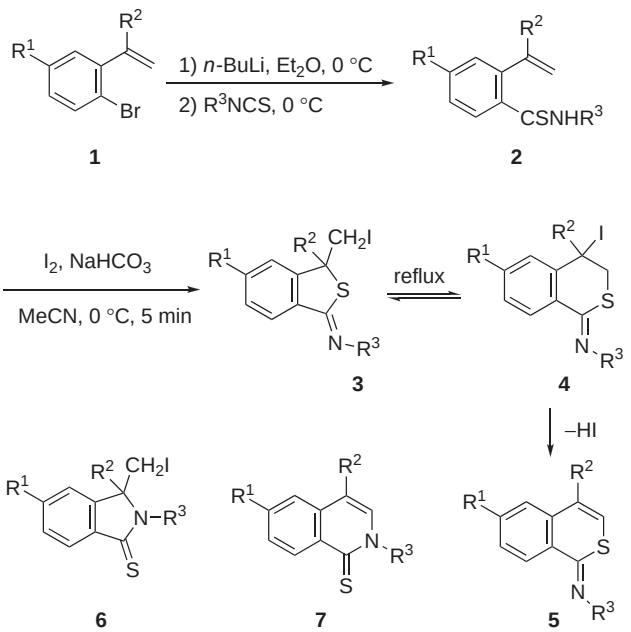
Efficient methods have been developed for the preparation of 1(3*H*)-imino-2-benzothiophene and 1-imino-1*H*-2-benzothiopyran derivatives. Treatment of secondary *o*-(vinyl)thiobenzamide derivatives with iodine in the presence of sodium hydrogencarbonate in acetonitrile at 0 °C gave the former derivatives. Similar treatment at reflux gave the latter derivatives.

We have recently reported that iodine-mediated cyclization of secondary *o*-vinylbenzamide derivatives affords 3-(iodomethyl)isoindolin-1-one derivatives.[1] We are interested in examining the reaction of secondary *o*-(vinyl)thiobenzamide derivatives with iodine under similar conditions, which should give 3-(iodomethyl)isoindolin-1-thione derivatives **6**. The reaction, however, gives 1(3*H*)-imino-2-benzothiophene derivatives **3**. We have also found that **3** can be transformed into 1-imino-1*H*-2-benzothiopyran derivatives **5** by elevating the reaction temperature. This paper reports convenient methods for the preparation of these heterocycles. Although these derivatives may be of potential interest from a biological point of view, there have been only a few reports on their syntheses.[2,3]

Preparation of **3** and **5** was carried out as shown in Scheme 1. The secondary *o*-(vinyl)thiobenzamide derivatives **2** were readily prepared by reacting the appropriate isothiocyanates with *o*-vinylphenyllithiums, generated in situ by treating *o*-bromostyrene derivatives with butyllithium in diethyl ether at 0 °C.[1] Moderate to good yields of the products **2** were obtained, as summarized in Table 1.

Initially, the reactions of these thioamides **2** with iodine were carried out in acetonitrile at 0 °C in the presence of sodium hydrogencarbonate. They proceeded very smoothly and were complete within 5 min. After the usual aqueous workup, followed by purification using preparative TLC on silica gel, **3**, not **6**, were obtained in fair to good yields, as shown in Table 1. One of the possible stereoisomers was obtained as a sole product in each reaction. Although the stereochemistry of 1-imino moiety of **3** is not yet clear, it was tentatively determined to be *Z*. The structure of **3** was assigned on the basis of ^{13}C NMR spectra of **3a** and **3h**. The spectra had signals assignable to the imino carbons at δ 165.25 and 164.59, respectively, while that of **2a** showed a signal assignable to the thiocarbonyl carbon at δ 198.52. Further confirmation of the structure was carried out by hydrolysis of **3**. In other words, subjection acid hydrolysis of **3a** and **3g** gave 2-benzothiophene-1(3*H*)-one derivatives **8a** and **8b**, respectively, in good yields, as shown in Scheme 2.

During the above investigation, a small quantity (ca. 2%) of



Scheme 1.

1-ethylimino-4-phenyl-1*H*-2-benzothiopyran (**5d**) was found in the reaction mixture for the preparation of **3d** from **2d**. It was hypothesized that **5d** was produced due to structural isomerization of **3d** via intermediate **4** (Scheme 1). Heating of mixtures of **2**, iodine, and sodium hydrogencarbonate in acetonitrile at reflux resulted in the formation of **5** in moderate to fair yields, as summarized in Table 2. Thus, it should be possible to transform isolated **3** into **5** under the same reaction conditions. For example, **3a** was heated in acetonitrile at reflux in the presence of iodine and sodium hydrogencarbonate to give **5a** in 86% yield. In the ^{13}C NMR spectra of **5a**, the signal at δ 156.79 could be assigned to the imino carbon atom, which supported the presence of the 1-imino-1*H*-2-benzothiopyran structure. This excludes the possibility of the thiolactam structure **7**, as described for the structure determination of **3**. As well, the stereochemistry of the imino moiety, i.e., *Z*, was only tentative.

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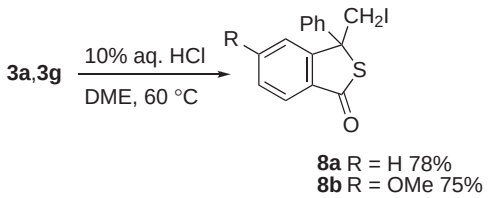
Table 1. Preparation of 1(3*H*)-Imino-2-benzothiophene Derivatives **3** via *o*-(Vinyl)thiobenzamide Derivatives **2**

Entry	**1**	R^3	**2** (Yield/%)[a)]	**3** (Yield/%)[a)]
1	**1a** (R^1 = H, R^2 = Ph)	Ph	**2a** (81)	**3a** (69)
2	**1a**	*m*-Tol	**2b** (77)	**3b** (56)
3	**1a**	4-BrC_6H_4	**2c** (77)	**3c** (61)
4	**1a**	Et	**2d** (68)	**3d** (62)
5	**1a**	*c*-Hex	**2e** (53)	**3e** (73)
6	**1a**	Adamantan-1-yl	**2f** (56)	**3f** (51)
7	**1b** (R^1 = OMe, R^2 = Ph)	Ph	**2g** (76)	**3g** (50)
8	**1c** (R^1 = H, R^2 = 4-ClC_6H_4)	Ph	**2h** (72)	**3h** (86)
9	**1c**	*c*-Hex	**2i** (59)	**3i** (56)
10	**1d** (R^1 = H, R^2 = Me)	Ph	**2j** (79)	**3j** (78)
11	**1d**	*c*-Hex	**2k** (71)	**3k** (77)

a) Isolated yield.



