JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

Palladium-Catalyzed Oxidative Sulfenylation of Indoles and Related Electron-Rich Heteroarenes with Aryl Boronic Acids and Elemental Sulfur

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Supporting Information

ABSTRACT: An efficient and convenient palladium-catalyzed C−H bond oxidative sulfenylation of indoles and related electron-rich heteroarenes with aryl boronic acids and elemental sulfur has been described. This procedure provides a useful and direct approach for the assembly of a wide range of structurally diverse 3-sulfenylheteroarenes with moderate to excellent yields from simple and readily available starting materials. Moreover, this synthetic protocol is suitable for *N*-protected and unprotected indoles. Notably, the construction of two C−S bonds in one step was also achieved in this transformation.

INTRODUCTION

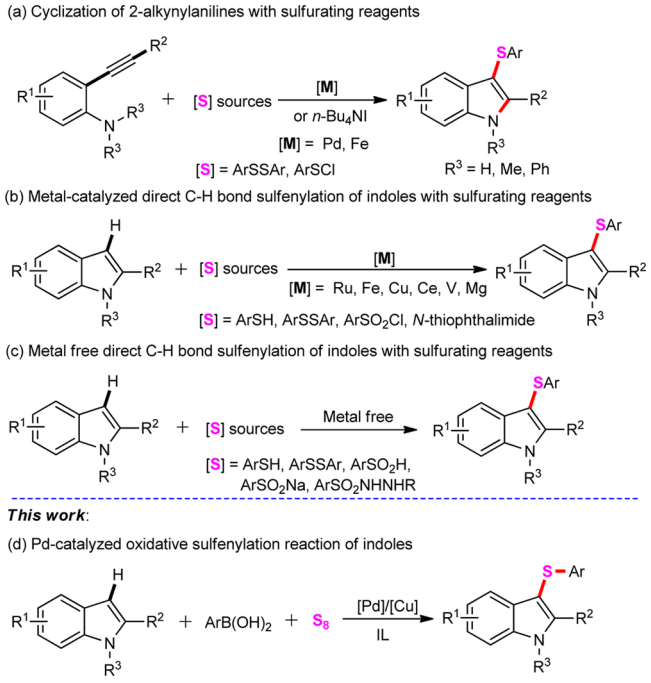
The development of practical and efficient synthetic methods for the synthesis of complex molecular skeletons from readily accessible starting materials has aroused substantial attention in recent years.[1] In this regard, the transition metal-catalyzed cross-coupling reaction has emerged as an attractive and powerful tool for the construction of carbon−carbon and/or carbon−heteroatom bonds in an atom- and step-economical manner over the past few decades.[2] Most notably, palladium-catalyzed processes play a significant role in this field because they usually proceed under mild reaction conditions, great functional group tolerance, and high chemo-, regio-, and stereoselectivity.[3] Consequently, considerable efforts have been made to develop efficient methods for the construction of C−C, C−O, C−N, and other C−heteroatom bonds in recent years. Despite the overall efficiency and versatility of this transformation, the development of practical and environmentally friendly synthetic methods for the straightforward construction of C−S bonds is less explored[4] and still highly desirable.

In addition, substituted indoles are versatile and important heterocyclic scaffolds in organic synthesis and are found in many natural products and pharmaceuticals.[5] As a subclass, 3-sulfenylindoles exhibit a broad spectrum of biological activities, which are important drugs assessed for the treatment of bacterial infection, cancer, HIV, obesity, heart diseases, and allergies.[6] Consequently, many representative synthetic methods have been developed for constructing this heterocyclic scaffold. Generically, two strategies are typically employed. Undoubtedly, 2-alkynylanilines are the most commonly used precursors to prepare this functionalized core backbone (Scheme 1a). For instance, Larock and co-workers reported a novel procedure for the synthesis of 3-sulfenylindoles via *n*-Bu_4NI-induced electrophilic cyclization of *N*,*N*-dialkyl-2-(1-alkynyl)anilines with arylsulfenyl chlorides.[7] Subsequently, Li and Zhang reported that 3-sulfenylindoles were synthesized by metal-involved annulations of 2-(1-alkynyl)benzenamines with disulfides.[8] On the other hand, direct C−H bond sulfenylation of the preexisting indole ring is a more convenient method for the formation of 3-sulfenylindoles. Among them, metal complexes of vanadium,[9] magnesium,[10] iron,[11] cerium,[12] copper,[13] and ruthenium[14] have been identified as extremely efficient catalysts for constructing these heterocyclic scaffolds. Various sulfenylating agents such as thiols, disulfides, arylsulfonyl chlorides, and *N*-thioimides are employed (Scheme 1b). Despite the significance, many of these approaches require foul-smelling, toxic, and unstable sulfenylating agents as starting materials. Considering the synthetic simplicity as well as environmentally benign process, providing a direct strategy for the synthesis of 3-sulfenylindoles via a transition metal-free protocol is still an urgent need. In recent years, several approaches for direct sulfenylation of indoles with activated sulfur reagents under transition metal-free conditions have been developed (Scheme 1c).[15] For instance, Tian and co-workers reported a nice protocol of iodine-catalyzed regioselective

Received: June 14, 2016
Published: August 8, 2016

DOI: 10.1021/acs.joc.6b01428
J. Org. Chem. 2016, 81, 7771−7783

Scheme 1. Representative Methods for the Synthesis of 3-Sulfenylindoles



sulfenylation of indoles with sulfonyl hydrazides.[15e] Subsequently, Deng and co-workers developed the iodine-catalyzed sulfenylation of free indoles with sodium sulfinates.[15g] Then, Braga and co-workers described a solvent and metal-free procedure for the synthesis of 3-sulfenylindoles from indoles using DMSO as an oxidant.[15l] However, thiols, disulfides, sulfonyl hydrazides, arylsulfonyl chlorides, and sodium sulfinates are still employed as sulfenylating agents. Therefore, the development of convenient and efficient synthetic methodologies for the construction of this heterocyclic motif under environmentally friendly reaction conditions is still highly desirable. Inspired by the aforementioned background and our longstanding interest in Pd-catalyzed coupling reactions in ionic liquids,[16] we disclose herein an efficient and concise route for the synthesis of 3-sulfenylindoles via palladium-catalyzed oxidative sulfenylation of indoles with aryl boronic acids and elemental sulfur (Scheme 1d).

RESULTS AND DISCUSSION

The reaction of indole (**1a**), phenylboronic acid (**2a**), and elemental sulfur (S_8) was employed as a model reaction to screen for the optimal reaction conditions, and the results are summarized in Table 1. Initially, several oxidants such as BQ, DDQ, $AgNO_3$, and Ag_2CO_3 were tested for the reaction (Table 1, entries 1−4), we found that Ag_2CO_3 was the best oxidant for this transformation. Subsequently, palladium catalysts were also examined. Other Pd catalysts, including $PdCl_2$, $Pd(PhCN)_2Cl_2$, and $Pd(TFA)_2$, were tested, and they were less effective than $Pd(OAc)_2$ (Table 1, entries 4−7). Furthermore, different copper salts were examined, including CuCl, CuBr, CuCN, and CuI, and CuI was the most effective catalyst for this transformation (Table 1, entries 7−10). As revealed in Table 1, bases such as K_2CO_3, K_3PO_4, KF, and Cs_2CO_3 were investigated (Table 1, entries 10−13). It was found that Cs_2CO_3 was the best base for the present sulfenylation reaction. Finally, different solvents were then screened to study the efficiency of this reaction (Table 1, entries 13−17). Notably, [Bmim]Cl was identified as the optimal solvent for the formation of **3aa** (Table 1, entry 17). Without $Pd(OAc)_2$ or CuI catalyst, the reaction could not occur at all (Table 1, entries 20 and 21). When the reaction was carried out under oxygen atmosphere, no product **3aa** was obtained (entry 22). Several kinds of borates and boronates were further investigated (Table 1, entries 23−26); however, only trace desired **3aa** was detected by GC-MS when phenylboronic acid pinacol ester (**2d**) was used (Table 1, entry 26).

With the optimized reaction conditions in hand, the scope and generality of the sulfenylation reaction was investigated using several structurally diverse indoles, phenylboronic acid (**2a**), and elemental sulfur (S_8). Representative results are summarized in Table 2. Generally, both electron-donating (Me, OMe, OBn) and electron-withdrawing (F, Cl, Br, CO_2Me, NO_2) substituents on the indole ring were transferred to the desired products in good to excellent yields (**3aa**−**3aw**). Pleasingly, 5,6-disubstituted (**1o**−**1s**) and 4,6-disubstituted (**1t**) indoles could also undergo this transformation to furnish the corresponding 3-phenylthioindoles in good yields (**3ao**−**3at**). Gratifyingly, this transformation was compatible with the Cl- and Br-substituted indole ring, which might allow for further synthetic transformations by transition metal-catalyzed coupling reactions. Additionally, C-2-substituted indoles proceeded smoothly to afford the corresponding 3-phenylthioindoles (**3au**−**3bb**) in moderate to good yields. Remarkably, 2-methyl-6,7-dihydro-1*H*-indol-4(5*H*)-one could be converted to the corresponding product **3bc** in 46% yield as well.

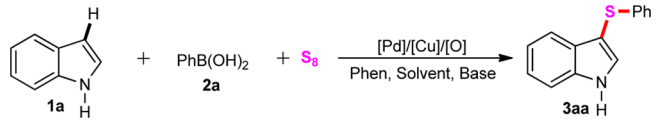
The sulfenylation reactions of several *N*-substituted indoles were then explored, which showed high tolerance to this reaction. Representative results are summarized in Table 3. To our delight, *N*-substituted indoles with methyl and phenyl groups could convert to the corresponding products **5a**−**5d** in moderate to good yields. Unfortunately, under the optimized conditions, *N*-acetylindole (**4e**) and *N*-Boc-indole (**4f**) failed to afford the desired products. The main reason is that acetyl and Boc groups are readily detached from indoles under basic conditions. Furthermore, various *N*-benzylindoles reacted well with phenylboronic acid (**2a**) and S_8 under the standard conditions to afford the target products **5h**−**5r** in moderate to good yields.

For the generality and scope of this reaction to be explored further, a wide array of aryl boronic acids were examined, and the results are summarized in Table 4. In general, under the optimized conditions, aryl boronic acids with either an electron-donating or -withdrawing group on the benzene ring were able to generate the corresponding 3-sulfenylindoles **6a**−**6m** in moderate to good yields. Gratifyingly, various functional groups, such as alkyl, fluoro, chloro, bromo, and cyano groups, were compatible with the reaction conditions. Remarkably, the electronic properties of the substituents on the benzene ring of aryl boronic acids did not have a significant influence on the reaction efficiency. Moreover, the heteroaryl boronic acids, such as thiophen-3-ylboronic acid (**2n**) and pyridin-4-ylboronic acid (**2o**), could be converted to the corresponding products **6n** and **6o** in 64 and 53% yields, respectively.

