

# Access to Substituted Dihydrothiopyrano[2,3-*b*]indoles via Sequential Rearrangements During *S*-Alkylation and Au-Catalyzed Hydroarylation on Indoline-2-thiones

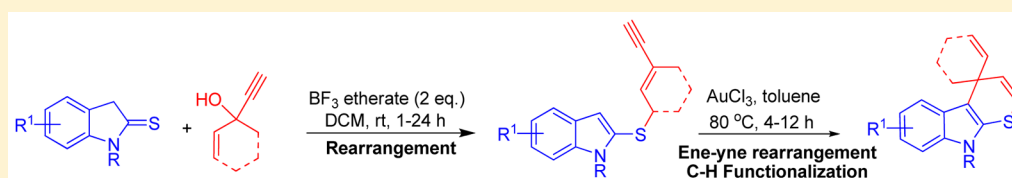
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## S Supporting Information



**ABSTRACT:** An efficient methodology for the synthesis of indole-fused dihydrothiopyrans has been developed from indoline-2-thiones. The protocol involves the synthesis of conjugated ene-yne-substituted indole-sulfides, a gold(III)-catalyzed rearrangement of the ene-yne side chain followed by intramolecular hydroarylation via C3–H functionalization of the indole core. This new synthesis of functionalized tricyclic indole derivatives through sequential rearrangements is quite general in nature

Transition-metal-catalyzed hydroarylation reactions have received considerable attention in recent years as an atom-economical approach for the functionalization of arenes, as well as for the creation of complex molecular architectures.<sup>1</sup> This ever-developing area has witnessed a remarkable growth in gold-catalyzed methodologies involving the addition of a wide variety of nucleophiles (C/N/O) to internal or terminal alkynes in an intra/intermolecular fashion.<sup>2</sup> Not surprisingly, this strategy has also emerged as a highly useful tool for the synthesis of novel heterocycles.<sup>3</sup>

Being structural constituents of several natural products, agrochemicals, pharmaceuticals, and organic materials, heterocycles with diverse substitution patterns are highly sought-after chemical entities. In particular, chemicals possessing an indole core are an extremely desirable subclass of heterocycles due to a wide range of biological activities associated with them.<sup>4</sup> A survey of the literature suggests the chemistry of *S*-containing heterocycles, thiopyran and fused-thiopyrans, has not been explored to the same extent as that of their pyran analogues. Recent reports have associated substituted thiopyran and fused-thiopyran scaffolds to anti-inflammatory, antibacterial, antihyperplasia, antipsychotic, analgesic, estrogen receptor modulator, and anticancer activities.<sup>5</sup> Certain thiopyran-fused indoles and their pharmaceutically acceptable salts have been shown to possess psychoanalytic and nootropic effects.<sup>6</sup> Considering the importance of functionalized indoles, developing an efficient synthesis process to access them remains an intense area of investigation. In this communication, we report a C–H activation-based two-step synthesis of dihydrothiopyrano[2,3-*b*]indole ring system starting from indoline-2-thiones. The

newly generated indole-fused thiopyran derivatives are structural analogues of a biologically active carbazole skeleton.<sup>7</sup>

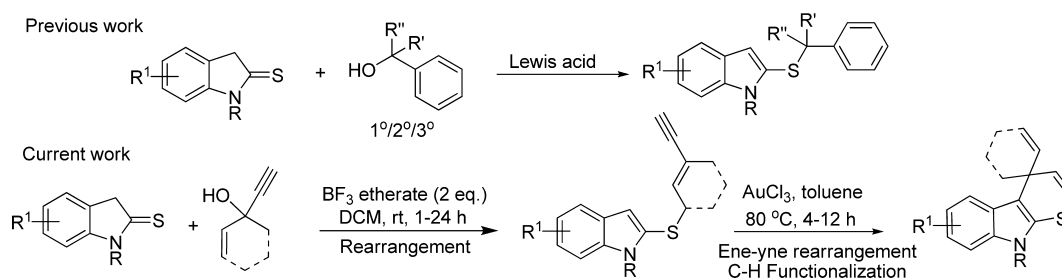
In a continuation of our efforts toward developing synthetic strategies to access diversely substituted indoles,<sup>8,9</sup> we explored the application of 2-(2-alkenylthio)indoles to the construction of indole-fused *S*-containing ring structures. We have recently reported an efficient process for chemoselective *S*-benzylation of indoline-2-thiones using benzyl alcohols in the presence of a catalytic amount of Lewis acids, leading to biologically relevant indole-based sulfides.<sup>9</sup> Mechanistically, the methodology supports the involvement of a resonance-stabilized benzylic carbocation in the *S*-benzylation process.<sup>9</sup> On the basis of these results, we envisaged that unsaturated aliphatic alcohols capable of producing resonance-stabilized carbocations may also undergo *S*-alkylation similar to the *S*-benzylation process to produce 2-(2-alkenylthio)indoles. Furthermore, an intramolecular hydroarylation carbocyclization with the 3-position of the indole core may lead to an indole-fused *S*-containing ring system. Herein, we wish to report an efficient two-step methodology for the synthesis of indole-fused dihydrothiopyrans starting from indoline-2-thiones via sequential rearrangements (Scheme 1).

To the best of our knowledge, the use of unsaturated aliphatic alcohols in the synthesis of *S*-alkenylated sulfides has not yet been reported. Hence, our initial investigation focused on the *S*-alkylation of indoline-2-thiones with the aid of unsaturated aliphatic alcohols. Inspired by our *S*-benzylation work,<sup>9</sup> we first employed rare earth metal triflates as a potential

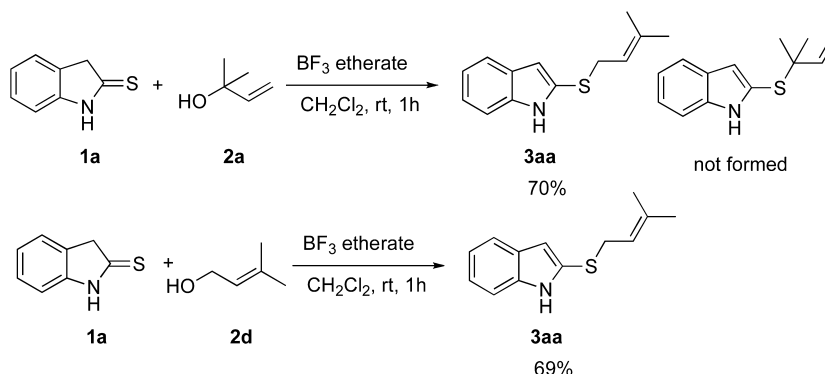
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**Scheme 1.** Synthesis of Indole-Based Sulfides Using Substituted Benzyl Alcohols (Previous Work, Ref 9) and Synthesis of Indole-Fused Dihydrothiopyrans Starting from Indoline-2-Thiones via Sequential Rearrangements (Current Work)



**Scheme 2.**  $\text{BF}_3$  Etherate-Mediated Alkylation of Indoline-2-thione (**1a**) using 2-Methylbut-3-en-2-ol (**2a**) and Prenyl Alcohol (**2d**)



catalyst for the S-alkylation of indoline-2-thione (**1a**) with 2-methylbut-3-en-2-ol (**2a**). Even after multiple attempts, the desired S-(2-alkenyl)indole could not be obtained under these conditions. Gratifyingly, the use of excess  $\text{BF}_3$  etherate in the reaction facilitated the formation of desired indole sulfide **3aa** in good yield. Interestingly, a rearrangement in the allyl side chain was observed in the isolated product (Scheme 2). It appears that the thermodynamically more stable, highly substituted alkene is the favored product under these conditions.