Scheme 2.

Table 2. Preparation of 1-Imino-1*H*-2-benzothiopyran Derivatives **5**

Entry	**2**	Time	**5** (Yield/%)[a)]
1	**2a**	0.5 h	**5a** (58)
2	**2b**	0.5 h	**5b** (52)
3	**2c**	0.5 h	**5c** (59)
4	**2d**	10 min	**5d** (54)
5	**2e**	1.5 h	**5e** (62)
6	**2f**	1.5 h	**5f** (45)
7	**2g**	0.5 h	**5g** (40)
8	**2h**	1 h	**5h** (55)
9	**2i**	40 min	**5i** (56)
10	**2j**	1.5 h	**5j** (63)
11	**2k**	2 h	**5k** (53)

a) Isolated yield.

In conclusion, we showed that the reaction of secondary *o*-(vinyl)thiobenzamides with iodine provides a short and efficient route to 1(3*H*)-imino-2-benzothiophene and 1-imino-1*H*-2-benzothiopyran derivatives. To the best of our knowledge, this is the first report on the general synthesis of these derivatives. The methods have advantages over the previous methods for the synthesis of these derivatives:[2,3] simple manipulations as well as the ready availability of the starting materials.

Experimental

General. The melting points were determined on a Laboratory Devices MEL-TEMP II melting-point apparatus and are uncorrected. The IR spectra were recorded on a Shimadzu FTIR-8300 spectrometer. The ^{1}H NMR spectra were determined using $SiMe_4$ as an internal reference in $CDCl_3$, unless stated otherwise, with a JEOL ECP500 FT NMR spectrometer operating at 500 MHz or a JEOL LA400 FT NMR spectrometer operating at 400 MHz. The ^{13}C NMR spectra were determined using $SiMe_4$ as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 125 MHz in $CDCl_3$. Low-resolution mass spectra were recorded on a JEOL AUTOMASS 20 spectrometer (Center for Joint Research and Development, this University). High-resolution MS analyses were performed on a JEOL JMS-AX505 HA spectrometer (Faculty of Agriculture, this University). Thin-layer chromatography (TLC) was carried out using Merck Kieselgel 60 PF_{254}. All of the solvents used were dried over the appropriate drying agents and distilled under argon prior to use.

Starting Materials. 1-Bromo-2-(1-phenylethenyl)benzene (**1a**),[4] (2-bromo-5-methoxyphenyl)phenylmethanone,[5] 2-bromophenyl(4-chlorophenyl)methanone,[6] and 1-bromo-2-(1-methylethenyl)benzene (**1d**)[7] were prepared by the appropriate reported methods. All other chemical used in this study were commercially available.

1-Bromo-4-methoxy-2-(1-phenylethenyl)benzene (1b): This compound was prepared by the reaction of (2-bromo-5-methoxyphenyl)phenylmethanone[5] with methylenetriphenylphosphorane in THF at 0 °C in 68% yield; a pale-yellow oil; R_f 0.35 (1:9 $CHCl_3$–hexane); IR (neat) 1591, 1568, 1464, and 1232 cm^{-1}; ^{1}H NMR (500 MHz) δ 3.81 (3H, s), 5.27 (1H, d, J = 0.9 Hz), 5.83 (1H, d, J = 0.9 Hz), 6.78 (1H, dd, J = 8.7 and 2.2 Hz), 6.87 (1H, d, J = 2.2 Hz), 7.25–7.34 (5H, m), and 7.47 (1H, d, J = 8.7 Hz). Found: C, 62.27; H, 4.64%. Calcd for $C_{15}H_{13}BrO$: C, 62.30; H, 4.53%.

1-Bromo-2-[1-(4-chlorophenyl)ethenyl]benzene (1c): This compound was prepared by the reaction of 2-bromophenyl(4-chlorophenyl)methanone[6] with methylenetriphenylphosphorane in THF at 0 °C in 73% yield; a colorless oil; R_f 0.71 (cyclohexane); IR (neat) 1616 cm^{-1}; ^{1}H NMR (500 MHz) δ 5.28 (1H, d, J = 0.9 Hz), 5.81 (1H, d, J = 0.9 Hz), 7.19 (2H, d, J = 8.7 Hz), 7.22 (1H, ddd, J = 8.2, 7.3, and 1.8 Hz), 7.26 (2H, d, J = 8.7 Hz), 7.30 (1H, dd, J = 7.3 and 1.8 Hz), 7.35 (1H, td, J = 7.3 and 1.4 Hz), and 7.59 (1H, dd, J = 8.2 and 1.4 Hz). Found: C, 57.18; H, 3.73%. Calcd for $C_{14}H_{10}ClBr$: C, 57.27; H, 3.43%.