Furthermore, the present synthetic route to 3-arylthioindoles was successfully applied to the synthesis of 3,3′-bis-(phenylthio)biindole. For instance, under the optimized conditions, the bissulfenylation of 1*H*,1′*H*-2,2′-biindole (**7**) provided desired product **8** in 41% yield (Scheme 2).

DOI: 10.1021/acs.joc.6b01428
J. Org. Chem. 2016, 81, 7771−7783

Table 1. Optimization of the Reaction Conditions[a]



entry	catalyst	CuX	oxidant	base	solvent	yield[b]
1	$Pd(OAc)_2$	CuI	BQ	K_2CO_3	DMF	24
2	$Pd(OAc)_2$	CuI	DDQ	K_2CO_3	DMF	13
3	$Pd(OAc)_2$	CuI	$AgNO_3$	K_2CO_3	DMF	37
4	$Pd(OAc)_2$	CuI	Ag_2CO_3	K_2CO_3	DMF	52
5	$PdCl_2$	CuI	Ag_2CO_3	K_2CO_3	DMF	36
6	$Pd(PhCN)_2Cl_2$	CuI	Ag_2CO_3	K_2CO_3	DMF	28
7	$Pd(TFA)_2$	CuI	Ag_2CO_3	K_2CO_3	DMF	17
8	$Pd(OAc)_2$	CuCl	Ag_2CO_3	K_2CO_3	DMF	9
9	$Pd(OAc)_2$	CuBr	Ag_2CO_3	K_2CO_3	DMF	21
10	$Pd(OAc)_2$	CuCN	Ag_2CO_3	K_2CO_3	DMF	trace
11	$Pd(OAc)_2$	CuI	Ag_2CO_3	K_3PO_4	DMF	45
12	$Pd(OAc)_2$	CuI	Ag_2CO_3	KF	DMF	36
13	$Pd(OAc)_2$	CuI	Ag_2CO_3	Cs_2CO_3	DMF	64
14	$Pd(OAc)_2$	CuI	Ag_2CO_3	Cs_2CO_3	DMSO	72
15	$Pd(OAc)_2$	CuI	Ag_2CO_3	Cs_2CO_3	Toluene	40
16	$Pd(OAc)_2$	CuI	Ag_2CO_3	Cs_2CO_3	1,4-dioxane	38
17	$Pd(OAc)_2$	CuI	Ag_2CO_3	Cs_2CO_3	[Bmim]Cl	89 (81)
18	$Pd(OAc)_2$	CuI	Ag_2CO_3		[Bmim]Cl	26
19[c]	$Pd(OAc)_2$	CuI	Ag_2CO_3	Cs_2CO_3	[Bmim]Cl	83
20		CuI	Ag_2CO_3	Cs_2CO_3	[Bmim]Cl	N.D.
21	$Pd(OAc)_2$		Ag_2CO_3	Cs_2CO_3	[Bmim]Cl	N.D.
22	$Pd(OAc)_2$	CuI	O_2	Cs_2CO_3	[Bmim]Cl	N.D.
23[d]	$Pd(OAc)_2$		Ag_2CO_3	Cs_2CO_3	[Bmim]Cl	N.D.
24[e]	$Pd(OAc)_2$		Ag_2CO_3	Cs_2CO_3	[Bmim]Cl	N.D.
25[e]	$Pd(OAc)_2$	CuI	Ag_2CO_3	Cs_2CO_3	[Bmim]Cl	N.D.
26[f]	$Pd(OAc)_2$	CuI	Ag_2CO_3	Cs_2CO_3	[Bmim]Cl	trace

[a]Unless otherwise noted, reactions were performed with **1a** (0.10 mmol), **2** (0.20 mmol), S_8 (0.30 mmol), catalyst (5 mol %), CuX (0.10 mmol), Phen (1,10-phenanthroline, 0.11 mmol), oxidant (0.20 mmol), base (0.20 mmol), and solvents (1 mL) under N_2 at 80 °C for 6 h. [Bmim]Cl: 1-butyl-3-methylimidazolium chloride. [b]Determined by GC using dodecane as the internal standard. The value in parentheses is the yield of isolated product. [c]Performed at 100 °C. [d]$PhB(OH)_2$ (**2a**) was replaced by Ph_3B (**2b**). [e]$PhB(OH)_2$ (**2a**) was replaced by $KPhBF_3$ (**2c**). [f]$PhB(OH)_2$ (**2a**) was replaced by phenylboronic acid pinacol ester (**2d**).

More importantly, other kinds of electron-rich heteroarenes were also tested under the present optimized conditions, and the results are listed in Table 5. Similarly, all of the tested imidazo[1,2-*a*]pyridine substrates could be converted to the desired sulfenylation products (**10a**−**10h**) in moderate to good yields.[17] However, when pyrrole (**9i**) was subjected to the standard conditions, only a trace amount of desired product **10i** was detected by GC-MS. Unfortunately, when furan was employed, no desired sulfenylation product **10j** was observed in the current conditions. To our delight, 2-phenylbenzofuran (**9k**) was found to be compatible with this protocol, thus providing **10k** in 46% yield.

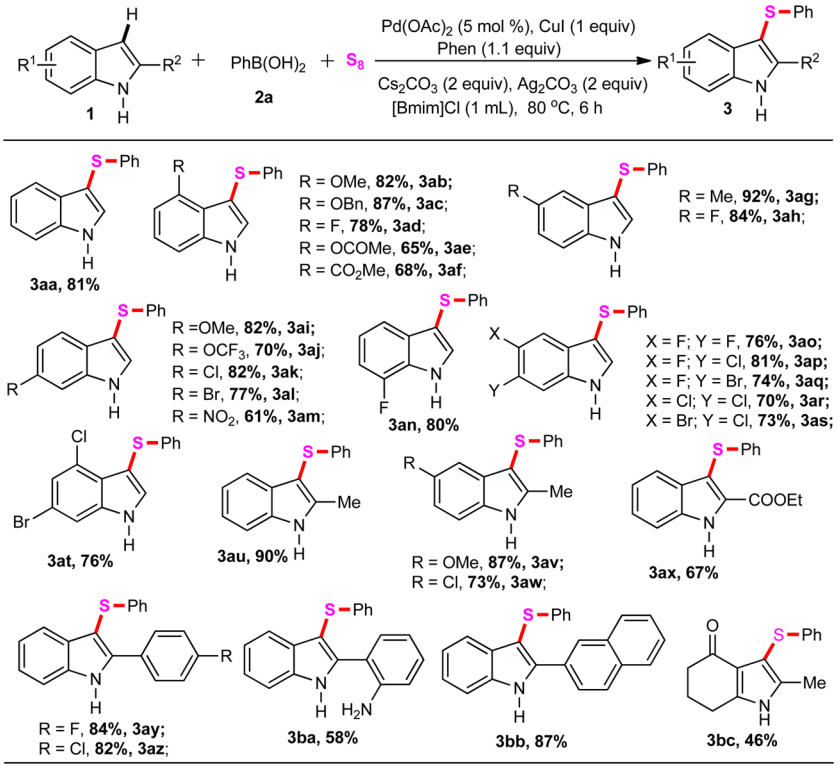
To demonstrate the efficiency and practicability of this protocol, we further examined the *N*-arylation reaction of the resultant products under basic conditions (Scheme 3). For instance, under mild conditions, 3-phenylthioindole **3aw** with benzyl bromide delivered *N*-benzyl 3-phenylthioindole **11** in 83% yield.[18] Further, *N*-phenyl 3-phenylthioindole (**12**) could also be achieved from **3aw** with iodobenzene by using Cu_2O as catalyst.[19]

To gain some insights into the mechanism of this transformation, several control experiments have been also conducted (Scheme 4). Under the standard conditions, when 3-methyl-1*H*-indole (**13**) was employed to react with phenylboronic acid (**2a**) and S_8; unfortunately, desired product **14** was obtained in 8% GC yield (eq 1). This result indicated that the sulfenylation of indoles mainly occurred at the 3-position. Subsequently, when treated with indole (**1a**) with 1,2-diphenyldisulfane (**15**) and benzenethiol (**16**) under the standard conditions, no desired product **3aa** could be detected by GC-MS (eq 2).[20] All of these results described above suggested that neither **15** nor **16** was a possible intermediate in this chemical process. When 3-iodo-indole (**17**) was used as the substrate under the redox-neutral conditions, desired product **3aa** was detected by GC-MS in 56% yield (eq 3). This result suggested that Ag_2CO_3 as the oxidant played a crucial role to complete the catalytic cycle. Moreover, when 2 equiv of radical inhibitor 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added to the reaction under the standard conditions, desired product **3aa** was also detected in 85% GC yield (eq 4). This observation demonstrated that the reaction should not be a radical pathway.

Although the direct sulfuration reactions of borates and boronates by elemental sulfur have been well-developed,[21] palladium-catalyzed oxidative sulfenylation reaction using elemental sulfur as sulfurating reagent remains relatively rare.[22] Further, more traditional nucleophile boron reagents like potassium phenyltrifluoroborate ($KPhBF_3$, **2c**) and phenyl-

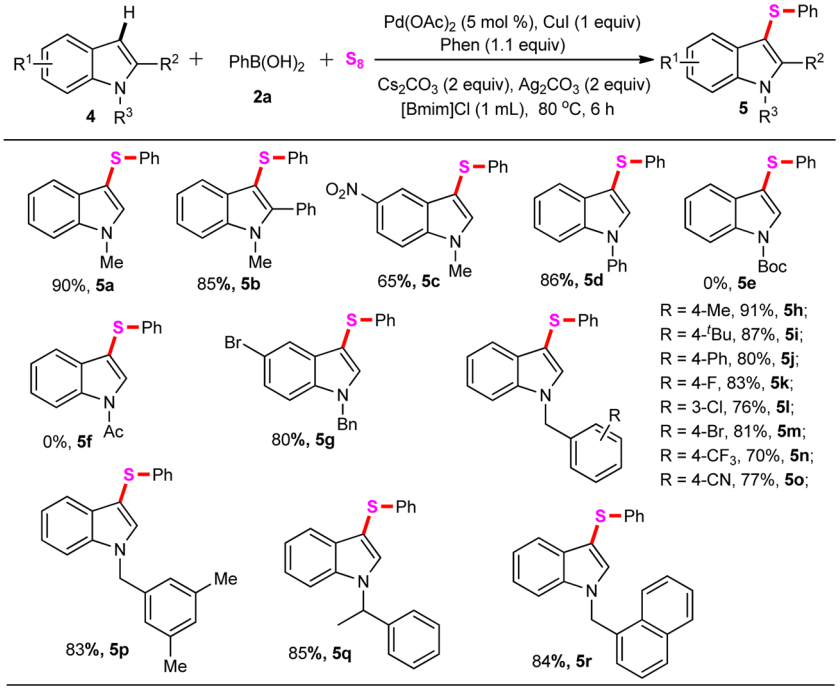
DOI: 10.1021/acs.joc.6b01428
J. Org. Chem. 2016, 81, 7771−7783

Table 2. Sulfenylation of Indoles with Phenylboronic Acid and S_8[a]



[a]Reactions were performed with **1** (0.20 mmol), **2a** (0.4 mmol), S_8 (0.60 mmol), $Pd(OAc)_2$ (5 mol %), CuI (0.20 mmol), Phen (0.22 mmol), Ag_2CO_3 (0.4 mmol), Cs_2CO_3 (0.4 mmol), and [Bmim]Cl (1 mL) under N_2 at 80 °C for 6 h. Yields refer to isolated yields.