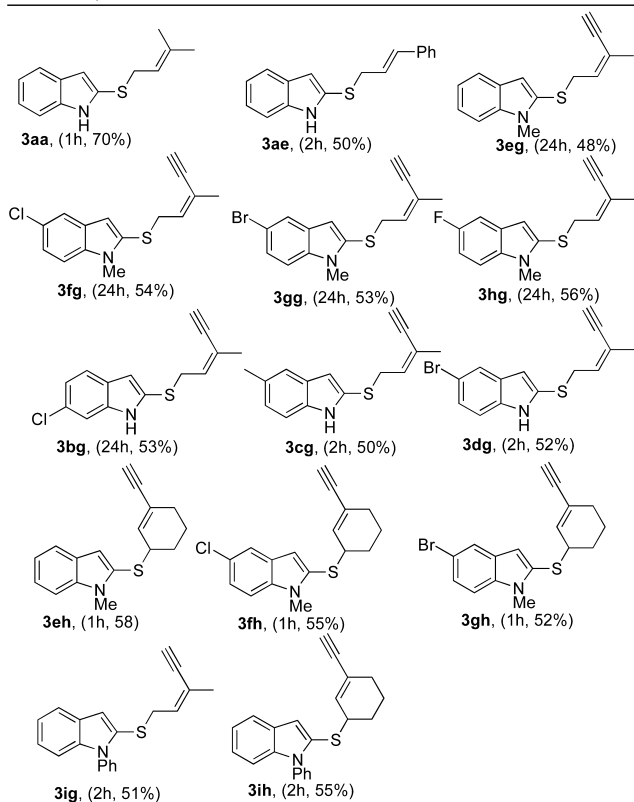
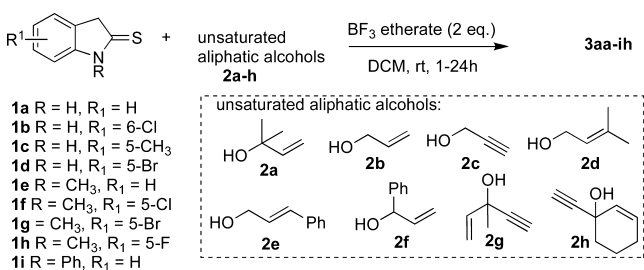
Encouraged by these results, we then proceeded to screen a range of substituted/unsubstituted allylic or propargylic alcohols with varying degrees of substitution ( $1^\circ/2^\circ/3^\circ$  alcohols) for the S-alkylation reaction. As presented in Table 1, only a select group of unsaturated alcohols, primarily substituted allyl alcohols, yielded S-(2-alkenylated) products (**3**). No reaction was observed in the cases of unsubstituted allyl/propargyl alcohols. Interestingly, the regioisomer of **2a**, prenyl alcohol (**2d**), when reacted with thione **1a**, also resulted in 2-(3-methylbut-2-enylthio)-indole (**3aa**) in 69% yield (Scheme 2). These results were further corroborated using isomeric alcohols **2e** and **2f**, both of which resulted in sulfide **3ae** in ~50% yield. Furthermore, irrespective of the degree of substitution of the reactant alcohol, we observed a consistent trend of rearrangement in the reactions of all of the substituted allyl alcohols, including 3-methylpent-1-en-4-yn-3-ol (**2g**) and 1-ethynylcyclohex-2-enol (**2h**)<sup>10</sup> under these conditions, in the synthesis of sulfides **3aa–ih** (Table 1). The sulfides obtained from alcohols **2g** and **2h** are of particular importance because they possess a conjugated ene-yne unsaturated system, which can be synthetically manipulated for further chemical transformations.

After acquiring all of the desired 2-(2-alkenylthio)indoles (**3aa–ih**), we attempted the metal-catalyzed hydroarylation

reaction to produce the indole-fused S-containing cyclized products. Initially, 2-(3-methylpent-2-en-4-ynylthio)-N-methylindole **3eg** was chosen as a model reactant to study the intramolecular cyclization reaction with the prospect of producing annulated products **I** and/or **II** as depicted in Scheme 3.

As shown in Table 2, the desired C–H activated carbocyclization step was screened using a range of potential metal catalysts in toluene at 80 °C. Initially, only reactions attempted with  $\text{AuCl}$ ,  $\text{AuCl}_3$ , and  $\text{ZnCl}_2$  resulted in product formation (Table 2, entries 1, 5, and 7).  $^1\text{H}$  and  $^{13}\text{C}$  NMR analysis of the product (liquid) revealed that the possible structure of the product may be dihydrothiopyrano[2,3-*b*]-N-methylindole. The exact positions of the substituents were established using 1D NOESY experiments. The two possible regioisomers of **4a** are shown in Figure 1 (A and B). The perturbations of the phenyl proton at position 5 (red dot) showed a strong NOE to the methyl and vinyl groups at position 4 (blue dot). This evidence supported regioisomer A. In addition, negative evidence was obtained by the perturbation of N- $\text{CH}_3$  protons (black dot), which showed only an NOE response to the phenyl proton at position 8 of the skeleton. Thus, on the basis of 1D NOESY experiments, the structure of **4a** was unambiguously assigned as 4,9-dimethyl-4-vinyl-4,9-dihydrothiopyrano[2,3-*b*]indole (regioisomer A).