Typical Procedure for the Preparation of *o*-(Vinyl)thiobenzamide Derivatives 2. *N*-Phenyl-2-(1-phenylethenyl)thiobenzamide (2a): To a stirred solution of **1a** (0.86 g, 3.3 mmol) in Et_2O (10 mL) at 0 °C was added dropwise *n*-BuLi (1.6 M in hexane; 3.7 mmol) (1 M = 1 mol dm^{-3}). After 1 h, PhNCS (0.49 g, 3.7 mmol) was added, and stirring was continued for an additional 20 min. The reaction mixture was quenched by adding saturated aqueous NH_4Cl (15 mL) and extracted with Et_2O three times (10 mL each). The combined extracts were washed with brine,

and dried over anhydrous Na_2SO_4, and the solvent was evaporated. The residual solid was recrystallized from Et_2O–CH_2Cl_2 to give **2a** (0.85 g, 81%): a pale-yellow solid; mp 154–159 °C; IR (KBr disk) 3360 and 1362 cm^{-1}; ^1H NMR (500 MHz) δ 5.49 (1H, d, $J = 0.9$ Hz), 5.80 (1H, s), 7.20 (1H, tt, $J = 7.3$ and 1.8 Hz), 7.24–7.29 (9H, m), 7.37 (1H, dd, $J = 7.3$ and 1.4 Hz), 7.44–7.49 (2H, m), 7.90 (1H, dd, $J = 7.3$ and 1.4 Hz), and 8.71 (1H, br s); ^{13}C NMR δ 116.10, 122.89, 126.67, 126.88, 128.32, 128.34, 128.43, 128.65, 130.11, 130.39, 130.94, 136.87, 138.58, 139.14, 142.92, 148.78, and 198.52. Found: C, 79.65; H, 5.45; N, 4.43%. Calcd for $C_{21}H_{17}NS$: C, 79.96; H, 5.43; N, 4.44%.

***N*-(3-Methylphenyl)-2-(1-phenylethenyl)thiobenzamide (2b):** A yellow solid; mp 69–71 °C (Et_2O–CH_2Cl_2); IR (KBr disk) 3298, 1609, and 1373 cm^{-1}; ^1H NMR (500 MHz) δ 2.28 (3H, s), 5.47 (1H, s), 5.80 (1H, s), 6.97 (1H, s), 7.01 (1H, d, $J = 7.8$ Hz), 7.04 (1H, d, $J = 7.8$ Hz), 7.17 (1H, t, $J = 7.8$ Hz), 7.25–7.29 (5H, m), 7.37 (1H, dd, $J = 7.3$ and 1.4 Hz), 7.42–7.49 (2H, m), 7.89 (1H, dd, $J = 7.3$ and 1.4 Hz), and 8.65 (1H, br s). Found: C, 80.16; H, 5.92; N, 4.25%. Calcd for $C_{22}H_{19}NS$: C, 80.20; H, 5.81; N, 4.25%.

***N*-(4-Bromophenyl)-2-(1-phenylethenyl)thiobenzamide (2c):** A yellow solid; mp 111–113 °C (hexane–Et_2O); IR (KBr disk) 3229 and 1362 cm^{-1}; ^1H NMR (500 MHz) δ 5.47 (1H, s), 5.80 (1H, s), 7.14 (2H, d, $J = 8.7$ Hz), 7.20–7.28 (5H, m), 7.37–7.40 (3H, m), 7.46 (1H, ddd, $J = 7.8$, 7.3, and 1.4 Hz), 7.49 (1H, ddd, $J = 7.8$, 7.3, and 1.4 Hz), 7.88 (1H, dd, $J = 7.8$ and 1.4 Hz), and 8.64 (1H, br s). Found: C, 64.06; H, 4.13; N, 3.46%. Calcd for $C_{21}H_{16}BrNS$: C, 63.96; H, 4.09; N, 3.55%.

***N*-Ethyl-2-(1-phenylethenyl)thiobenzamide (2d):** A yellow solid; mp 69–70 °C (hexane); IR (KBr disk) 3250 and 1387 cm^{-1}; ^1H NMR (500 MHz) δ 1.01 (3H, t, $J = 7.3$ Hz), 3.35–3.40 (2H, m), 5.41 (1H, s), 5.78 (1H, s), 7.16 (1H, br s), 7.27–7.31 (6H, m), 7.38–7.43 (2H, m), and 7.76 (1H, dd, $J = 7.3$ and 1.8 Hz). Found: C, 76.17; H, 6.41; N, 5.19%. Calcd for $C_{17}H_{17}NS$: C, 76.36; H, 6.41; N, 5.24%.

***N*-Cyclohexyl-2-(1-phenylethenyl)thiobenzamide (2e):** A yellow solid; mp 117–120 °C (hexane–Et_2O); IR (KBr disk) 3362 and 1387 cm^{-1}; ^1H NMR (500 MHz) δ 0.88–1.83 (10H, m), 4.16–4.20 (1H, m), 5.39 (1H, d, $J = 0.9$ Hz), 5.84 (1H, d, $J = 0.9$ Hz), 7.14 (1H, br s), 7.21–7.33 (6H, m), 7.36–7.40 (2H, m), and 7.73–7.77 (1H, m). Found: C, 78.46; H, 7.27; N, 4.29%. Calcd for $C_{21}H_{23}NS$: C, 78.46; H, 7.21; N, 4.36%.

***N*-(Adamantan-1-yl)-2-(1-phenylethenyl)thiobenzamide (2f):** A yellow solid; mp 40–41 °C (Et_2O–CH_2Cl_2); IR (KBr disk) 3366 and 1391 cm^{-1}; ^1H NMR (500 MHz) δ 1.54–1.62 (6H, m), 1.95–1.99 (9H, m), 5.40 (1H, d, $J = 0.9$ Hz), 5.90 (1H, d, $J = 0.9$ Hz), 6.99 (1H, br s), 7.18–7.22 (1H, m), 7.27–7.39 (7H, m), and 7.72–7.77 (1H, m). Found: C, 80.17; H, 7.45; N, 3.59%. Calcd for $C_{25}H_{27}NS$: C, 80.38; H, 7.29; N, 3.75%.