Table 3. Sulfenylation of *N*-Substituted Indoles with Phenylboronic Acid and S_8[a]

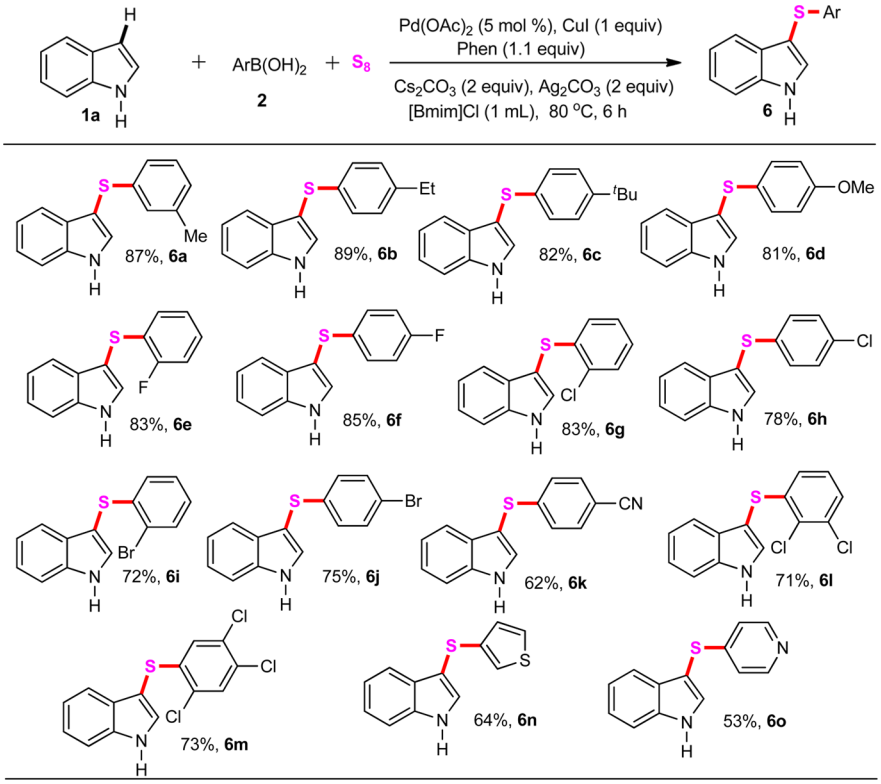


[a]Reactions were performed with **4** (0.20 mmol), **2a** (0.4 mmol), S_8 (0.60 mmol), $Pd(OAc)_2$ (5 mol %), CuI (0.20 mmol), Phen (0.22 mmol), Ag_2CO_3 (0.4 mmol), Cs_2CO_3 (0.4 mmol), and [Bmim]Cl (1 mL) under N_2 at 80 °C for 6 h. Yields refer to isolated yields.

boronic acid pinacol ester (**2d**) were ineffective in our current catalytic system.[21] Additionally, disulfides were not possible intermediates according to the control experiments and our previous reports.[22] Hence, these observations indicated that the current protocol is different from the previous postulated process. As a consequence, on the basis of the above observations and relevant reports in the literature, a tentative mechanism of this transformation is illustrated in Scheme 5.

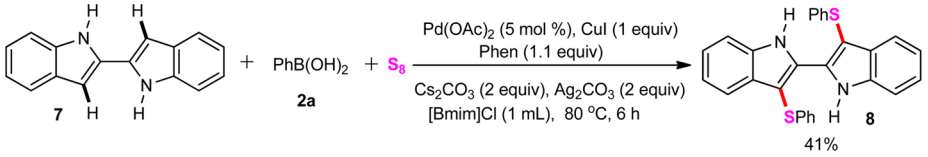
DOI: 10.1021/acs.joc.6b01428
J. Org. Chem. 2016, 81, 7771−7783

Table 4. Sulfenylation of 1a with Aryl Boronic Acids 2 and S_8[a]



[a]Reactions were performed with **1a** (0.20 mmol), **2** (0.4 mmol), S_8 (0.60 mmol), $Pd(OAc)_2$ (5 mol %), CuI (0.20 mmol), Phen (0.22 mmol), Ag_2CO_3 (0.4 mmol), Cs_2CO_3 (0.4 mmol), and [Bmim]Cl (1 mL) under N_2 at 80 °C for 6 h. Yields refer to isolated yields.

Scheme 2. Sulfenylation of 1*H*,1′*H*-2,2′-Biindole



Initially, vinyl-palladium intermediate **I** was generated by electrophilic palladation of heteroarenes.[23,24] Simultaneously, organocopper thiolate complex intermediate **II** from aryl boronic acid, S_8, and CuI was formed.[25] Subsequently, intermediate **I** could undergo transmetalation with intermediate **II** to produce intermediate **III**.[22] On the other hand, organocopper thiolate complexes are frequently accompanied by side-reactions to give a handful of thiol derivatives.[20] Finally, a reductive elimination produced the target products and Ag(I) oxidized Pd(0) to Pd(II) active species to complete the catalytic cycle.[26] A silver mirror reaction was observed when the reaction was finished.

CONCLUSIONS

In summary, we have successfully accomplished an efficient and convenient strategy for the synthesis of structurally diverse 3-sulfenylheteroarenes by a palladium-catalyzed C−H bond oxidative sulfenylation of indoles and related electron-rich heteroarenes with aryl boronic acids and elemental sulfur. Importantly, readily available indoles without preactivation, broad substrate scopes, and excellent functional group compatibility make this protocol practical and attractive. Moreover, the chemistry described herein represents an efficient synthetic approach for accessing biologically important 3-sulfenylindole derivatives.

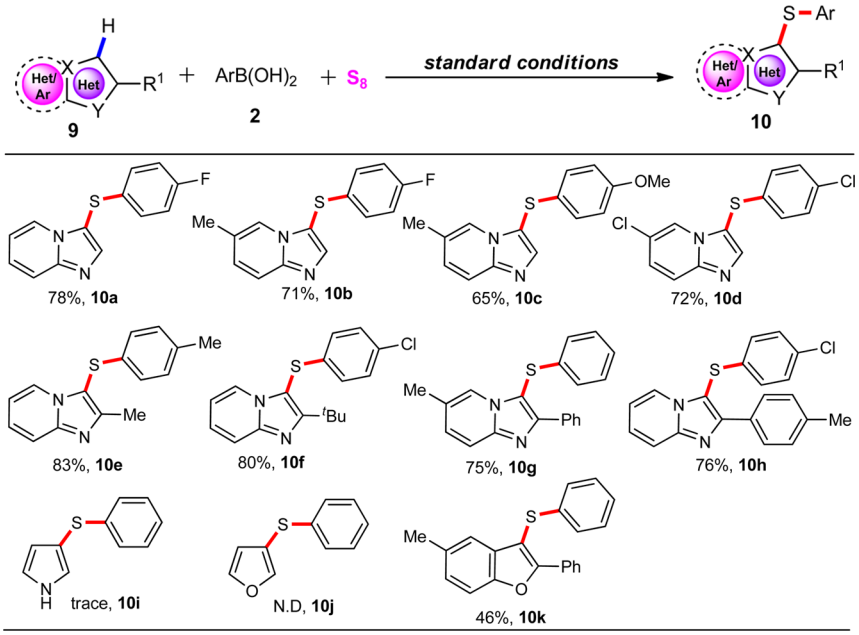
EXPERIMENTAL SECTION

General Methods. Melting points were measured by a melting point instrument and were uncorrected. ^1H and ^{13}C NMR spectra were recorded by using a 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.24 and 77.0 ppm, respectively, and chloroform is used as a solvent with TMS as the internal standard. IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with an infrared spectrometer. GC-MS was obtained using electron ionization. The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). TLC was performed by using commercially available 100−400 mesh silica gel plates (GF_{254}). Unless otherwise noted, all purchased chemicals were used without further purification.

General Procedure for Sulfenylation of Indoles. A mixture of $Pd(OAc)_2$ (5 mol %), indoles (0.20 mmol), and [Bmim]Cl (1 mL) was added to an Schlenk tube equipped with a stir-bar and stirred at room temperature for 15 min. A balloon filled with N_2 was connected to the Schlenk tube via the side tube and purged three times. Then, aryl boronic acids (0.4 mmol), elemental sulfur (0.60 mmol), CuI (0.40 mmol), Phen (0.44 mmol), Ag_2CO_3 (0.4 mmol), and Cs_2CO_3 (0.4 mmol) were quickly added to the tube under N_2 atmosphere and stirred at 80 °C for 6 h. After the reaction was finished, the N_2 gas was released carefully, and the reaction was quenched by water and

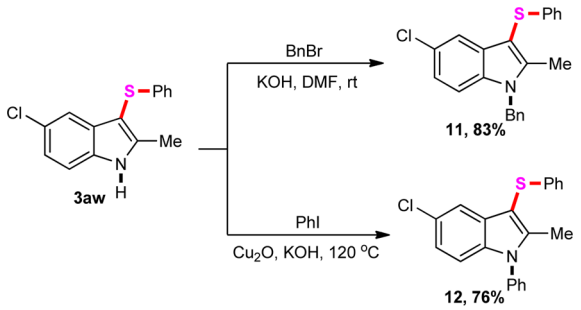
DOI: 10.1021/acs.joc.6b01428
J. Org. Chem. 2016, 81, 7771−7783

Table 5. Sulfenylation of 9 with Aryl Boronic Acids 2 and S_8[a]

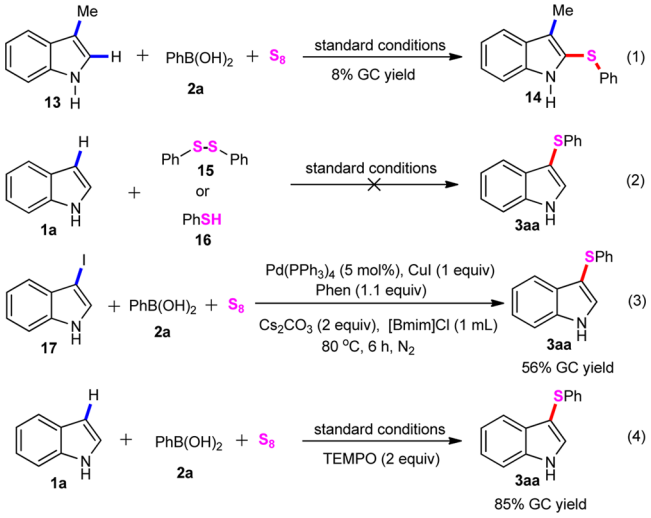


[a]Reactions were performed with **9** (0.20 mmol), **2** (0.4 mmol), S_8 (0.60 mmol), $Pd(OAc)_2$ (5 mol %), CuI (0.20 mmol), Phen (0.22 mmol), Ag_2CO_3 (0.4 mmol), Cs_2CO_3 (0.4 mmol), and [Bmim]Cl (1 mL) under N_2 at 80 °C for 6 h. Yields refer to isolated yields. N.D = not determined.