Once the isolated product was fully characterized, the effect of a cocatalyst on the product yield was studied. On the basis of literature reports,<sup>11</sup> a combination of  $\text{AuCl}(\text{PPh}_3)$  and  $\text{AgOTf}$  was employed as a catalyst for our desired cyclization. However, this isolated yield of **4a** was found to be lower than that of  $\text{AuCl}_3$  alone (Table 2, entry 16). These results led us to select  $\text{AuCl}_3$  as the catalyst of choice for the cyclization step and set out to optimize other reaction parameters, such as temperature, solvent, and catalyst concentration. A loss in yield of **4a** was

**Table 1.** BF<sub>3</sub> Etherate-Mediated Alkylation of Indoline-2-thiones Using Unsaturated Aliphatic Alcohols<sup>a</sup>

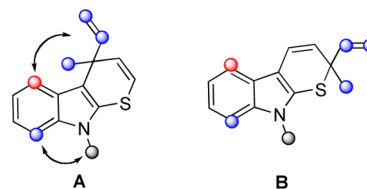
<sup>a</sup>Reaction conditions: **1** (1.0 mmol), **2** (1.0 mmol), BF<sub>3</sub> etherate (2.0 mmol), dichloromethane (40 mL), rt; yields are based on the amounts of starting materials utilized in the reaction and are unoptimized.

observed when the reaction temperature was increased to 110 °C (Table 2, entry 8). Changing the solvent of the reaction did not appear to have a significant impact on the product yields. In general, reactions performed in toluene provided superior results among the tested solvents (Table 2, entries 9–12). Catalyst loading had a profound impact on the reaction outcome. The use of 2 mol % of AuCl<sub>3</sub> resulted in 50% yield of cyclized product **4a**, whereas the use of 10 mol % of AuCl<sub>3</sub> provided 76% of **4a** (Table 2, entries 5, 13, and 14). Overall, after a thorough screening, we determined that 10 mol % of

**Table 2.** Optimization of Metal-Catalyzed Hydroarylation Reaction<sup>a</sup>

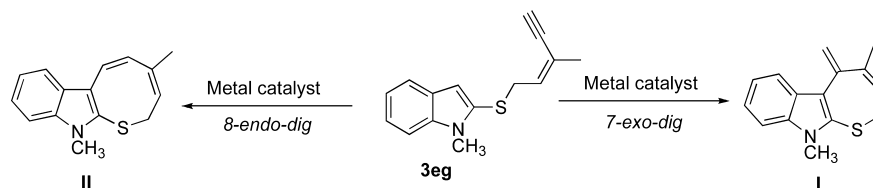
| entry | catalyst (mol %)                        | solvent      | temperature (°C) | yield (%) |
|-------|---|--------------|------------------|-----------|
| 1     | AuCl <sub>3</sub> (5)                   | toluene      | 80               | 55        |
| 2     | CuCl (5)                                | toluene      | 80               | <i>b</i>  |
| 3     | FeCl <sub>3</sub> (5)                   | toluene      | 80               | <i>b</i>  |
| 4     | PdCl <sub>2</sub> (5)                   | toluene      | 80               | <i>b</i>  |
| 5     | AuCl <sub>3</sub> (5)                   | toluene      | 80               | 62        |
| 6     | NiCl <sub>2</sub> (5)                   | toluene      | 80               | <i>b</i>  |
| 7     | ZnCl <sub>2</sub> (5)                   | toluene      | 80               | 46        |
| 8     | AuCl <sub>3</sub> (5)                   | toluene      | 110              | 45        |
| 9     | AuCl <sub>3</sub> (5)                   | acetonitrile | 80               | 50        |
| 10    | AuCl <sub>3</sub> (5)                   | DMF          | 80               | 55        |
| 11    | AuCl <sub>3</sub> (5)                   | DMSO         | 80               | 40        |
| 12    | AuCl <sub>3</sub> (5)                   | 1,4-dioxane  | 80               | 26        |
| 13    | AuCl <sub>3</sub> (2)                   | toluene      | 80               | 50        |
| 14    | ZnCl <sub>2</sub>                       | toluene      | 80               | 32        |
| 15    | AuCl <sub>3</sub> ·PPh <sub>3</sub> (5) | toluene      | 80               | 48%       |
| 16    | AuCl(PPh <sub>3</sub> )/AgOTf (5/5)     | toluene      | 80               | 54%       |
| 17    | AuCl <sub>3</sub> (10)                  | toluene      | 80               | 76        |

<sup>a</sup>Reaction conditions: **3eg** (40 mg, 0.16 mmol), catalyst (2–10 mol %), solvent (2 mL), 80 °C, 12 h. <sup>b</sup>No reaction.

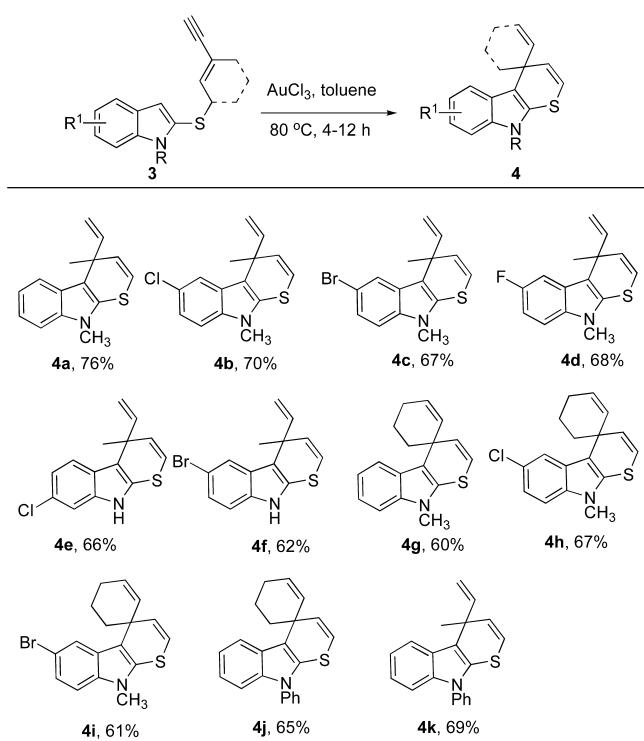
**Figure 1.** Possible regioisomers of compound **4a**.

AuCl<sub>3</sub> in toluene at 80 °C is the optimal condition for the synthesis of **4a** from **3eg**.

Next, the optimized conditions were used to study the scope of the C–H activation-mediated carbocyclization reaction. As shown in Table 3, differently substituted 2-(2-alkenylthio)indoles (**3**) were subjected to these conditions to obtain diverse indole-fused dihydrothiopyrans (**4**). Among the various substrates studied, no specific substitution effects were observed in the reaction outcome, and all dihydrothiopyran derivatives were prepared in good yields (54–76%). Owing to the nucleophilic nature of position 1 of the indole core in the case of unsubstituted 2-(2-alkenylthio)indoles (e.g., **3bg**), a competition between position 1 and 3 was anticipated in the