4-Methoxy-*N*-phenyl-2-(1-phenylethenyl)thiobenzamide (2g): This product was purified by preparative TLC on silica gel; a yellow viscous oil; R_f 0.42 (1:4 THF–hexane); IR (neat) 3343 and 1360 cm^{-1}; ^1H NMR (500 MHz) δ 3.89 (3H, s), 5.50 (1H, s), 5.82 (1H, s), 6.87 (1H, d, $J = 2.7$ Hz), 6.98 (1H, dd, $J = 8.7$ and 2.7 Hz), 7.16–7.28 (10H, m), 7.96 (1H, d, $J = 8.7$ Hz), and 8.74 (1H, br s). Found: C, 76.37; H, 5.66; N, 3.88%. Calcd for $C_{22}H_{19}NOS$: C, 76.49; H, 5.54; N, 4.05%.

2-[1-(4-Chlorophenyl)ethenyl]-*N*-phenylthiobenzamide (2h): A yellow solid; mp 128–130 °C (hexane–Et_2O); IR (KBr disk) 3364 and 1358 cm^{-1}; ^1H NMR (400 MHz) δ 5.47 (1H, s), 5.75 (1H, s), 7.15 (2H, d, $J = 8.6$ Hz), 7.19–7.23 (3H, m), 7.31–7.37 (5H, m), 7.44–7.50 (2H, m), 7.86 (1H, dd, $J = 7.7$ and 2.2 Hz), and 8.65 (1H, br s). Found: C, 72.03; H, 4.53; N, 3.91%. Calcd for $C_{21}H_{16}ClNS$: C, 72.09; H, 4.61; N, 4.00%.

2-[1-(4-Chlorophenyl)ethenyl]-*N*-cyclohexylthiobenzamide (2i): A yellow solid; mp 98–100 °C (hexane–Et_2O); IR (KBr disk) 3366 and 1385 cm^{-1}; ^1H NMR (500 MHz) δ 0.93–1.00 (2H, m), 1.08–1.16 (1H, m), 1.28–1.36 (2H, m), 1.55–1.62 (3H, m), 1.82–1.85 (2H, m), 4.17–4.21 (1H, m), 5.41 (1H, s), 5.79 (1H, s), 7.04–7.12 (1H, br), 7.21–7.27 (5H, m), 7.37–7.41 (2H, m), and 7.66–7.70 (1H, m). Found: C, 70.86; H, 6.50; N, 3.87%. Calcd for $C_{21}H_{22}ClNS$: C, 70.86; H, 6.23; N, 3.94%.

2-(1-Methylethenyl)-*N*-phenylthiobenzamide (2j): A yellow solid; mp 98–100 °C (hexane–Et_2O); IR (KBr disk) 3204 and 1373 cm^{-1}; ^1H NMR (500 MHz) δ 2.10 (3H, s), 5.26 (1H, d, $J = 1.4$ Hz), 5.30 (1H, d, $J = 1.4$ Hz), 7.25 (1H, dd, $J = 7.8$ and 1.4 Hz), 7.30 (1H, t, $J = 7.3$ Hz), 7.36 (1H, ddd, $J = 7.8$, 7.3, and 1.4 Hz), 7.40 (1H, ddd, $J = 7.8$, 7.3, and 1.4 Hz), 7.45 (2H, dd, $J = 7.8$ and 7.3 Hz), 7.79 (2H, d, $J = 7.8$ Hz), 7.87 (1H, dd, $J = 7.8$ and 1.4 Hz), and 9.03 (1H, br s). Found: C, 75.85; H, 5.92; N, 5.38%. Calcd for $C_{16}H_{15}NS$: C, 75.85; H, 5.97; N, 5.53%.

***N*-Cyclohexyl-2-(1-methylethenyl)thiobenzamide (2k):** A pale-yellow solid; mp 71–74 °C (hexane–Et_2O); IR (KBr disk) 3263 and 1387 cm^{-1}; ^1H NMR (500 MHz) δ 1.21–1.31 (3H, m), 1.42–1.50 (2H, m), 1.65–1.68 (1H, m), 1.71–1.75 (2H, m), 2.04 (3H, d, $J = 0.9$ Hz), 2.11–2.17 (2H, m), 4.48–4.52 (1H, m), 5.13 (1H, q, $J = 0.9$ Hz), 5.20 (1H, q, $J = 0.9$ Hz), 7.16 (1H, dd, $J = 7.3$ and 1.4 Hz), 7.29 (1H, td, $J = 7.3$ and 1.4 Hz), 7.33 (1H, td, $J = 7.3$ and 1.4 Hz), 7.44 (1H, br s), and 7.76 (1H, dd, $J = 7.3$ and 1.4 Hz). Found: C, 73.95; H, 8.41; N, 5.15%. Calcd for $C_{16}H_{21}NS$: C, 74.08; H, 8.16; N, 5.40%.

Typical Procedure for the Preparation of 2-Benzothiophene Derivatives 3. 3-Iodomethyl-3-pheny-1(3*H*)-phenylimino-2-benzothiophene (3a): To a stirred solution of **2a** (0.85 g, 2.7 mmol) in MeCN (20 mL) containing $NaHCO_3$ (0.90 g, 11 mmol) at 0 °C was added I_2 (2.7 g, 11 mmol) in portions. After 5 min, 10% aqueous $Na_2S_2O_3$ was added dropwise until the color of iodine disappeared. The acetonitrile was evaporated, and the organic materials were extracted with Et_2O three times (15 mL each). The combined extracts were washed with saturated aqueous $NaHCO_3$, and dried over anhydrous K_2CO_3, and the solvent was evaporated. The residue was purified by column chromatography on silica gel to give **3a** (0.82 g, 69%): a yellow viscous oil; R_f 0.30 (14:1 THF–hexane); IR (neat) 1622 cm^{-1}; ^1H NMR (400 MHz) δ 4.21 (1H, d, $J = 10.5$ Hz), 4.24 (1H, d, $J = 10.5$ Hz), 7.14 (2H, d, $J = 7.8$ Hz), 7.26–7.39 (9H, m), 7.51–7.56 (2H, m), and 8.13 (1H, dd, $J = 8.2$ and 1.8 Hz); ^{13}C NMR δ 17.82, 66.43, 120.35, 123.88, 124.93, 125.30, 127.05, 127.91, 128.69, 129.03, 129.17, 131.50, 138.22, 140.64, 149.36, 151.55, and 165.25; MS m/z (%) 441 (M^+, 100). Found: C, 57.09; H, 3.67; N, 3.13%. Calcd for $C_{21}H_{16}INS$: C, 57.15; H, 3.65; N, 3.17%.