Scheme 3. *N*-Arylation of 3-Phenylthioindole 3aw



Scheme 4. Control Experiments



extracted with CH_2Cl_2 three times. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The residue was purified by flash column chromatography on silica gel (hexanes/ethyl acetate) to afford the desired products.

3-(Phenylthio)-1H-indole (***3aa***).[15d] Yield of 81% (36.5 mg) as a white solid; mp 148.4−149.8 °C; R_f = 0.32 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.48−7.37 (m, 2H), 7.24 (d, J = 9.6 Hz, 1H), 7.18−7.08 (m, 5H), 7.04 (t, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 136.5, 130.7, 129.1, 128.7, 125.9, 124.8, 123.1, 120.9, 119.7, 111.6, 102.9 ppm; ν_{max} (KBr)/cm^{-1} 3408, 3026, 1654, 1600, 1454, 1400, 742; MS (EI) m/z 77, 148, 165, 193, 225; HRMS-ESI (m/z) calcd for $C_{14}H_{11}NNaS$ [M + Na]$^+$ 248.0504, found 248.0508.

4-Methoxy-3-(phenylthio)-1H-indole (***3ab***). Yield of 82% (41.8 mg) as a yellow solid; mp 78.4−79.8 °C; R_f = 0.28 (4:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.23−7.20 (m, 1H), 7.18−7.12 (m, 5H), 7.07−7.01 (m, 1H), 6.97 (d, J = 8.0 Hz, 1H), 6.52 (d, J = 7.6 Hz, 1H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 140.7, 138.5, 129.6, 128.5, 126.5, 124.7, 123.9, 118.6, 104.9, 102.5, 101.6, 55.6 ppm; ν_{max} (KBr)/cm^{-1} 3410, 3034, 1658, 1604, 1560, 1448, 1280, 1092, 746; MS (EI) m/z 119, 207, 240, 255; HRMS-ESI (m/z) calcd for $C_{15}H_{13}NNaOS$ [M + Na]$^+$ 278.0610, found 278.0609.

4-(Benzyloxy)-3-(phenylthio)-1H-indole (***3ac***). Yield of 87% (57.6 mg) as a green oil; R_f = 0.30 (4:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.23−7.16 (m, 4H), 7.13−7.05 (m, 7H), 7.01 (t, J = 6.8 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 6.56 (d, J = 7.6 Hz, 1H), 5.00 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 141.1, 138.7, 137.2, 130.3, 128.6, 128.2, 127.4, 127.1, 125.8, 124.4, 123.9, 118.8, 105.1, 102.6, 101.7, 69.9 ppm; ν_{max} (KBr)/cm^{-1} 3404, 3028, 1658, 1624, 1560, 1444, 1276, 1042, 753; MS (EI) m/z 91, 207, 240, 298, 331; HRMS-ESI (m/z) calcd for $C_{21}H_{17}NNaOS$ [M + Na]$^+$ 354.0923, found 354.0925.

4-Fluoro-3-(phenylthio)-1H-indole (***3ad***).[15a] Yield of 78% (37.9 mg) as a yellow solid; mp 137.2−138.5 °C; R_f = 0.40 (5:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.36 (d, J = 2.4 Hz, 1H), 7.20−7.12 (m, 6H), 7.07 (ddd, J = 8.4, 6.0, 2.8 Hz, 1H), 6.82−6.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9 (d, J = 248.7 Hz), 139.7, 139.4 (d, J = 10.0 Hz), 131.1, 128.8, 126.4, 125.1, 123.7 (d, J = 7.7 Hz), 117.7 (d, J = 18.0 Hz), 107.8 (d, J = 4.1 Hz), 106.4 (d, J = 19.0 Hz), 101.4 (d, J = 2.1 Hz) ppm; ν_{max} (KBr)/cm^{-1} 3396, 3024, 1656, 1625, 1438, 1404, 740; MS (EI) m/z 95, 122, 166, 211, 243; HRMS-ESI (m/z) calcd for $C_{14}H_{10}FNNaS$ [M + Na]$^+$ 266.0410, found 266.0406.

DOI: 10.1021/acs.joc.6b01428
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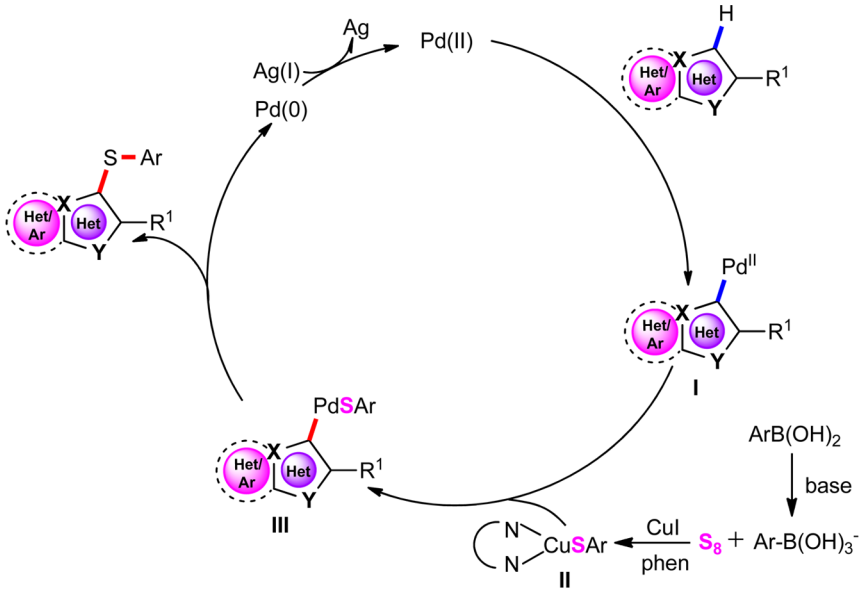
Scheme 5. Plausible Mechanism



3-(Phenylthio)-1H-indol-4-yl acetate (***3ae***). Yield of 65% (36.8 mg) as a white solid; mp 124.7−126.3 °C; R_f = 0.25 (2:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.15 (ddd, J = 4.8, 4.0, 1.6 Hz, 5H), 7.05 (td, J = 7.2, 1.2 Hz, 3H), 6.80 (dd, J = 5.2, 3.2 Hz, 1H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 143.8, 140.4, 138.7, 132.5, 128.7, 125.2, 124.7, 123.1, 121.0, 114.0, 110.2, 99.7, 20.8 ppm; ν_{max} (KBr)/cm^{-1} 3400, 3028, 1686, 1653, 1600, 1540, 1427, 1403, 744; MS (EI) m/z 109, 163, 208, 241, 283; HRMS-ESI (m/z) calcd for $C_{16}H_{13}NNaO_2S$ [M + Na]$^+$ 306.0559, found 306.0564.

Methyl 3-(Phenylthio)-1H-indole-4-carboxylate (***3af***). Yield of 68% (38.5 mg) as a white solid; mp 122.3−123.5 °C; R_f = 0.23 (2:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (s, 1H), 7.45 (dd, J = 7.6, 3.2 Hz, 2H), 7.36 (s, 1H), 7.20 (t, J = 7.6 Hz, 1H), 7.13−7.08 (m, 2H), 7.05−6.97 (m, 3H), 3.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 140.2, 137.6, 134.0, 128.6, 125.6, 125.4, 125.2, 124.6, 122.2, 122.1, 115.3, 101.9, 51.9 ppm; ν_{max} (KBr)/cm^{-1} 3408, 3035, 2946, 1683, 1636, 1526, 1425, 763; MS (EI) m/z 111, 152, 196, 223, 283; HRMS-ESI (m/z) calcd for $C_{16}H_{13}NNaO_2S$ [M + Na]$^+$ 306.0559, found 306.0565.

5-Methyl-3-(phenylthio)-1H-indole (***3ag***).[15c] Yield of 92% (43.9 mg) as a white solid; mp 135.6−137.2 °C; R_f = 0.36 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.39 (d, J = 7.2 Hz, 2H), 7.28 (d, J = 8.0 Hz, 1H), 7.15 (t, J = 7.2 Hz, 2H), 7.11−6.99 (m, 4H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 134.8, 130.9, 130.5, 129.4, 128.7, 125.7, 124.8, 124.7, 119.2, 111.3, 101.9, 21.5 ppm; ν_{max} (KBr)/cm^{-1} 3404, 3033, 2915, 1623, 1538, 1447, 1220, 748; MS (EI) m/z 118, 162, 206, 223, 239; HRMS-ESI (m/z) calcd for $C_{15}H_{13}NNaS$ [M + Na]$^+$ 262.0661, found 262.0654.

5-Fluoro-3-(phenylthio)-1H-indole (***3ah***).[15e] Yield of 84% (40.8 mg) as a yellow solid; mp 114.2−115.5 °C; R_f = 0.36 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, DMSO) δ 11.83 (s, 1H), 7.86 (d, J = 2.4 Hz, 1H), 7.67−7.37 (m, 1H), 7.21 (td, J = 8.0, 1.6 Hz, 2H), 7.15−6.97 (m, 5H); ^{13}C NMR (100 MHz, DMSO) δ 157.7 (d, J = 232.6 Hz), 138.8, 134.4, 133.3, 129.3 (d, J = 9.8 Hz), 128.8, 125.4, 124.9, 113.6 (d, J = 9.6 Hz), 110.4 (d, J = 26.0 Hz), 103.0 (d, J = 23.6 Hz), 99.6 (d, J = 4.6 Hz) ppm; ν_{max} (KBr)/cm^{-1} 3388, 3024, 1653, 1600, 1546, 1438, 1411, 748; MS (EI) m/z 95, 139, 166, 211, 243; HRMS-ESI (m/z) calcd for $C_{14}H_{11}FNS$ [M + H]$^+$ 244.0591, found 244.0586.