**Scheme 3.** Chemical Structures of the Expected Annulation Products from Sulfide **3eg**

**Table 3. Synthesis of Dihydrothiopyrano[2,3-*b*]indoles from 2-(2-Alkenylthio)indoles<sup>a</sup>**

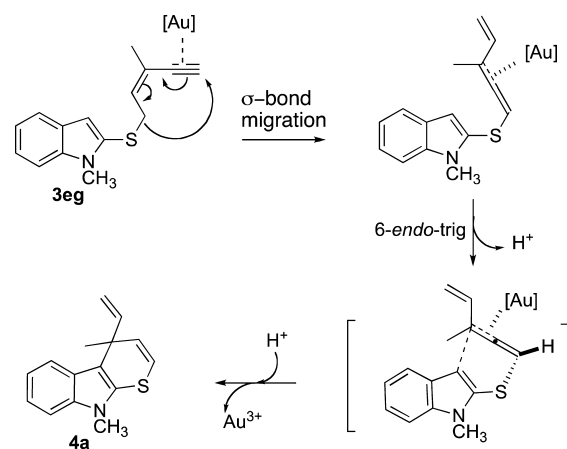


<sup>a</sup>Reaction conditions: **3** (0.16 mmol), AuCl<sub>3</sub> (10 mol %), toluene (2 mL), 80 °C.

cyclization process. In the past, gold-catalyzed reactions of indoles have been preferred using *N*-alkylated substrates to circumvent such issues.<sup>12</sup> Remarkably, no interference of indole nitrogen was observed in the current investigation. The synthesis of *N*-unsubstituted analogues of indole-fused dihydrothiopyrans (**4e–f**) was achieved directly without requiring additional protection and deprotection steps, reflecting the regioselective nature of the reaction. Furthermore, under the optimized reaction conditions, cyclization was only feasible from substrates possessing a conjugated ene-yne side chain. Prenyl-substituted sulfide (2-(3-methylbut-2-enylthio)indole, **3aa**) was found to be unreactive in these conditions. Overall, the new synthesis of functionalized tricyclic indole derivatives appears to be quite general in nature. Further chemical manipulations at positions 1, 5, and 6 can be conveniently performed using the strategically placed vital functional groups (nitrogen, methyl, bromine, and chlorine) at these sites in compound **3**. These transformations could easily lead to analogues of biologically active carbazole alkaloids.<sup>7</sup> In addition, the vinyl group of product **4** could also be exploited for the creation of new C–C bonds.<sup>13</sup>

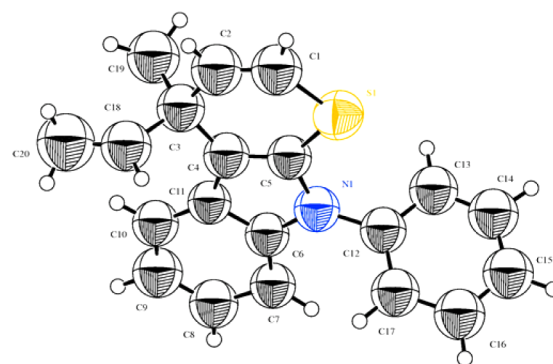
The actual mechanism for the formation of product **4** might be complicated. A simplified mechanism for the observed 6-*endo*-trig carbocyclization is outlined in Scheme 4. Typically, gold-catalyzed intramolecular hydroarylation of alkynes begins with nucleophilic attack at the alkyne/allenic carbon activated with cationic gold.<sup>11</sup> The apparent formation of an *S*-containing six-membered ring in **4a–k** suggested that, prior to the hydroarylation step, rearrangement of the conjugated ene-yne manifold present on sulfur takes place, as depicted in Scheme 4. In addition to 1D NOESY correlations, the creation of a spiro ring in products **4g–j** provide further evidence in favor of the

**Scheme 4. Proposed Mechanism for AuCl<sub>3</sub>-Mediated Formation of Dihydrothiopyrano[2,3-*b*]indoles**



proposed rearrangement. We are currently investigating in detail the different aspects of the rearrangement of a conjugated ene-yne side chain under these conditions.

The structures of the indole-fused thiopyran products (**4a–k**) were confirmed using X-ray crystallographic data of compound **4k**, as shown in Figure 2.<sup>14</sup>



**Figure 2.** ORTEP representation of **4k** (ellipsoids drawn at 40%).

In conclusion, we have developed an efficient methodology for the formation of a dihydrothiopyrano[2,3-*b*]indole skeleton starting from indoline-2-thione in two steps. First, a regioselective BF<sub>3</sub> etherate-catalyzed alkylation of thione using unsaturated alcohols results in 2-(2-alkenylthio)indole. Subsequently, a Au(III)-mediated reaction of 2-(2-alkenylthio)indole allowed access to an indole-fused dihydrothiopyran framework via sequential rearrangement of the ene-yne side chain and intramolecular hydroarylation at the C<sub>3</sub> position of the indole core.

## EXPERIMENTAL SECTION

**General.** All reagents and solvents were used as supplied by commercial sources without further purification. Melting points were measured using a MEL-TEMP II apparatus and are uncorrected. Precoated fluorescent silica gel TLC plates were used to monitor the progress of the reactions. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained by a 300 MHz FT-NMR spectrometer. Chemical shifts of the <sup>1</sup>H NMR spectra are reported in parts per million (ppm) downfield from tetramethylsilane. IR spectra were recorded on an FT-IR spectrometer, and the values are expressed in cm<sup>-1</sup>. HR-ESIMS spectra were obtained using a micrOTOF mass analyzer and ESI positive ionization source.

**General Procedure for the Synthesis of Compounds 3aa–ih.**

BF<sub>3</sub> etherate (2.01 mmol) was added dropwise to solution of appropriate indolin-2-thione (1.0 mmol) and alcohol (1.0 mmol) in dichloromethane (40 mL). The reaction mixture was stirred at room temperature (see Table 1 for reaction times). Excess dichloromethane was evaporated using rotavap after the reaction was complete. The residue was subjected to column chromatography (2% ethyl acetate in hexanes) to obtain compounds 3aa–ih.

**2-(3-Methylbut-2-enylthio)-1H-indole (3aa).** Light yellow liquid (70%, 153 mg); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.09 (s, 1H), 7.57 (d, J = 7.7 Hz, 1H), 7.33 (d, J = 7.8 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.11 (t, J = 7.3 Hz, 1H), 6.65 (s, 1H), 5.36 (t, J = 7.4 Hz, 1H), 3.48 (d, J = 7.9 Hz, 2H), 1.74 (s, 3H), 1.47 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 137.1, 136.8, 128.9, 128.6, 122.5, 120.2, 120.0, 119.9, 110.5, 109.0, 35.1, 25.7, 17.5; FT-IR ν<sub>max</sub> (neat) 3396, 2965, 2912, 1439, 1337, 1226, 741 cm<sup>-1</sup>; HRMS (m/z) calcd for C<sub>13</sub>H<sub>15</sub>NS 218.0998 [M + H]<sup>+</sup>, found 218.0997.