3-Iodomethyl-1(3*H*)-(3-methylphenyl)imino-3-phenyl-2-benzothiophene (3b): A yellow viscous oil; R_f 0.26 (1:1 hexane–Et_2O); IR (neat) 1615 cm^{-1}; ^1H NMR (400 MHz) δ 2.36 (3H, s), 4.22 (2H, s), 6.94–6.97 (3H, m), 7.23–7.33 (4H, m), 7.37–7.39 (3H, m), 7.51–7.54 (2H, m), and 8.12 (1H, dd, $J = 7.7$ and 1.5 Hz); MS m/z (%) 455 (M^+, 86) and 328 (100). Found: m/z 455.0219. Calcd for $C_{22}H_{18}INS$: M, 455.0205.

1(3*H*)-(4-Bromophenyl)imino-3-iodomethyl-3-phenyl-2-benzothiophene (3c): A yellow solid; mp 155–158 °C (hexane); IR (KBr disk) 1618 cm^{-1}; ^1H NMR (500 MHz) δ 4.19 (1H, d, $J = 10.5$ Hz), 4.25 (1H, d, $J = 10.5$ Hz), 7.03 (2H, d, $J = 8.7$ Hz), 7.25–7.39 (6H, m), 7.48 (2H, d, $J = 8.7$ Hz), 7.50–7.57 (2H, m), and 8.10 (1H, dd, $J = 7.8$ and 1.4 Hz); MS m/z (%) 519 (M^+,

100). Found: C, 48.29; H, 2.98; N, 2.71%. Calcd for $C_{21}H_{15}BrINS$: C, 48.48; H, 2.91; N, 2.69%.

1(3*H*)-Ethylimino-3-iodomethyl-3-phenyl-2-benzothiophene (3d): A yellow oil; R_f 0.38 (1:5 Et_2O–hexane); IR (neat) 1634 cm^{-1}; ^1H NMR (500 MHz) δ 1.40 (3H, t, $J = 7.3$ Hz), 3.46–3.56 (2H, m), 4.18 (1H, d, $J = 12.0$ Hz), 4.26 (1H, d, $J = 12.0$ Hz), 7.26–7.34 (4H, m), 7.40–7.47 (4H, m), and 7.96 (1H, dd, $J =$ 7.3 and 1.4 Hz); MS m/z (%) 393 (M^+, 22) and 266 (100). Found: C, 51.91; H, 4.17; N, 3.27%. Calcd for $C_{17}H_{16}INS$: C, 51.92; H, 4.10; N, 3.56%.

1(3*H*)-Cyclohexylimino-3-iodomethyl-3-phenyl-2-benzothiophene (3e): A pale-yellow solid; mp 114–116 °C (hexane–Et_2O); IR (KBr disk) 1632 cm^{-1}; ^1H NMR (500 MHz) δ 1.27–1.96 (10H, m), 3.16–3.21 (1H, m), 4.20 (1H, d, $J = 10.5$ Hz), 4.25 (1H, d, $J = 10.5$ Hz), 7.25–7.34 (4H, m), 7.40–7.45 (4H, m), and 7.98 (1H, dd, $J = 6.9$ and 2.3 Hz); MS m/z (%) 447 (M^+, 35) and 320 (100). Found: C, 56.34; H, 5.14; N, 2.98%. Calcd for $C_{21}H_{22}INS$: C, 56.38; H, 4.96; N, 3.13%.

1(3*H*)-(Adamantan-1-yl)imino-3-iodomethyl-3-phenyl-2-benzothiophene (3f): A yellow solid; mp 40–41 °C (hexane–Et_2O); IR (neat) 1624 cm^{-1}; ^1H NMR (500 MHz) δ 1.69–1.75 (6H, m), 2.04–2.15 (9H, m), 4.22 (1H, d, $J = 10.5$ Hz), 4.24 (1H, d, $J =$ 10.5 Hz), 7.25–7.30 (2H, m), 7.32 (2H, dd, $J = 7.8$ and 7.3 Hz), 7.39–7.44 (4H, m), and 7.94 (1H, dd, $J = 7.3$ and 1.4 Hz); MS m/z (%) 499 (M^+, 9.5), 372 (38), and 135 (100). Found: C, 59.93; H, 5.31; N, 2.84%. Calcd for $C_{25}H_{26}INS$: C, 60.12; H, 5.25; N, 2.80%.

3-Iodomethyl-5-methoxy-3-phenyl-1(3*H*)-phenylimino-2-benzothiophene (3g): A pale-yellow solid; mp 134 °C (hexane–CH_2Cl_2); IR (KBr disk) 1618 cm^{-1}; ^1H NMR (500 MHz) δ 3.85 (3H, s), 4.19 (1H, d, $J = 10.5$ Hz), 4.21 (1H, d, $J = 10.5$ Hz), 6.85 (1H, d, $J = 2.3$ Hz), 7.07 (1H, dd, $J = 8.7$ and 2.3 Hz), 7.11–7.14 (3H, m), 7.26–7.39 (7H, m), and 8.03 (1H, d, $J = 8.7$ Hz); MS m/z (%) 471 (M^+, 88) and 344 (100). Found: C, 56.02; H, 3.91; N, 3.02%. Calcd for $C_{22}H_{18}INOS$: C, 56.06; H, 3.85; N, 2.97%.