6-Methoxy-3-(phenylthio)-1H-indole (***3ai***).[12] Yield of 82% (41.8 mg) as a yellow solid; mp 111.6−113.2 °C; R_f = 0.28 (4:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.34 (s, 1H), 7.17−7.13 (m, 2H), 7.10 (d, J = 7.6 Hz, 2H), 7.05 (d, J = 6.8 Hz, 1H), 6.89 (s, 1H), 6.82 (d, J = 8.8 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 139.3, 137.3, 129.4, 128.7, 125.8, 124.7, 123.3, 120.3, 110.8, 102.8, 95.1, 55.7 ppm; ν_{max} (KBr)/cm^{-1} 3408, 3026, 2934, 1627, 1524, 1457, 1286, 756; MS (EI) m/z 135, 184, 212, 240, 255; HRMS-ESI (m/z) calcd for $C_{15}H_{13}NNaOS$ [M + Na]$^+$ 278.0610, found 278.0608.

3-(Phenylthio)-6-(trifluoromethoxy)-1H-indole (***3aj***). Yield of 70% (43.3 mg) as a yellow solid; mp 125.6−127.4 °C; R_f = 0.31 (4:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.49 (d, J = 1.6 Hz, 1H), 7.28 (s, 1H), 7.17 (t, J = 7.6 Hz, 2H), 7.13−7.06 (m, 3H), 7.03 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 138.6, 136.1, 131.9, 128.9, 126.1, 125.1, 122.0, 120.7 (q, J = 256.2 Hz), 120.5, 115.1, 104.7, 103.5 ppm; ν_{max} (KBr)/cm^{-1} 3386, 3028, 1633, 1536, 1457, 1409, 752; MS (EI) m/z 135, 184, 223, 277, 309; HRMS-ESI (m/z) calcd for $C_{15}H_{11}F_3NOS$ [M + H]$^+$ 310.0508, found 310.0509.

6-Chloro-3-(phenylthio)-1H-indole (***3ak***).[15d] Yield of 82% (42.5 mg) as a white solid; mp 103.3−104.7 °C; R_f = 0.38 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 7.6 Hz, 1H), 7.15 (t, J = 7.2 Hz, 2H), 7.07 (dd, J = 13.6, 7.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 133.8, 131.2, 130.6, 128.8, 126.1, 125.1, 122.5, 121.7, 118.4, 117.0, 104.5 ppm; ν_{max} (KBr)/cm^{-1} 3398, 3056, 1722, 1635, 1538, 1453, 746; MS (EI) m/z 111, 146, 182, 224, 259; HRMS-ESI (m/z) calcd for $C_{14}H_{10}ClNNaS$ [M + Na]$^+$ 282.0115, found 282.0113.

6-Bromo-3-(phenylthio)-1H-indole (***3al***).[6e] Yield of 77% (46.7 mg) as a white solid; mp 144.8−146.5 °C; R_f = 0.38 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.57 (d, J = 1.6 Hz, 1H), 7.44 (t, J = 5.2 Hz, 2H), 7.30−7.21 (m, 1H), 7.19−7.12 (m, 2H), 7.10−7.01 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 137.3, 131.1, 128.8, 128.0, 126.0, 125.1, 124.3, 121.0, 116.7, 114.6, 103.6 ppm; ν_{max} (KBr)/cm^{-1} 3402, 3036, 1637, 1542, 1456, 1405, 755; MS (EI) m/z 112, 152, 191, 224, 271, 303; HRMS-ESI (m/z) calcd for $C_{14}H_{10}BrNNaS$ [M + Na]$^+$ 325.9610, found 325.9604.

6-Nitro-3-(phenylthio)-1H-indole (***3am***). Yield of 61% (32.9 mg) as a yellow solid; mp 147.5−148.7 °C; R_f = 0.26 (1:4 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.43 (d, J = 1.6 Hz, 1H), 8.05 (dd, J = 8.8, 2.0 Hz, 1H), 7.77 (d, J = 2.4 Hz, 1H), 7.67 (d, J = 8.8 Hz, 1H), 7.22−7.14 (m, 2H), 7.10 (dd, J = 7.2, 5.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 137.9, 135.7, 135.1, 134.0, 128.9, 126.3, 125.5, 119.9, 116.4, 108.6, 105.1 ppm; ν_{max} (KBr)/cm^{-1} 3394, 3026, 1646, 1578, 1436, 1404, 746; MS (EI) m/z 120, 191, 224, 240, 270; HRMS-ESI (m/z) calcd for $C_{14}H_{10}N_2NaO_2S$ [M + Na]$^+$ 293.0355, found 293.0358.

DOI: 10.1021/acs.joc.6b01428
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7-Fluoro-3-(phenylthio)-1H-indole (**3an**). Yield of 80% (38.8 mg) as a yellow solid; mp 114.4−115.2 °C; R_f = 0.35 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.44 (d, J = 2.4 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.15 (t, J = 7.6 Hz, 2H), 7.09 (d, J = 7.6 Hz, 2H), 7.04 (ddd, J = 12.8, 7.2, 5.6 Hz, 2H), 6.95 (dd, J = 10.8, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6 (d, J = 243.6 Hz), 138.7, 132.6 (d, J = 4.4 Hz), 131.2, 128.8, 126.1, 125.0, 124.9 (d, J = 13.6 Hz), 121.2 (d, J = 6.1 Hz), 115.4 (d, J = 3.5 Hz), 107.9 (d, J = 15.8 Hz), 104.1 (d, J = 2.9 Hz) ppm; ν_{max} (KBr)/cm $^{-1}$ 3408, 3046, 1644, 1618, 1543, 1425, 750; MS (EI) m/z 95, 122, 166, 183, 211, 243; HRMS-ESI (m/z) calcd for $C_{14}H_{11}FNS$ $[M + H]^+$ 244.0591, found 244.0587.

5,6-Difluoro-3-(phenylthio)-1H-indole (**3ao**). Yield of 76% (39.7 mg) as a white solid; mp 157.0−158.6 °C; R_f = 0.32 (8:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.48 (d, J = 2.4 Hz, 1H), 7.31 (dd, J = 10.2, 7.6 Hz, 1H), 7.23−7.14 (m, 3H), 7.08 (dd, J = 5.2, 3.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7 (dd, J = 242.9, 16.0 Hz), 147.4 (dd, J = 240.6, 14.9 Hz), 138.4, 131.9 (d, J = 3.3 Hz), 131.3 (d, J = 10.6 Hz), 128.9, 126.0, 125.2, 124.8 (dd, J = 8.1, 1.3 Hz), 106.5 (dd, J = 19.8, 1.0 Hz), 103.6 (dd, J = 4.3, 1.3 Hz), 99.7 (d, J = 22.2 Hz) ppm; ν_{max} (KBr)/cm^{-1} 3402, 3034, 1653, 1616, 1568, 1524, 1419, 748; MS (EI) m/z 77, 113, 184, 201, 229, 261; HRMS-ESI (m/z) calcd for $C_{14}H_9F_2NNaS$ $[M + Na]^+$ 284.0316, found 284.0311.

6-Chloro-5-fluoro-3-(phenylthio)-1H-indole (**3ap**). Yield of 81% (44.9 mg) as a yellow solid; mp 165.4−167.2 °C; R_f = 0.34 (8:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.50 (d, J = 2.4 Hz, 1H), 7.44 (d, J = 6.0 Hz, 1H), 7.31 (d, J = 9.2 Hz, 1H), 7.21−7.13 (m, 2H), 7.08 (dd, J = 7.2, 5.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9 (d, J = 239.1 Hz), 138.3, 132.6, 128.9, 128.6, 128.4 (d, J = 8.8 Hz), 126.1, 125.2, 117.3 (d, J = 21.5 Hz), 112.9, 105.9 (d, J = 24.1 Hz), 103.8 (d, J = 4.5 Hz) ppm; ν_{max} (KBr)/cm^{-1} 3384, 3026, 1646, 1628, 1544, 1411, 1400, 753; MS (EI) m/z 77, 121, 173, 242, 277; HRMS-ESI (m/z) calcd for $C_{14}H_9ClFNNaS$ $[M + Na]^+$ 300.0020, found 300.0027.

6-Bromo-5-fluoro-3-(phenylthio)-1H-indole (**3aq**). Yield of 74% (47.5 mg) as a white solid; mp 153.1−154.3 °C; R_f = 0.34 (8:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.59 (d, J = 5.2 Hz, 1H), 7.49 (s, 1H), 7.30 (d, J = 8.8 Hz, 1H), 7.17 (t, J = 7.2 Hz, 2H), 7.08 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6 (d, J = 238.8 Hz), 138.3, 133.2, 132.6, 129.3 (d, J = 8.8 Hz), 128.9, 126.1, 125.2, 115.8, 105.7 (d, J = 25.4 Hz), 104.8 (d, J = 25.0 Hz), 103.8 (d, J = 4.8 Hz) ppm; ν_{max} (KBr)/cm $^{-1}$ 3392, 3031, 1647, 1623, 1554, 1447, 1408, 748; MS (EI) m/z 77, 121, 183, 242, 289, 321; HRMS-ESI (m/z) calcd for $C_{14}H_9BrFNNaS$ $[M + Na]^+$ 343.9515, found 343.9513.

5,6-Dichloro-3-(phenylthio)-1H-indole (**3ar**). Yield of 70% (41.0 mg) as a yellow solid; mp 148.6−150.2 °C; R_f = 0.35 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.66 (s, 1H), 7.52 (s, 1H), 7.48 (d, J = 2.0 Hz, 1H), 7.18 (t, J = 7.6 Hz, 2H), 7.08 (t, J = 8.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 135.1, 132.5, 128.9, 128.8, 127.2, 126.0, 125.4, 125.3, 120.7, 113.2, 103.3 ppm; ν_{max} (KBr)/cm $^{-1}$ 3402, 3025, 1648, 1615, 1536, 1443, 1400, 746; MS (EI) m/z 112, 223, 258, 293; HRMS-ESI (m/z) calcd for $C_{14}H_9Cl_2NNaS$ $[M + Na]^+$ 315.9725, found 315.9730.