**2-(Cinnamylthio)-1H-indole (3ae).** Colorless oil (50%, 134 mg); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.10 (s, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.37–7.11 (m, 8H), 6.74 (s, 1H), 6.35 (s, 2H), 3.64 (s, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 137.1, 136.7, 133.1, 128.7, 128.6, 128.2, 127.8, 126.4, 125.6, 122.7, 120.4, 120.1, 110.7, 109.7, 39.9; FT-IR ν<sub>max</sub> (neat) 3393, 1487, 1435, 1337, 1228, 962, 736, 696 cm<sup>-1</sup>; HRMS (m/z) calcd for C<sub>17</sub>H<sub>16</sub>NS 266.0998 [M + H]<sup>+</sup>, found 266.0985.

**(Z)-1-Methyl-2-(3-methylpent-2-en-4-ynylthio)-1H-indole (3eg).** Pale yellow liquid (48%, 116 mg); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.58 (d, J = 7.4 Hz, 1H), 7.23 (d, J = 7.9 Hz, 1H), 7.13 (d, J = 6.4 Hz, 2H), 6.70 (s, 1H), 5.81 (t, J = 7.6 Hz, 1H), 3.83 (s, 3H), 3.61 (d, J = 7.7 Hz, 2H), 3.00 (s, 1H), 1.84 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 138.4, 133.1, 130.2, 127.4, 122.23, 120.7, 120.3, 119.6, 109.51, 109.4, 81.8, 81.6, 36.4, 29.9, 22.8; FT-IR ν<sub>max</sub> (neat) 3276, 3049, 2921, 1706, 1610, 1457, 1323, 735 cm<sup>-1</sup>; HRMS (m/z) calcd for C<sub>15</sub>H<sub>15</sub>NS 242.0998 [M + H]<sup>+</sup>, found 242.0986.

**(Z)-5-Chloro-1-methyl-2-(3-methylpent-2-en-4-ynylthio)-1H-indole (3fg).** Colorless liquid (54%, 150 mg); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.53 (s, 1H), 7.18 (s, 2H), 6.61 (s, 1H), 5.79 (t, J = 7.5 Hz, 1H), 3.79 (s, 3H), 3.61 (d, J = 7.7 Hz, 2H), 2.97 (s, 1H), 1.83 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 136.7, 132.8, 132.0, 128.3, 125.3, 122.4, 121.0, 119.5, 110.4, 108.6, 81.8, 81.5, 36.1, 30.1, 22.8; FT-IR ν<sub>max</sub> (neat) 3286, 2920, 1452, 1320, 788 cm<sup>-1</sup>; HRMS (m/z) calcd for C<sub>15</sub>H<sub>14</sub>ClNS 276.0608 [M + H]<sup>+</sup>, found 276.0619.

**(Z)-5-Bromo-1-methyl-2-(3-methylpent-2-en-4-ynylthio)-1H-indole (3gg).** Liquid (53%, 171 mg); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.69 (s, 1H), 7.30 (d, J = 8.5 Hz, 1H), 7.14 (d, J = 8.5 Hz, 1H), 6.61 (s, 1H), 5.79 (t, J = 7.5 Hz, 1H), 3.78 (s, 3H), 3.62 (d, J = 7.7 Hz, 2H), 2.98 (s, 1H), 1.83 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 136.9, 132.8, 131.9, 128.9, 124.9, 122.6, 121.0, 112.9, 110.9, 108.5, 81.8, 81.5, 36.1, 30.0, 22.8; FT-IR ν<sub>max</sub> (neat) 3283, 2919, 1714, 1606, 1455, 1318, 786 cm<sup>-1</sup>; HRMS (m/z) calcd for C<sub>15</sub>H<sub>14</sub>BrNS 320.0103 [M + H]<sup>+</sup>, found 320.0101.

**(Z)-5-Fluoro-1-methyl-2-(3-methylpent-2-en-4-ynylthio)-1H-indole (3hg).** Yellow liquid (56%, 146 mg); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.22 (d, J = 9.1 Hz, 2H), 6.99 (t, J = 8.8 Hz, 1H), 6.64 (s, 1H), 5.80 (t, J = 7.6 Hz, 1H), 3.81 (s, 3H), 3.62 (d, J = 7.6 Hz, 2H), 2.99 (s, 1H), 1.84 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 157.9 (d, J<sub>C-F</sub> = 234.5 Hz), 135.0, 132.9, 132.1, 127.5 (d, J<sub>C-F</sub> = 10.2 Hz), 120.9, 110.6 (d, J<sub>C-F</sub> = 26.4 Hz), 110.06 (d, J<sub>C-F</sub> = 9.6 Hz), 108.9 (d, J<sub>C-F</sub> = 4.8 Hz), 104.9 (d, J<sub>C-F</sub> = 23.3 Hz), 81.8, 81.5, 36.2, 30.1, 22.8; FT-IR ν<sub>max</sub> (neat) 3290, 2922, 1620, 1456, 1328, 844, 786 cm<sup>-1</sup>; HRMS (m/z) calcd for C<sub>15</sub>H<sub>14</sub>FNS 260.0904 [M + H]<sup>+</sup>, found 260.0892.

**(Z)-6-Chloro-2-(3-methylpent-2-en-4-ynylthio)-1H-indole (3bg).** Colorless liquid (53%, 140 mg); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.11 (s, 1H), 7.45 (d, J = 8.3 Hz, 1H), 7.31 (s, 1H), 7.07 (d, J = 8.0 Hz, 1H), 6.60 (s, 1H), 5.83 (t, J = 7.7 Hz, 1H), 3.69 (d, J = 7.7 Hz, 2H), 3.07 (s, 1H), 1.85 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 137.4, 133.6, 128.8, 128.4, 127.2, 121.0, 120.8, 120.7, 110.4, 109.1, 82.2, 81.6, 36.0, 22.84; FT-IR ν<sub>max</sub> (neat) 3403, 3284, 2919, 1608, 1435, 1333, 807 cm<sup>-1</sup>; HRMS (m/z) calcd for C<sub>14</sub>H<sub>12</sub>ClNS 262.0452 [M + H]<sup>+</sup>, found 262.0448.

**(Z)-5-Methyl-2-(3-methylpent-2-en-4-ynylthio)-1H-indole (3cg).**

Pale yellow liquid (50%, 122 mg); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.06 (s, 1H), 7.37 (s, 1H), 7.22 (d, J = 8.1 Hz, 1H), 7.04 (d, J = 8.0 Hz, 1H), 6.58 (s, 1H), 5.85 (t, J = 7.5 Hz, 1H), 3.69 (d, J = 7.6 Hz, 2H), 3.10 (s, 1H), 2.46 (s, 3H), 1.87 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 135.6, 133.9, 129.3, 128.9, 127.8, 124.2, 120.4, 119.8, 110.2, 108.7, 82.2, 81.8, 36.2, 22.8, 21.5; FT-IR ν<sub>max</sub> (neat) 3392, 3281, 2918, 1442, 1325, 793 cm<sup>-1</sup>; HRMS (m/z) calcd for C<sub>15</sub>H<sub>15</sub>NS 242.0998 [M + H]<sup>+</sup>, found 242.0991.