3-(4-Chlorophenyl)-3-iodomethyl-1(3*H*)-phenylimino-2-benzothiophene (3h): A yellow solid; mp 84–87 °C (hexane–Et_2O); IR (KBr disk) 1620 cm^{-1}; ^1H NMR (500 MHz) δ 4.16 (1H, d, $J = 10.5$ Hz), 4.17 (1H, d, $J = 10.5$ Hz), 7.13 (2H, d, $J = 7.8$ Hz), 7.16 (1H, t, $J = 7.3$ Hz), 7.28 (2H, d, $J = 8.7$ Hz), 7.32 (2H, d, $J = 8.7$ Hz), 7.34–7.40 (3H, m), 7.52–7.56 (2H, m), and 8.13 (1H, dd, $J = 7.3$ and 1.4 Hz); ^{13}C NMR δ 17.08, 65.84, 120.29, 124.06, 125.05, 125.14, 128.55, 128.82, 129.21 (two overlapped C's), 131.62, 133.88, 138.09, 139.34, 148.94, 151.43, and 164.59; MS m/z (%) 475 (M^+, 11), 348 (72), and 334 (100). Found: C, 52.73; H, 3.22; N, 2.87%. Calcd for $C_{21}H_{15}ClINS$: C, 53.01; H, 3.18; N, 2.94%.

3-(4-Chlorophenyl)-1(3*H*)-cyclohexylimino-3-iodomethyl-2-benzothiophene (3i): A pale-yellow solid; mp 113 °C (decomp) (hexane–Et_2O); IR (KBr disk) 1624 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 1.19–1.37 (3H, m), 1.43–1.50 (2H, m), 1.59–1.62 (1H, m), 1.74–1.82 (4H, m), 3.10–3.14 (1H, m), 4.35 (1H, d, $J =$ 11.0 Hz), 4.86 (1H, d, $J = 11.0$ Hz), 7.39 (2H, d, $J = 8.7$ Hz), 7.43–7.46 (2H, m), 7.48 (2H, d, $J = 8.7$ Hz), 7.53 (1H, dd, $J =$ 7.8 and 7.3 Hz), and 7.78 (1H, d, $J = 7.8$ Hz); MS m/z (%) 481 (M^+, 1.1) and 354 (100). Found: C, 52.32; H, 4.40; N, 2.69%. Calcd for $C_{21}H_{21}ClINS$: C, 52.35; H, 4.39; N, 2.91%.

3-Iodomethyl-3-methyl-1(3*H*)-phenylimino-2-benzothiophene (3j): A yellow oil; R_f 0.37 (1:5 THF–hexane); IR (neat) 1622 cm^{-1}; ^1H NMR (500 MHz) δ 1.98 (3H, s), 3.70 (1H, d, $J = 10.1$ Hz), 3.79 (1H, d, $J = 10.1$ Hz), 7.13 (2H, dd, $J = 8.2$ and 1.4 Hz), 7.17 (1H, t, $J = 7.3$ Hz), 7.40 (2H, dd, $J = 8.2$ and 7.3 Hz), 7.45 (1H, d, $J = 7.8$ Hz), 7.49 (1H, t, $J = 7.3$ Hz), 7.57 (1H, ddd, $J =$ 7.8, 7.3, and 1.4 Hz), and 8.05 (1H, d, $J = 7.8$ Hz); MS m/z (%) 379 (M^+, 100). Found: C, 50.38; H, 3.73; N, 3.72%. Calcd for $C_{16}H_{14}INS$: C, 50.67; H, 3.72; N, 3.69%.

1(3*H*)-Cyclohexylimino-3-iodomethyl-3-methyl-2-benzothiophene (3k): A pale-yellow oil; R_f 0.53 (1:4 THF–hexane); IR (neat) 1639 and 1622 cm^{-1}; ^1H NMR (500 MHz) δ 1.24–1.44 (3H, m), 1.47–1.59 (2H, m), 1.62–1.69 (1H, m), 1.81–1.92 (4H, m), 1.98 (3H, s), 3.15–3.21 (1H, m), 3.68 (1H, d, $J = 10.0$ Hz), 3.79 (1H, d, $J = 10.0$ Hz), 7.37–7.40 (2H, m), 7.47 (1H, td, $J = 7.3$ and 1.4 Hz), and 7.91 (1H, dd, $J = 7.3$ and 1.4 Hz); MS m/z (%) 385 (M^+, 1.2) and 258 (100). Found: m/z 385.0378. Calcd for $C_{16}H_{20}INS$: M, 385.0361.

Typical Procedure for the Preparation of 1*H*-2-Benzothiopyran Derivatives 5. 4-Phenyl-1-phenylimino-1*H*-2-benzothiopyran (5a): To a stirring mixture of **2a** (0.54 g, 1.7 mmol) in MeCN (12 mL) containing $NaHCO_3$ (0.57 g, 6.8 mmol) at room temperature was added I_2 (1.7 g, 6.8 mmol) in portions; the mixture was heated at reflux for 30 min. After cooling to room temperature, the reaction mixture was worked up in a manner similar to that described for the preparation of **3a**. The crude product was purified by preparative TLC on silica gel to give **5a** (0.31 g, 58%): a white solid; mp 118–119 °C (Et_2O–CH_2Cl_2); IR (KBr disk) 1564 cm^{-1}; ^1H NMR (400 MHz) δ 6.54 (1H, s), 6.97 (2H, dd, $J = 7.8$ and 1.1 Hz), 7.16 (1H, t, $J = 7.3$ Hz), 7.28 (1H, dd, $J = 7.7$ and 1.4 Hz), 7.33 (2H, dd, $J = 8.0$ and 1.8 Hz), 7.37–7.52 (7H, m), and 8.61 (1H, dd, $J = 7.7$ and 1.8 Hz); ^{13}C NMR δ 119.61, 119.86, 124.25, 126.21, 127.76, 128.18, 128.53, 128.77, 129.16, 129.38, 129.74, 131.27, 133.20, 134.94, 139.81, 151.03, and 156.79; MS m/z (%) 313 (M^+, 100). Found: C, 80.37; H, 4.79; N, 4.40; S, 10.36%. Calcd for $C_{21}H_{15}NS$: C, 80.48; H, 4.82; N, 4.47; S, 10.23%.