5-Bromo-6-chloro-3-(phenylthio)-1H-indole (**3as**). Yield of 73% (49.2 mg) as a white solid; mp 154.7−156.0 °C; R_f = 0.35 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.84 (s, 1H), 7.54 (s, 1H), 7.46 (s, 1H), 7.18 (t, J = 7.2 Hz, 2H), 7.08 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 135.8, 132.4, 129.5, 128.9, 128.8, 126.0, 125.3, 124.1, 114.7, 113.1, 103.1 ppm; ν_{max} (KBr)/cm^{-1} 3402, 3032, 1654, 1623, 1546, 1510, 1436, 1405, 748; MS (EI) m/z 111, 223, 258, 307, 337; HRMS-ESI (m/z) calcd for $C_{14}H_9BrClNNaS$ $[M + Na]^+$ 359.9220, found 359.9223.

6-Bromo-4-chloro-3-(phenylthio)-1H-indole (**3at**). Yield of 76% (51.2 mg) as a green solid; mp 133.5−134.8 °C; R_f = 0.35 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.42 (d, J = 13.6 Hz, 2H), 7.24 (s, 1H), 7.18 (d, J = 7.6 Hz, 2H), 7.11−7.04 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 138.4, 133.0, 128.8, 127.8, 126.0, 125.1, 125.0, 124.3, 115.9, 113.5, 103.7 ppm; ν_{max} (KBr)/cm^{-1} 3396, 3025, 1662, 1635, 1547, 1523, 1448, 1410, 744; MS (EI) m/z 111, 154, 223, 258, 304, 337; HRMS-ESI (m/z) calcd for $C_{14}H_9BrClNNaS$ $[M + Na]^+$ 359.9220, found 359.9217.

2-Methyl-3-(phenylthio)-1H-indole (**3au**).[15d] Yield of 90% (43.0 mg) as a white solid; mp 112.3−113.9 °C; R_f = 0.34 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.19−7.17 (m, 1H), 7.16−7.08 (m, 3H), 7.02 (dd, J = 11.6, 5.6 Hz, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 139.4, 135.5, 130.3, 128.7, 125.6, 124.6, 122.2, 120.7, 119.0, 110.7, 99.4, 12.2 ppm; ν_{max} (KBr)/cm^{-1} 3398, 2924, 1722, 1583, 1524, 1445, 1411, 747; MS (EI) m/z 77, 118, 162, 206, 239; HRMS-ESI (m/z) calcd for $C_{15}H_{13}NNaS$ $[M + Na]^+$ 262.0661, found 262.0665.

5-Methoxy-2-methyl-3-(phenylthio)-1H-indole (**3av**).[15a] Yield of 87% (46.8 mg) as a colorless solid; mp 130.2−131.5 °C; R_f = 0.25 (5:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.20−7.10 (m, 3H), 7.06−6.98 (m, 4H), 6.82 (d, J = 8.8 Hz, 1H), 3.77 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 141.8, 139.4, 131.2, 130.3, 128.7, 125.4, 124.5, 112.2, 111.5, 100.9, 98.9, 55.8, 12.2 ppm; ν_{max} (KBr)/cm^{-1} 3386, 3048, 2961, 1592, 1456, 1419, 1356, 752; MS (EI) m/z 118, 148, 192, 239, 269; HRMS-ESI (m/z) calcd for $C_{16}H_{16}NOS$ $[M + H]^+$ 270.0947, found 270.0946.

5-Chloro-2-methyl-3-(phenylthio)-1H-indole (**3aw**).[15a] Yield of 73% (39.8 mg) as a pink solid; mp 140.8−141.9 °C; R_f = 0.36 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.51 (s, 1H), 7.21 (d, J = 8.4 Hz, 1H), 7.17−7.10 (m, 3H), 7.05 (d, J = 7.2 Hz, 1H), 7.01 (d, J = 8.0 Hz, 2H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 138.8, 133.8, 131.6, 128.8, 126.7, 125.6, 124.8, 122.5, 118.5, 111.7, 99.5, 12.2 ppm; ν_{max} (KBr)/cm^{-1} 3394, 3056, 1708, 1583, 1448, 1360, 744; MS (EI) m/z 119, 152, 196, 238, 273; HRMS-ESI (m/z) calcd for $C_{15}H_{12}ClNNaS$ $[M + Na]^+$ 296.0271, found 296.0274.

Ethyl 3-(Phenylthio)-1H-indole-2-carboxylate (**3ax**).[15e] Yield of 67% (39.8 mg) as a white solid; mp 106.3−107.5 °C; R_f = 0.26 (2:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.40−7.31 (m, 1H), 7.21−7.12 (m, 5H), 7.09 (dq, J = 8.8, 4.4 Hz, 1H), 4.38 (q, J = 7.2 Hz, 2H), 1.31 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 137.9, 135.7, 130.1, 128.7, 127.3, 126.1, 125.3, 121.8, 121.5, 112.0, 110.6, 61.4, 14.2 ppm; ν_{max} (KBr)/cm^{-1} 3368, 3054, 2928, 1684, 1505, 1444, 1368, 744; MS (EI) m/z 105, 146, 223, 297; HRMS-ESI (m/z) calcd for $C_{17}H_{15}NNaO_2S$ $[M + Na]^+$ 320.0716, found 320.0723.

2-(4-Fluorophenyl)-3-(phenylthio)-1H-indole (**3ay**).[15a] Yield of 84% (53.6 mg) as a yellow oil; R_f = 0.32 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.76−7.65 (m, 2H), 7.62 (d, J = 7.6 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H), 7.20−7.00 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9 (d, J = 249.5 Hz), 141.1, 139.1, 135.8, 131.1, 130.2 (d, J = 8.1 Hz), 128.9, 127.6 (d, J = 3.4 Hz), 125.6, 124.8, 123.5, 121.3, 120.0, 115.9 (d, J = 21.7 Hz), 111.2, 99.5 ppm; ν_{max} (KBr)/cm^{-1} 3396, 3058, 1648, 1583, 1504, 1452, 748; MS (EI) m/z 77, 121, 183, 242, 287, 319; HRMS-ESI (m/z) calcd for $C_{20}H_{14}FNNaS$ $[M + Na]^+$ 342.0723, found 342.0725.

2-(4-Chlorophenyl)-3-(phenylthio)-1H-indole (**3az**). Yield of 82% (54.9 mg) as a yellow oil; R_f = 0.33 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.62 (t, J = 6.8 Hz, 3H), 7.44−7.32 (m, 3H), 7.26 (t, J = 7.6 Hz, 1H), 7.14 (dd, J = 14.4, 7.6 Hz, 3H), 7.04 (dd, J = 16.0, 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 138.9, 135.9, 134.7, 131.2, 129.8, 129.4, 129.0, 128.9, 125.6, 124.9, 123.7, 121.4, 120.1, 111.3, 100.1 ppm; ν_{max} (KBr)/cm^{-1} 3384, 3048, 1652, 1560, 1512, 1437, 1410, 746; MS (EI) m/z 121, 190, 267, 303, 335; HRMS-ESI (m/z) calcd for $C_{20}H_{14}ClNNaS$ $[M + Na]^+$ 358.0428, found 358.0431.

2-(3-(Phenylthio)-1H-indol-2-yl)aniline (**3ba**). Yield of 58% (36.7 mg) as a yellow oil; R_f = 0.21 (5:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.26 (d, J = 7.2 Hz, 2H), 7.20−7.10 (m, 4H), 7.07 (d, J = 7.2 Hz, 2H), 7.02 (t, J = 7.0 Hz, 1H), 6.81−6.72 (m, 2H), 3.54 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 140.4, 138.9, 136.0, 131.5, 130.3, 130.2, 128.8, 125.8, 124.7, 123.2, 121.0, 119.8, 118.9,

DOI: 10.1021/acs.joc.6b01428
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117.4, 116.5, 111.3, 101.0 ppm; ν_{max} (KBr)/cm^{-1} 3408, 3026, 1658, 1503, 1437, 1411, 756; MS (EI) m/z 104, 152, 180, 283, 316; HRMS-ESI (m/z) calcd for $C_{20}H_{17}N_2S$ [M + H]$^+$ 317.1107, found 317.1103.

2-(Naphthalen-2-yl)-3-(phenylthio)-1H-indole (**3bb**).[15e] Yield of 87% (61.1 mg) as a white solid; mp 96.5−97.8 °C; R_f = 0.30 (8:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.14 (s, 1H), 7.90−7.83 (m, 2H), 7.79 (ddd, J = 9.0, 6.0, 3.2 Hz, 2H), 7.66 (d, J = 8.0 Hz, 1H), 7.50−7.44 (m, 2H), 7.42 (d, J = 8.0 Hz, 1H), 7.27 (t, J = 7.2 Hz, 1H), 7.18 (d, J = 8.0 Hz, 1H), 7.16−7.11 (m, 4H), 7.03 (ddd, J = 8.4, 6.0, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 139.3, 136.0, 133.2, 133.2, 131.4, 128.9, 128.4, 128.4, 127.8, 127.5, 126.7, 126.6, 125.8, 125.7, 124.8, 123.5, 121.3, 120.0, 111.2, 100.1 ppm; ν_{max} (KBr)/cm^{-1} 3386, 3035, 1649, 1594, 1526, 1502, 1437, 745; MS (EI) m/z 120, 175, 215, 273, 318, 351; HRMS-ESI (m/z) calcd for $C_{24}H_{18}NS$ [M + H]$^+$ 352.1154, found 352.1159.

2-Methyl-3-(phenylthio)-6,7-dihydro-1H-indol-4(5H)-one (**3bc**). Yield of 46% (23.6 mg) as a white solid; mp 248.7−250.4 °C; R_f = 0.18 (1:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.14 (t, J = 7.6 Hz, 2H), 7.10−6.96 (m, 3H), 2.76 (t, J = 6.4 Hz, 2H), 2.47−2.39 (m, 2H), 2.23 (s, 3H), 2.16−2.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 143.7, 139.4, 135.1, 128.5, 126.2, 124.6, 120.2, 104.4, 38.6, 23.7, 23.2, 11.0 ppm; ν_{max} (KBr)/cm^{-1} 3384, 2928, 2850, 1650, 1555, 1508, 1452, 1407, 749; MS (EI) m/z 115, 180, 202, 228, 257; HRMS-ESI (m/z) calcd for $C_{15}H_{16}NOS$ [M + H]$^+$ 258.0947, found 258.0940.

1-Methyl-3-(phenylthio)-1H-indole (**5a**).[15d] Yield of 90% (43.0 mg) as a white solid; mp 84.7−86.4 °C; R_f = 0.46 (50:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.6 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.24 (d, J = 10.0 Hz, 2H), 7.17−7.07 (m, 5H), 7.01 (dd, J = 9.6, 4.4 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 137.6, 135.1, 129.9, 128.7, 125.8, 124.7, 122.6, 120.6, 119.8, 109.8, 100.6, 33.1 ppm; ν_{max} (KBr)/cm^{-1} 3032, 1612, 1506, 1450, 1378, 746; MS (EI) m/z 118, 162, 207, 239; HRMS-ESI (m/z) calcd for $C_{15}H_{13}NNaS$ [M + Na]$^+$ 262.0661, found 262.0661.