**(Z)-5-Bromo-2-(3-methylpent-2-en-4-ynylthio)-1H-indole (3dg).**

Pale yellow liquid (52%, 160 mg); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.19 (s, 1H), 7.68 (s, 1H), 7.22 (dd, J = 25.5, 8.0 Hz, 2H), 6.56 (s, 1H), 5.83 (t, J = 7.3 Hz, 1H), 3.70 (d, J = 7.7 Hz, 2H), 3.07 (s, 1H), 1.85 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 135.7, 133.5, 130.3, 129.7, 125.3, 122.6, 120.8, 113.2, 111.9, 108.1, 82.3, 81.6, 35.9, 22.8; FT-IR ν<sub>max</sub> (neat) 3193, 2964, 1435, 1021, 793 cm<sup>-1</sup>. HRMS (m/z) calcd for C<sub>14</sub>H<sub>13</sub>BrNS 305.9952 [M + H]<sup>+</sup>, found 305.9947.

**2-((3-Ethynylcyclohex-2-en-1-yl)thio)-1-methyl-1H-indole (3eh).**

Yellow liquid (58%, 145 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.64–7.60 (m, 1H), 7.34 (dd, J = 8.2, 0.8 Hz, 1H), 7.28 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 7.15 (ddd, J = 8.0, 6.9, 1.2 Hz, 1H), 6.80 (d, J = 0.8 Hz, 1H), 3.86 (s, 3H), 3.71–3.64 (m, 1H), 2.94 (s, 1H), 2.22–2.14 (m, 3H), 1.97–1.90 (m, 1H), 1.89–1.84 (m, 1H), 1.83–1.76 (m, 1H), 1.70–1.63 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.4, 134.6, 129.9, 127.3, 123.0, 122.5, 120.5, 119.8, 110.4, 109.7, 84.49, 76.8, 46.4, 29.9, 29.0, 27.6, 19.2; HRMS (m/z) calcd for C<sub>17</sub>H<sub>18</sub>NS 268.1160 [M + H]<sup>+</sup>, found 268.1154.

**(Z)-2-(3-Methylpent-2-en-4-ynylthio)-1-phenyl-1H-indole (3ig).**

Pale yellow liquid (51%, 156 mg); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.58–7.43 (m, 5H), 7.17 (s, 4H), 6.81 (s, 1H), 5.68 (t, J = 7.6 Hz, 1H), 3.48 (d, J = 7.7 Hz, 2H), 3.04 (s, 1H), 1.82 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 139.2, 137.4, 133.3, 131.6, 129.1, 128.5, 128.0, 127.7, 122.5, 120.4, 120.3, 120.0, 110.3, 109.1, 82.1, 81.7, 35.6, 22.8; FT-IR ν<sub>max</sub> (neat) 3278, 3046, 2920, 1496, 741, 695 cm<sup>-1</sup>; HRMS (m/z) calcd for C<sub>20</sub>H<sub>18</sub>NS 304.1160 [M + H]<sup>+</sup>, found 304.1154.

**2-(3-Ethynylcyclohex-2-enylthio)-1-phenyl-1H-indole (3fh).**

Pale yellow liquid (55%, 167 mg); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.60–7.41 (m, 6H), 7.17 (d, J = 6.0 Hz, 3H), 6.89 (s, 1H), 5.94 (d, J = 3.8 Hz, 1H), 3.46 (s, 1H), 2.88 (s, 1H), 1.79–1.43 (m, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 139.2, 137.3, 134.4, 130.7, 129.1, 128.6, 127.9, 127.5, 122.8, 120.5, 120.2, 111.0, 110.6, 84.4, 77.2, 45.6, 28.9, 27.4, 18.9; FT-IR ν<sub>max</sub> (neat) 3291, 3011, 2942, 1472, 772 cm<sup>-1</sup>; HRMS (m/z) calcd for C<sub>22</sub>H<sub>20</sub>NS 330.1316 [M + H]<sup>+</sup>, found 330.1311.

**5-Bromo-2-((3-ethynylcyclohex-2-en-1-yl)thio)-1-methyl-1H-indole (3gh).**

Colorless oil (55%, 189 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.73–7.71 (m, 1H), 7.34 (dd, J = 8.7, 1.9 Hz, 1H), 7.19 (d, J = 8.7 Hz, 1H), 6.70 (d, J = 0.8 Hz, 1H), 3.82 (s, 3H), 3.71–3.67 (m, 1H), 2.93 (s, 1H), 2.21–2.16 (m, 3H), 1.93–1.84 (m, 2H), 1.81–1.73 (m, 1H), 1.72–1.63 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.9, 134.3, 131.6, 128.8, 125.2, 123.3, 122.8, 113.1, 111.1, 109.3, 84.3, 76.9, 46.3, 30.1, 28.9, 27.6, 19.1; HRMS (m/z) calcd for C<sub>17</sub>H<sub>17</sub>BrNS 346.0256 [M + H]<sup>+</sup>, found 346.0260.

**5-Chloro-2-(3-ethynylcyclohex-2-enylthio)-1-methyl-1H-indole (3ih).**

Colorless liquid (55%, 182 mg); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.56 (s, 1H), 7.21 (s, 2H), 6.70 (s, 1H), 6.20 (s, 1H), 3.82 (s, 3H), 2.92 (s, 1H), 2.18 (s, 2H), 1.99–1.56 (m, 5H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 136.7, 134.3, 131.7, 128.1, 125.6, 123.3, 122.7, 119.7, 110.7, 109.5, 84.3, 77.2, 46.3, 30.2, 29.0, 27.7, 19.2; FT-IR ν<sub>max</sub> (neat) 3287, 2931, 1451, 1220, 790 cm<sup>-1</sup>; HRMS (m/z) calcd for C<sub>17</sub>H<sub>17</sub>ClNS 302.0765 [M + H]<sup>+</sup>, found 302.0755.

**General Procedure for the Synthesis of Compounds 4a–k.**

AuCl<sub>3</sub> (10 mol %, 0.016 mmol) was added to a solution of the appropriate indole sulfide (0.16 mmol) in toluene. The reaction mixture was stirred at 80 °C for 4–12 h. After the reaction was complete, excess toluene was evaporated using rotavap. The residue was subjected to column chromatography (2% ethyl acetate in hexanes) to obtain compounds 4a–k.