1-(3-Methylphenyl)imino-4-phenyl-1*H*-2-benzothiopyran (5b): A pale-yellow solid; mp 92 °C (Et_2O); IR (KBr disk) 1568 cm^{-1}; ^1H NMR (400 MHz) δ 2.38 (3H, s), 6.54 (1H, s), 6.76–6.78 (2H, m), 6.98 (1H, d, $J = 7.3$ Hz), 7.26–7.34 (4H, m), 7.39–7.49 (5H, m), and 8.59 (1H, d, $J = 7.3$ Hz); MS m/z (%) 327 (M^+, 99.6) and 210 (100). Found: C, 80.59; H, 5.31; N, 4.14%. Calcd for $C_{22}H_{17}NS$: C, 80.70; H, 5.23; N, 4.28%.

1-(4-Bromophenyl)imino-4-phenyl-1*H*-2-benzothiopyran (5c): A yellow solid; mp 47–49 °C (hexane–Et_2O); IR (KBr disk) 1560 cm^{-1}; ^1H NMR (400 MHz) δ 6.55 (1H, s), 6.86 (2H, d, $J = 8.8$ Hz), 7.26–7.54 (10H, m), and 8.59 (1H, d, $J = 7.3$ Hz); MS m/z (%) 391 (M^+, 71) and 210 (100). Found: C, 64.18; H, 3.61; N, 3.49%. Calcd for $C_{21}H_{14}BrNS$: C, 64.29; H, 3.60; N, 3.57%.

1-Ethylimino-4-phenyl-1*H*-2-benzothiopyran (5d): A yellow oil; R_f 0.58 (1:5 Et_2O–hexane); IR (neat) 1605 and 1568 cm^{-1}; ^1H NMR (500 MHz) δ 1.47 (3H, t, $J = 7.3$ Hz), 3.44 (2H, q, $J = 7.3$ Hz), 6.65 (1H, s), 7.21 (1H, dd, $J = 7.8$ and 1.4 Hz), 7.35 (2H, dd, $J = 7.8$ and 1.4 Hz), 7.37–7.45 (5H, m), and 8.46 (1H, dd, $J = 7.8$ and 1.8 Hz); MS m/z (%) 265 (M^+, 75) and 210 (100). Found: m/z 265.0946. Calcd for $C_{17}H_{15}NS$: M, 265.0925.

1-Cyclohexylimino-4-phenyl-1*H*-2-benzothiopyran (5e): A yellow oil; R_f 0.57 (1:15 THF–hexane); IR (neat) 1605 and 1573 cm^{-1}; ^1H NMR (500 MHz) δ 1.33–1.48 (3H, m), 1.54–1.61 (2H, m), 1.68–1.71 (1H, m), 1.85–1.87 (4H, m), 3.54–3.58 (1H, m), 6.61 (1H, s), 7.18 (1H, dd, $J = 7.8$ and 1.4 Hz), 7.33–7.44 (7H, m), and 8.41 (1H, dd, $J = 7.8$ and 1.4 Hz); MS m/z (%) 319 (M^+, 37), 286 (90), and 236 (100). Found: C, 78.55; H, 6.54; N, 4.53%. Calcd for $C_{21}H_{21}NS$: C, 78.95; H, 6.63; N, 4.38%.

1-(Adamantan-1-yl)imino-4-phenyl-1*H*-2-benzothiopyran (5f): A pale-yellow viscous oil; R_f 0.33 (1:7 C_6H_6–hexane); IR (neat)

1604 and 1578 cm^{-1}; ^{1}H NMR (500 MHz) δ 1.72–1.79 (6H, m), 2.12–2.24 (9H, m), 6.58 (1H, s), 7.15 (1H, dd, $J = 7.8$ and 1.4 Hz), 7.31–7.44 (7H, m), and 8.37 (1H, dd, $J = 7.8$ and 1.4 Hz); MS m/z (%) 371 (M^+, 24) and 135 (100). Found: m/z 371.1704. Calcd for $C_{25}H_{25}NS$: M, 371.1708.

6-Methoxy-4-phenyl-1-phenylimino-1*H*-2-benzothiopyran (5g): A yellow solid; mp 178 °C (hexane–Et_2O); IR (KBr disk) 1603 and 1556 cm^{-1}; ^{1}H NMR (500 MHz) δ 3.74 (3H, s), 6.56 (1H, s), 6.74 (1H, d, $J = 2.3$ Hz), 6.97 (2H, d, $J = 8.2$ Hz), 7.05 (1H, dd, $J = 8.7$ and 2.3 Hz), 7.16 (1H, t, $J = 7.3$ Hz), 7.33–7.45 (7H, m), and 8.58 (1H, d, $J = 8.7$ Hz); MS m/z (%) 343 (M^+, 100). Found: C, 76.87; H, 5.05; N, 4.06%. Calcd for $C_{22}H_{17}NOS$: C, 76.94; H, 4.99; N, 4.08%.

4-(4-Chlorophenyl)-1-phenylimino-1*H*-2-benzothiopyran (5h): A yellow solid; mp 126–128 °C (hexane–Et_2O); IR (KBr disk) 1568 cm^{-1}; ^{1}H NMR (500 MHz) δ 6.53 (1H, s), 6.96 (2H, dd, $J =$ 8.2 and 0.9 Hz), 7.17 (1H, t, $J = 7.3$ Hz), 7.24 (1H, dd, $J = 7.8$ and 1.4 Hz), 7.27 (2H, d, $J = 8.2$ Hz), 7.40–7.53 (6H, m), and 8.61 (1H, dd, $J = 7.8$ and 1.4 Hz); MS m/z (%) 347 (M^+, 100). Found: C, 72.21; H, 4.11; N, 3.95%. Calcd for $C_{21}H_{14}ClNS$: C, 72.51; H, 4.06; N, 4.03%.