1-Methyl-2-phenyl-3-(phenylthio)-1H-indole (**5b**).[7b] Yield of 85% (53.6 mg) as a yellow solid; mp 95.7−97.5 °C; R_f = 0.44 (50:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.0 Hz, 1H), 7.42−7.34 (m, 6H), 7.29 (t, J = 7.6 Hz, 1H), 7.20−7.14 (m, 1H), 7.09 (t, J = 7.6 Hz, 2H), 7.03 (d, J = 7.6 Hz, 2H), 6.98 (t, J = 7.2 Hz, 1H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 140.1, 137.7, 130.7, 130.6, 129.9, 128.8, 128.7, 128.4, 125.7, 124.5, 122.9, 121.1, 119.9, 109.9, 99.8, 31.8 ppm; ν_{max} (KBr)/cm $^{-1}$ 3044, 1630, 1504, 1400, 1381, 748; MS (EI) m/z 118, 165, 204, 283, 315; HRMS-ESI (m/z) calcd for $C_{21}H_{17}NNaS$ [M + Na]$^+$ 338.0974, found 338.0979.

1-Methyl-5-nitro-3-(phenylthio)-1H-indole (**5c**). Yield of 65% (36.9 mg) as a yellow solid; mp 183.4−185.2 °C; R_f = 0.32 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 2.0 Hz, 1H), 8.16 (dd, J = 9.0, 2.0 Hz, 1H), 7.48 (s, 1H), 7.40 (d, J = 8.8 Hz, 1H), 7.21−7.14 (m, 2H), 7.14−7.05 (m, 3H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 140.3, 138.2, 137.9, 129.4, 128.9, 126.4, 125.5, 118.3, 116.9, 109.9, 104.9, 33.6 ppm; ν_{max} (KBr)/cm^{-1} 3038, 1626, 1456, 1410, 1376, 757; MS (EI) m/z 118, 165, 207, 238, 284; HRMS-ESI (m/z) calcd for $C_{15}H_{12}N_2NaO_2S$ [M + Na]$^+$ 307.0512, found 307.0517.

1-Phenyl-3-(phenylthio)-1H-indole (**5d**).[15h] Yield of 86% (51.8 mg) as a yellow oil; R_f = 0.34 (50:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.6 Hz, 1H), 7.61−7.55 (m, 2H), 7.52 (d, J = 4.4 Hz, 4H), 7.43−7.35 (m, 1H), 7.26 (d, J = 7.6 Hz, 1H), 7.22−7.14 (m, 5H), 7.06 (d, J = 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 138.9, 136.8, 133.9, 130.3, 129.8, 128.8, 127.2, 126.2, 125.0, 124.5, 123.4, 121.4, 120.1, 111.0, 104.1 ppm; ν_{max} (KBr)/cm^{-1} 3040, 1624, 1600, 1508, 1406, 744; MS (EI) m/z 77, 121, 165, 223, 269, 301; HRMS-ESI (m/z) calcd for $C_{20}H_{15}NNaS$ [M + Na]$^+$ 324.0817, found 324.0821.

1-Benzyl-5-bromo-3-(phenylthio)-1H-indole (**5g**). Yield of 80% (62.9 mg) as a yellow oil; R_f = 0.32 (50:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.34 (s, 1H), 7.27 (t, J = 7.6 Hz, 4H), 7.17−7.12 (m, 3H), 7.11−7.00 (m, 5H), 5.25 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 136.2, 135.8, 135.7, 131.9, 129.1, 128.9, 128.8, 128.2, 126.9, 125.9, 125.1, 122.5, 114.5, 111.9, 101.3, 50.7 ppm; ν_{max} (KBr)/cm^{-1} 3026, 1620, 1600, 1466, 1454, 1405, 748; MS (EI) m/z 91, 223, 302, 360, 393; HRMS-ESI (m/z) calcd for $C_{21}H_{16}BrNNaS$ [M + Na]$^+$ 416.0079, found 416.0079.

1-(4-Methylbenzyl)-3-(phenylthio)-1H-indole (**5h**). Yield of 91% (59.8 mg) as a yellow oil; R_f = 0.35 (50:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.0 Hz, 1H), 7.35−7.30 (m, 2H), 7.20 (dd, J = 11.2, 4.0 Hz, 1H), 7.15−7.07 (m, 7H), 7.06−6.98 (m, 3H), 5.23 (s, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 137.8, 137.3, 134.5, 133.6, 130.2, 129.7, 128.8, 127.2, 125.8, 124.8, 122.8, 120.8, 119.9, 110.4, 101.3, 50.3, 21.2 ppm; ν_{max} (KBr)/cm^{-1} 3036, 1646, 1610, 1473, 1454, 1410, 780; MS (EI) m/z 77, 105, 224, 296, 329; HRMS-ESI (m/z) calcd for $C_{22}H_{19}NNaS$ [M + Na]$^+$ 352.1130, found 352.1128.

1-(4-(tert-Butyl)benzyl)-3-(phenylthio)-1H-indole (**5i**). Yield of 87% (64.6 mg) as a yellow solid; mp 118.8−119.3 °C; R_f = 0.35 (50:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.0 Hz, 1H), 7.34 (dd, J = 10.8, 8.0 Hz, 4H), 7.23−7.18 (m, 1H), 7.16−7.06 (m, 7H), 7.05−6.96 (m, 1H), 5.28 (s, 2H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 139.6, 137.3, 134.5, 133.6, 130.1, 128.7, 126.9, 125.9, 125.8, 124.7, 122.7, 120.7, 119.9, 110.3, 101.3, 50.2, 34.6, 31.4 ppm; ν_{max} (KBr)/cm^{-1} 3036, 2936, 1638, 1602, 1446, 1410, 1264, 756; MS (EI) m/z 117, 147, 224, 338, 371; HRMS-ESI (m/z) calcd for $C_{25}H_{25}NNaS$ [M + Na]$^+$ 394.1600, found 394.1598.

1-([1,1′-Biphenyl]-4-ylmethyl)-3-(phenylthio)-1H-indole (**5j**). Yield of 80% (62.6 mg) as a yellow solid; mp 145.3−146.5 °C; R_f = 0.38 (50:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 8.0 Hz, 4H), 7.44−7.32 (m, 5H), 7.24 (t, J = 5.2 Hz, 3H), 7.19−7.09 (m, 5H), 7.04 (t, J = 7.0 Hz, 1H), 5.39 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 140.5, 139.5, 137.2, 135.6, 134.4, 130.1, 128.8, 128.7, 127.7, 127.6, 127.5, 127.1, 125.8, 124.7, 122.8, 120.8, 119.9, 110.3, 101.6, 50.2 ppm; ν_{max} (KBr)/cm^{-1} 3042, 2930, 1632, 1445, 1408, 746; MS (EI) m/z 117, 167, 224, 308, 391; HRMS-ESI (m/z) calcd for $C_{27}H_{21}NNaS$ [M + Na]$^+$ 414.1287, found 414.1281.

1-(4-Fluorobenzyl)-3-(phenylthio)-1H-indole (**5k**). Yield of 83% (55.3 mg) as a white solid; mp 140.2−141.8 °C; R_f = 0.30 (50:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.0 Hz, 1H), 7.31 (s, 1H), 7.27 (d, J = 8.4 Hz, 1H), 7.20 (dd, J = 11.2, 4.0 Hz, 1H), 7.13−7.04 (m, 7H), 7.03−6.91 (m, 3H), 5.20 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, J = 246.6 Hz), 139.5, 137.1, 134.3, 132.5 (d, J = 3.2 Hz), 130.2, 128.8, 128.7, 125.9, 124.9, 123.0, 120.9, 120.1, 115.9 (d, J = 21.7 Hz), 110.3, 101.8, 49.8 ppm; ν_{max} (KBr)/cm^{-1} 3038, 2926, 1646, 1610, 1454, 1410, 763; MS (EI) m/z 109, 165, 224, 300, 333; HRMS-ESI (m/z) calcd for $C_{21}H_{16}FNNaS$ [M + Na]$^+$ 356.0880, found 356.0876.

1-(3-Chlorobenzyl)-3-(phenylthio)-1H-indole (**5l**). Yield of 76% (53.0 mg) as a yellow oil; R_f = 0.33 (50:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.0 Hz, 1H), 7.34 (s, 1H), 7.27 (d, J = 8.0 Hz, 1H), 7.22 (ddd, J = 9.6, 5.2, 2.0 Hz, 3H), 7.12 (m, 6H), 7.02 (ddd, J = 6.4, 3.2, 16.0 Hz, 1H), 6.96 (d, J = 7.2 Hz, 1H), 5.24 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 138.8, 137.1, 134.9, 134.4, 130.3, 130.1, 128.8, 128.3, 127.1, 125.9, 125.0, 124.9, 123.1, 121.0, 120.1, 110.2, 102.1, 49.9 ppm; ν_{max} (KBr)/cm^{-1} 3040, 2928, 1652, 1608, 1450, 1400, 758; MS (EI) m/z 117, 197, 224, 316, 349; HRMS-ESI (m/z) calcd for $C_{21}H_{17}ClNS$ [M + H]$^+$ 350.0765, found 350.0757.

1-(4-Bromobenzyl)-3-(phenylthio)-1H-indole (**5m**). Yield of 81% (63.7 mg) as a yellow solid; mp 139.7−141.5 °C; R_f = 0.33 (50:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.38 (s, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.24 (d, J = 5.6 Hz, 1H), 7.16 (t, J = 7.6 Hz, 3H), 7.10 (t, J = 4.2 Hz, 2H), 7.06 (d, J = 7.2 Hz, 1H), 7.02 (d, J = 8.4 Hz, 2H), 5.30 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 137.0, 135.7, 134.2, 132.1, 130.1, 128.7, 128.6, 125.9, 124.8, 122.9, 121.9, 120.9, 120.0, 110.1, 102.0, 49.9 ppm; ν_{max} (KBr)/cm $^{-1}$ 3048, 2933, 1656, 1445, 1406, 744; MS (EI) m/z 90, 169, 224, 314, 360, 393; HRMS-ESI (m/z) calcd for $C_{21}H_{17}BrNS$ [M + H]$^+$ 394.0260, found 394.0256.