**4,9-Dimethyl-4-vinyl-4,9-dihydrothiopyrano[2,3-b]indole (4a).**

Light yellow liquid (76%, 30.5 mg); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.70 (d, J = 7.7 Hz, 1H), 7.33 (d, J = 7.8 Hz, 1H), 7.26 (t, J = 7.4 Hz,

1H), 7.18 (t,  $J = 7.1$  Hz, 1H), 6.38 (dd,  $J = 16.8, 10.7$  Hz, 1H), 6.19 (d,  $J = 9.9$  Hz, 1H), 5.71 (d,  $J = 9.9$  Hz, 1H), 5.28–5.18 (m, 2H), 3.71 (s, 3H), 1.82 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  144.8, 137.6, 129.8, 126.1, 124.9, 120.7, 119.5, 119.1, 112.3, 110.8, 109.3, 108.3, 41.2, 29.9, 27.7; FT-IR  $\nu_{\text{max}}$  (neat) 2962, 2923, 1613, 1462, 1405, 1326, 992, 914, 735  $\text{cm}^{-1}$ ; HRMS ( $m/z$ ) calcd for  $\text{C}_{15}\text{H}_{15}\text{NS}$  242.0998 [ $\text{M} + \text{H}$ ] $^+$ , found 242.0987.

**6-Chloro-4,9-dimethyl-4-vinyl-4,9-dihydrothiopyrano[2,3-*b*]indole (4b).** Colorless liquid (70%, 31.5 mg);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (s, 1H), 7.11 (dd,  $J = 20.8, 8.6$  Hz, 2H), 6.20 (dd,  $J = 17.0, 10.2$  Hz, 1H), 6.09 (d,  $J = 10.1$  Hz, 1H), 5.60 (d,  $J = 9.8$  Hz, 1H), 5.12 (t,  $J = 12.4$  Hz, 2H), 3.62 (s, 3H), 1.65 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  144.3, 136.0, 129.8, 127.1, 126.8, 124.8, 120.8, 118.8, 112.7, 110.5, 109.2, 108.9, 41.0, 30.1, 27.2; FT-IR  $\nu_{\text{max}}$  (neat) 2924, 1615, 1463, 1423, 1362, 1330, 995, 914, 710  $\text{cm}^{-1}$ ; HRMS ( $m/z$ ) calcd for  $\text{C}_{15}\text{H}_{14}\text{ClNS}$  276.0608 [ $\text{M} + \text{H}$ ] $^+$ , found 276.0614.

**6-Bromo-4,9-dimethyl-4-vinyl-4,9-dihydrothiopyrano[2,3-*b*]indole (4c).** Pale yellow liquid (67%, 35 mg);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (s, 1H), 7.21 (d,  $J = 8.7$  Hz, 1H), 7.10 (d,  $J = 8.3$  Hz, 1H), 6.20 (dd,  $J = 17.3, 10.5$  Hz, 1H), 6.09 (d,  $J = 10.1$  Hz, 1H), 5.60 (d,  $J = 10.1$  Hz, 1H), 5.12 (t,  $J = 13.0$  Hz, 2H), 3.62 (s, 3H), 1.65 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  144.3, 136.3, 129.8, 127.7, 126.7, 123.4, 121.8, 112.8, 112.3, 110.5, 109.6, 108.9, 41.0, 30.1, 27.2; FT-IR  $\nu_{\text{max}}$  (neat) 2961, 2922, 1613, 1461, 1422, 1363, 1329, 992, 922, 713  $\text{cm}^{-1}$ ; HRMS ( $m/z$ ) calcd for  $\text{C}_{15}\text{H}_{14}\text{BrNS}$  320.0103 [ $\text{M} + \text{H}$ ] $^+$ , found 320.0103.

**6-Fluoro-4,9-dimethyl-4-vinyl-4,9-dihydrothiopyrano[2,3-*b*]indole (4d).** Pale yellow liquid (68%, 28.6 mg);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.21 (d,  $J = 10.1$  Hz, 1H), 7.17–7.10 (m, 1H), 6.87 (t,  $J = 9.0$  Hz, 1H), 6.20 (dd,  $J = 17.0, 10.5$  Hz, 1H), 6.10 (d,  $J = 9.8$  Hz, 1H), 5.61 (d,  $J = 9.9$  Hz, 1H), 5.17–5.06 (m, 2H), 3.63 (s, 3H), 1.65 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  157.3 (d,  $J_{\text{C-F}} = 234.2$  Hz), 144.3, 134.2, 129.7, 126.9, 126.3 (d,  $J_{\text{C-F}} = 10.2$  Hz), 112.5, 110.6, 109.2, 108.8 (d,  $J_{\text{C-F}} = 3.2$  Hz), 108.6 (d,  $J_{\text{C-F}} = 13.0$  Hz), 104.6 (d,  $J_{\text{C-F}} = 24.4$  Hz); FT-IR  $\nu_{\text{max}}$  (neat) 2967, 2919, 1619, 1573, 1473, 1425, 1334, 989, 918, 712  $\text{cm}^{-1}$ ; HRMS ( $m/z$ ) calcd for  $\text{C}_{15}\text{H}_{14}\text{FNS}$  260.0904 [ $\text{M} + \text{H}$ ] $^+$ , found 260.0916.

**7-Chloro-4-methyl-4-vinyl-4,9-dihydrothiopyrano[2,3-*b*]indole (4e).** Pale yellow liquid (66%, 27.8 mg);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (s, 1H), 7.43 (d,  $J = 8.5$  Hz, 1H), 7.25 (s, 1H), 7.01 (d,  $J = 8.4$  Hz, 1H), 6.19 (dd,  $J = 17.4, 10.4$  Hz, 1H), 6.07 (d,  $J = 9.9$  Hz, 1H), 5.59 (d,  $J = 9.9$  Hz, 1H), 5.11 (t,  $J = 12.3$  Hz, 2H), 1.66 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  144.2, 136.7, 129.5, 129.4, 127.2, 124.9, 123.0, 120.2, 112.7, 110.9, 110.9, 110.2, 40.7, 27.0; FT-IR  $\nu_{\text{max}}$  (neat) 2965, 2925, 1737, 1697, 1608, 1446, 1406, 1367, 1320, 991, 918, 719  $\text{cm}^{-1}$ ; HRMS ( $m/z$ ) calcd for  $\text{C}_{14}\text{H}_{12}\text{ClNS}$  262.0452 [ $\text{M} + \text{H}$ ] $^+$ , found 262.0441.

**6-Bromo-4-methyl-4-vinyl-4,9-dihydrothiopyrano[2,3-*b*]indole (4f).** Yellow liquid (62%, 30.4 mg);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (s, 1H), 7.64 (s, 1H), 7.16 (dd,  $J = 17.1, 8.8$  Hz, 2H), 6.19 (dd,  $J = 16.9, 10.7$  Hz, 1H), 6.06 (d,  $J = 9.8$  Hz, 1H), 5.59 (d,  $J = 10.3$  Hz, 1H), 5.13 (t,  $J = 13.8$  Hz, 2H), 1.65 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  144.0, 135.0, 129.5, 128.1, 124.0, 123.8, 121.9, 113.0, 112.9, 111.56, 110.8, 110.5, 40.6, 27.0; FT-IR  $\nu_{\text{max}}$  (neat) 3193, 2964, 1435, 1042, 793  $\text{cm}^{-1}$ ; HRMS ( $m/z$ ) calcd for  $\text{C}_{14}\text{H}_{13}\text{BrNS}$  305.9952 [ $\text{M} + \text{H}$ ] $^+$ , found 305.9947.