4-(4-Chlorophenyl)-1-cyclohexylimino-1*H*-2-benzothiopyran (5i): A pale-yellow solid; mp 98–100 °C (hexane–Et_2O); IR (KBr disk) 1601 and 1574 cm^{-1}; ^{1}H NMR (500 MHz) δ 1.24–1.47 (3H, m), 1.54–1.61 (2H, m), 1.67–1.72 (1H, m), 1.82–1.88 (4H, m), 3.52–3.58 (1H, m), 6.59 (1H, s), 7.12 (1H, dd, $J = 7.8$ and 1.4 Hz), 7.26 (2H, d, $J = 7.8$ Hz), 7.37 (1H, ddd, $J = 7.8$, 7.3, and 1.4 Hz), 7.38–7.47 (3H, m), and 8.40 (1H, dd, $J = 7.8$ and 1.4 Hz); ^{13}C NMR δ 24.66, 25.91, 32.38, 61.40, 120.10, 126.47, 127.56, 128.69, 128.72, 130.13, 130.18, 130.70, 132.32, 133.62, 133.90, 138.69, and 149.67; MS m/z (%) 353 (M^+, 29) 271 (100). Found: C, 71.23; H, 5.63; N, 4.05%. Calcd for $C_{21}H_{20}$-ClNS: C, 71.27; H, 5.70; N, 3.96%.

4-Methyl-1-phenylimino-1*H*-2-benzothiopyran (5j): A yellow solid; mp 80–81 °C (hexane); IR (KBr disk) 1562 cm^{-1}; ^{1}H NMR (500 MHz) δ 2.32 (3H, d, $J = 1.4$ Hz), 6.43 (1H, q, $J =$ 1.4 Hz), 6.93 (2H, dd, $J = 8.2$ and 0.9 Hz), 7.15 (1H, t, $J = 7.3$ Hz), 7.41 (2H, dd, $J = 8.2$ and 7.3 Hz), 7.51 (1H, ddd, $J = 8.2$, 7.3, and 1.4 Hz), 7.58–7.64 (2H, m), and 8.60 (1H, dd, $J = 8.2$ and 0.9 Hz); ^{13}C NMR δ 21.30, 117.50, 119.64, 124.09, 125.51, 126.28, 128.54, 129.10, 129.69 (two overlapped C's), 131.50, 135.32, 151.19, and 157.44; MS m/z (%) 251 (M^+, 83) and 149 (100). Found: C, 76.39; H, 5.50; N, 5.77%. Calcd for $C_{16}H_{13}NS$: C, 76.46; H, 5.21; N, 5.57%.

1-Cyclohexylimino-4-methyl-1*H*-2-benzothiopyran (5k): A yellow oil; R_f 0.59 (1:9 THF–hexane); IR (neat) 1571 cm^{-1}; ^{1}H NMR (500 MHz) δ 1.29–1.45 (3H, m), 1.49–1.56 (2H, m) 1.66–1.69 (1H, m), 1.82–1.86 (4H, m), 2.28 (3H, d, $J = 1.4$ Hz), 3.46–3.52 (1H, m), 6.48 (1H, q, $J = 1.4$ Hz), 7.38–7.41 (1H, m), 7.48–7.50 (2H, m), and 8.42 (1H, dd, $J = 7.3$ and 0.9 Hz); MS m/z (%) 257 (M^+, 100). Found: C, 74.61; H, 7.49; N, 5.50%. Calcd for $C_{16}H_{19}NS$: C, 74.66; H, 7.44; N, 5.44%.

3-Iodomethyl-3-phenyl-2-benzothiophen-1(3*H*)-one (8a). A solution of **3a** (0.15 g, 0.35 mmol) in DME/10% aqueous HCl (3 mL, 2:1) was heated at 60 °C for 2 h. After cooling, the mixture was diluted by adding Et_2O and water (15 mL each), and the layers were separated. The aqueous layer was extracted with Et_2O twice (5 mL each), and the combined extracts were dried over anhydrous K_2CO_3. Evaporation of the solvent gave a residue, which was purified by preparative TLC on silica gel to give **8a** (0.10 g, 78%): a yellow oil; R_f 0.35 (1:5 Et_2O–hexane); IR (neat) 1693 cm^{-1}; ^{1}H NMR (500 MHz) δ 4.24 (1H, d, $J = 10.5$ Hz), 4.33 (1H, d, $J = 10.5$ Hz), 7.29–7.37 (3H, m), 7.39–7.43 (3H, m), 7.54 (1H, t, $J = 7.3$ Hz), 7.65 (1H, ddd, $J = 7.8$, 7.3, and 0.9 Hz), and 7.84 (1H, d, $J = 7.8$ Hz); MS m/z (%) 366 (M^+, 0.4) and 239 (100). Found: C, 49.16; H, 3.30%. Calcd for $C_{15}H_{11}IOS$: C, 49.20; H, 3.03%.

3-Iodomethyl-5-methoxy-3-phenyl-2-benzothiophen-1(3*H*)-one (8b). This compound was prepared by the same procedure as described above for the preparation of **8a**. **8b**: a pale-yellow oil; R_f 0.21 (1:7 THF–hexane); IR (neat) 1682 cm^{-1}; ^{1}H NMR (500 MHz) δ 3.85 (3H, s), 4.23 (1H, d, $J = 11.0$ Hz), 4.28 (1H, d, $J =$ 11.0 Hz), 6.85 (1H, d, $J = 1.8$ Hz), 7.05 (1H, dd, $J = 8.7$ and 1.8 Hz), 7.29–7.37 (3H, m), 7.40 (2H, d, $J = 7.8$ Hz), and 7.76 (1H, d, $J = 8.7$ Hz); MS m/z (%) 396 (M^+, 0.1) and 268 (100). Found: C, 48.38; H, 3.55%. Calcd for $C_{16}H_{13}IO_2S$: C, 48.50; H, 3.31%.

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