**9'-Methyl-9'-H-spiro[cyclohex[2]ene-1,4'-thiopyrano[2,3-*b*]indole] (4g).** Pale yellow liquid (60%, 24.5 mg);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (d,  $J = 7.2$  Hz, 1H), 7.26 (d,  $J = 7.9$  Hz, 1H), 7.16 (t,  $J = 6.8$  Hz, 1H), 7.07 (d,  $J = 6.9$  Hz, 1H), 6.11 (d,  $J = 9.7$  Hz, 1H), 5.99–5.84 (m, 3H), 3.66 (s, 1H), 2.37–2.16 (m, 3H), 2.06–1.69 (m, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  137.7, 134.1, 129.7, 126.3, 125.9, 125.3, 120.6, 119.3, 118.9, 110.8, 110.3, 108.2, 38.7, 36.8, 29.9, 24.7, 18.6; FT-IR  $\nu_{\text{max}}$  (neat) 3005, 2926, 1606, 1463, 1424, 1325, 727  $\text{cm}^{-1}$ ; HRMS ( $m/z$ ) calcd for  $\text{C}_{17}\text{H}_{17}\text{NS}$  268.1154 [ $\text{M} + \text{H}$ ] $^+$ , found 268.1161.

**6'-Chloro-9'-methyl-9'-H-spiro[cyclohex[2]ene-1,4'-thiopyrano[2,3-*b*]indole] (4h).** Colorless liquid (67%, 32.4 mg);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (s, 1H), 7.18–7.01 (m, 2H), 6.08 (d,  $J = 8.6$  Hz, 1H), 5.97–5.78 (m, 3H), 3.61 (s, 3H), 2.32–2.07 (m, 3H), 2.02–1.67

(m, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  136.1, 133.6, 129.8, 127.2, 126.5, 124.7, 120.7, 118.6, 110.6, 110.1, 109.1, 38.5, 36.7, 30.1, 24.6, 18.5; FT-IR  $\nu_{\text{max}}$  (neat) 3018, 2930, 2850, 1609, 1462, 1421, 1329, 730  $\text{cm}^{-1}$ ; HRMS ( $m/z$ ) calcd for  $\text{C}_{17}\text{H}_{16}\text{ClNS}$  302.0765 [ $\text{M} + \text{H}$ ] $^+$ , found 302.0766.

**6'-Bromo-9'-methyl-9'-H-spiro[cyclohex[2]ene-1,4'-thiopyrano[2,3-*b*]indole] (4i).** Pale yellow liquid (61%, 34.2 mg);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 (s, 1H), 7.20 (d,  $J = 8.6$  Hz, 1H), 7.09 (d,  $J = 8.6$  Hz, 1H), 6.09 (d,  $J = 9.9$  Hz, 1H), 5.87 (dd,  $J = 26.0, 10.4$  Hz, 3H), 3.62 (s, 3H), 2.29–2.06 (m, 3H), 2.01–1.67 (m, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  136.4, 133.59, 129.9, 127.89, 127.1, 126.5, 123.3, 121.7, 112.4, 110.63, 110.0, 109.5, 38.5, 36.8, 30.1, 24.6, 18.5; FT-IR  $\nu_{\text{max}}$  (neat) 3022, 2929, 1462, 1237, 786  $\text{cm}^{-1}$ ; HRMS ( $m/z$ ) calcd for  $\text{C}_{17}\text{H}_{17}\text{BrNS}$  346.0265 [ $\text{M} + \text{H}$ ] $^+$ , found 346.0260.

**9'-Phenyl-9'-H-spiro[cyclohex[2]ene-1,4'-thiopyrano[2,3-*b*]indole] (4j).** Pale yellow liquid (65%, 34.5 mg);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74–7.65 (m, 1H), 7.60–7.51 (m, 2H), 7.47 (d,  $J = 7.2$  Hz, 3H), 7.25–7.16 (m, 1H), 7.09 (dd,  $J = 6.0, 3.2$  Hz, 2H), 6.05 (d,  $J = 9.9$  Hz, 1H), 5.97–5.87 (m, 3H), 2.44–2.18 (m, 3H), 2.10–1.76 (m, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  138.1, 136.7, 134.0, 129.5, 129.1, 128.0, 127.3, 126.7, 126.1, 125.5, 121.2, 119.7, 119.4, 111.9, 111.5, 109.4, 38.7, 36.6, 24.7, 18.6; FT-IR  $\nu_{\text{max}}$  (neat) 3044, 2926, 1497, 1447, 736, 695  $\text{cm}^{-1}$ ; HRMS ( $m/z$ ) calcd for  $\text{C}_{22}\text{H}_{20}\text{NS}$  330.1316 [ $\text{M} + \text{H}$ ] $^+$ , found 330.1311.

**4-Methyl-9-phenyl-4-vinyl-4,9-dihydrothiopyrano[2,3-*b*]indole (4k).** Pale yellow liquid (69%, 34.5 mg);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (dd,  $J = 6.0, 3.2$  Hz, 1H), 7.54 (d,  $J = 6.8$  Hz, 2H), 7.50–7.44 (m, 3H), 7.19 (dt,  $J = 7.3, 3.7$  Hz, 1H), 7.13–7.06 (m, 2H), 6.34 (dd,  $J = 17.3, 10.4$  Hz, 1H), 6.07 (d,  $J = 10.0$  Hz, 1H), 5.61 (d,  $J = 10.0$  Hz, 1H), 5.19 (dd,  $J = 13.9, 6.3$  Hz, 2H), 1.77 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  144.7, 138.1, 136.7, 129.5, 129.2, 128.1, 127.4, 126.5, 125.2, 121.3, 119.8, 119.6, 112.4, 111.5, 110.8, 109.5, 41.2, 27.1; FT-IR  $\nu_{\text{max}}$  (neat) 3045, 2962, 2922, 1594, 1497, 1447, 737, 696  $\text{cm}^{-1}$ ; HRMS ( $m/z$ ) calcd for  $\text{C}_{20}\text{H}_{18}\text{NS}$  304.1160 [ $\text{M} + \text{H}$ ] $^+$ , found 304.1154.

## ■ ASSOCIATED CONTENT

### Supporting Information

Copies of  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra for products **3aa–3ih** and **4a–k**, X-ray crystallographic data, and crystal structure of compound **4k**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jo5025943.

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### Notes

The authors declare no competing financial interest.

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