DOI: 10.1021/acs.joc.6b01428
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3-(Phenylthio)-1-(4-(trifluoromethyl)benzyl)-1H-indole (**5n**). Yield of 70% (53.6 mg) as a white solid; mp 147.4−149.2 °C; R_f = 0.42 (25:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 8.0 Hz, 2H), 7.40 (s, 1H), 7.24 (t, J = 7.2 Hz, 4H), 7.19−7.14 (m, 3H), 7.11 (d, J = 6.8 Hz, 2H), 7.05 (t, J = 7.2 Hz, 1H), 5.40 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 139.2, 137.0, 134.2, 130.3 (q, J = 32.8 Hz), 128.8, 127.1, 125.9 (q, J = 3.6 Hz), 125.8, 125.3, 124.9, 123.9 (q, J = 270.4 Hz), 123.1, 121.0, 120.1, 110.1, 102.4, 49.9 ppm; ν_{max} (KBr)/cm^{-1} 3042, 2928, 1666, 1608, 1453, 1410, 746; MS (EI) m/z 109, 159, 224, 272, 383; HRMS-ESI (m/z) calcd for $C_{22}H_{16}F_3NNaS$ [M + Na]$^+$ 406.0848, found 406.0847.

4-((3-(Phenylthio)-1H-indol-1-yl)methyl)benzonitrile (**5o**). Yield of 77% (52.4 mg) as a yellow oil; R_f = 0.37 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 8.4 Hz, 2H), 7.37 (s, 1H), 7.24−7.20 (m, 2H), 7.19−7.08 (m, 7H), 7.05 (t, J = 7.2 Hz, 1H), 5.37 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 139.1, 136.9, 134.2, 132.8, 130.1, 128.8, 127.3, 126.0, 125.0, 123.3, 121.2, 120.2, 118.4 111.9, 110.0, 102.7, 50.0 ppm; ν_{max} (KBr)/cm^{-1} 3038, 2934, 2246, 1651, 1610, 1454, 1413, 749; MS (EI) m/z 116, 165, 224, 307, 340; HRMS-ESI (m/z) calcd for $C_{22}H_{16}N_2NaS$ [M + Na]$^+$ 363.0926, found 363.0931.

1-(3,5-Dimethylbenzyl)-3-(phenylthio)-1H-indole (**5p**). Yield of 83% (56.9 mg) as a yellow oil; R_f = 0.40 (50:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.23 (dd, J = 14.0, 5.6 Hz, 2H), 7.14 (dd, J = 15.2, 7.6 Hz, 3H), 7.07 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 4.8 Hz, 2H), 6.94 (d, J = 7.6 Hz, 1H), 6.82 (d, J = 7.6 Hz, 1H), 5.23 (s, 2H), 2.30 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 138.1, 137.3, 136.0, 134.1, 131.6, 131.1, 130.1, 128.7, 128.3, 127.2, 125.7, 124.7, 122.7, 120.8, 119.9, 110.2, 101.1, 48.4, 21.1, 19.1 ppm; ν_{max} (KBr)/cm^{-1} 3042, 2936, 1655, 1600, 1452, 1417, 1362, 746; MS (EI) m/z 91, 119, 224, 310, 343; HRMS-ESI (m/z) calcd for $C_{23}H_{21}NNaS$ [M + Na]$^+$ 366.1287, found 366.1291.

1-(1-Phenylethyl)-3-(phenylthio)-1H-indole (**5q**). Yield of 85% (55.9 mg) as a yellow oil; R_f = 0.38 (50:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.6 Hz, 1H), 7.56 (s, 1H), 7.32−7.22 (m, 4H), 7.19−7.07 (m, 8H), 7.06−6.99 (m, 1H), 5.67 (q, J = 7.2 Hz, 1H), 1.92 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 139.7, 137.1, 131.5, 130.2, 128.9, 128.7, 127.8, 125.9, 125.7, 124.7, 122.6, 120.8, 119.9, 110.7, 101.2, 55.5, 21.9 ppm; ν_{max} (KBr)/cm^{-1} 3039, 2932, 1653, 1607, 1454, 1413, 1374, 747; MS (EI) m/z 77, 105, 165, 225, 296, 329; HRMS-ESI (m/z) calcd for $C_{22}H_{19}NNaS$ [M + Na]$^+$ 352.1130, found 352.1130.

1-(Naphthalen-1-ylmethyl)-3-(phenylthio)-1H-indole (**5r**). Yield of 84% (61.3 mg) as a green oil; R_f = 0.35 (50:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, J = 10.2, 5.6 Hz, 2H), 7.79 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.52−7.45 (m, 2H), 7.37 (d, J = 8.2 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.25−7.20 (m, 2H), 7.16 (t, J = 7.2 Hz, 1H), 7.13−7.04 (m, 4H), 7.00 (t, J = 6.4 Hz, 2H), 5.69 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 137.4, 134.5, 133.8, 131.6, 131.0, 130.1, 129.1, 128.9, 128.8, 126.9, 126.2, 125.8, 125.7, 125.6, 124.8, 122.9, 122.6, 120.9, 120.1, 110.2, 101.6, 48.3 ppm; ν_{max} (KBr)/cm^{-1} 3040, 2930, 1654, 1634, 1603, 1455, 1408, 748; MS (EI) m/z 115, 141, 224, 302, 365; HRMS-ESI (m/z) calcd for $C_{25}H_{19}NNaS$ [M + Na]$^+$ 388.1130, found 388.1131.

3-(m-Tolylthio)-1H-indole (**6a**).[15g] Yield of 87% (41.6 mg) as a white solid; mp 123.2−124.8 °C; R_f = 0.34 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.40 (d, J = 2.0 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 7.02 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 8.0 Hz, 2H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 135.5, 134.7, 130.5, 129.5, 129.1, 126.3, 123.0, 122.7, 120.9, 120.4, 119.7, 111.6, 103.5, 20.9 ppm; ν_{max} (KBr)/cm^{-1} 3402, 3035, 2926, 1768, 1627, 1583, 1445, 1220, 744; MS (EI) m/z 77, 121, 148, 207, 239; HRMS-ESI (m/z) calcd for $C_{15}H_{13}NNaS$ [M + Na]$^+$ 262.0661, found 262.0656.

3-((4-Ethylphenyl)thio)-1H-indole (**6b**).[15f] Yield of 89% (45.0 mg) as a white solid; mp 116.2−117.4 °C; R_f = 0.34 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.40−7.35 (m, 2H), 7.23−7.20 (m, 1H), 7.14 (t, J = 7.6 Hz, 1H), 7.06−7.02 (m, 2H), 6.98 (d, J = 8.0 Hz, 2H), 2.53 (q, J = 7.6 Hz, 2H), 1.15 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 136.5, 135.8, 130.6, 129.2, 128.4, 126.3, 123.0, 120.9, 119.7, 111.6, 103.4, 28.3, 15.6 ppm; ν_{max} (KBr)/cm^{-1} 3408, 3052, 2938, 1635, 1569, 1453, 1226, 744; MS (EI) m/z 121, 148, 224, 253; HRMS-ESI (m/z) calcd for $C_{16}H_{16}NS$ [M + H]$^+$ 254.0998, found 254.0997.

3-((4-(tert-Butyl)phenyl)thio)-1H-indole (**6c**).[15f] Yield of 82% (46.1 mg) as a white solid; mp 136.1−137.5 °C; R_f = 0.35 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 2.4 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.18 (dd, J = 13.2, 8.0 Hz, 2H), 7.12−7.09 (m, 2H), 6.98 (d, J = 8.4 Hz, 2H), 1.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 136.5, 135.7, 130.6, 125.8, 125.8, 123.0, 122.7, 120.8, 119.8, 111.5, 103.4, 34.3, 31.3 ppm; ν_{max} (KBr)/cm^{-1} 3396, 3037, 2935, 1656, 1558, 1460, 1404, 1230, 746; MS (EI) m/z 77, 119, 148, 225, 266, 281; HRMS-ESI (m/z) calcd for $C_{18}H_{19}NNaS$ [M + Na]$^+$ 304.1130, found 304.1133.

3-((4-Methoxyphenyl)thio)-1H-indole (**6d**).[15f] Yield of 81% (41.3 mg) as a yellow solid; mp 110.2−111.5 °C; R_f = 0.28 (4:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.40 (d, J = 2.4 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.22 (d, J = 7.2 Hz, 1H), 7.14 (dd, J = 11.6, 8.0 Hz, 3H), 6.72 (d, J = 8.8 Hz, 2H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 136.5, 130.1, 129.6, 129.0, 128.6, 122.9, 120.8, 119.6, 114.5, 111.6, 104.6, 55.4 ppm; ν_{max} (KBr)/cm^{-1} 3383, 3046, 2961, 1648, 1583, 1452, 745; MS (EI) m/z 77, 120, 180, 240, 255; HRMS-ESI (m/z) calcd for $C_{15}H_{13}NNaOS$ [M + Na]$^+$ 278.0610, found 278.0614.

3-((2-Fluorophenyl)thio)-1H-indole (**6e**).[15c] Yield of 83% (40.3 mg) as a white solid; mp 145.6−146.9 °C; R_f = 0.34 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.46 (s, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H), 7.17 (t, J = 7.6 Hz, 1H), 7.06−6.96 (m, 2H), 6.79 (dt, J = 21.2, 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1 (d, J = 243.5 Hz), 136.5, 131.2, 129.1, 128.1 (d, J = 2.5 Hz), 126.6, 126.3 (d, J = 7.4 Hz), 124.4 (d, J = 3.4 Hz), 123.2, 121.1, 119.5, 115.1 (d, J = 21.1 Hz), 111.7, 100.8 ppm; ν_{max} (KBr)/cm^{-1} 3402, 3035, 1626, 1580, 1439, 1412, 748; MS (EI) m/z 77, 121, 148, 183, 243; HRMS-ESI (m/z) calcd for $C_{14}H_{10}FNNaS$ [M + Na]$^+$ 266.0410, found 266.0411.

3-((4-Fluorophenyl)thio)-1H-indole (**6f**).[15f] Yield of 85% (41.3 mg) as a white solid; mp 137.5−138.7 °C; R_f = 0.34 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.44−7.36 (m, 2H), 7.25 (t, J = 7.6 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 7.12−7.03 (m, 2H), 6.84 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0 (d, J = 244.0 Hz), 136.5, 134.1 (d, J = 3.1 Hz), 130.5, 128.9, 127.9 (d, J = 7.8 Hz), 123.2, 121.0, 119.6, 115.8 (d, J = 22.0 Hz), 111.7, 103.4 ppm; ν_{max} (KBr)/cm^{-1} 3400, 3028, 1633, 1584, 1526, 1443, 1406, 746; MS (EI) m/z 77, 121, 148, 211, 243; HRMS-ESI (m/z) calcd for $C_{14}H_{10}FNNaS$ [M + Na]$^+$ 266.0410, found 266.0415.

3-((2-Chlorophenyl)thio)-1H-indole (**6g**).[15g] Yield of 83% (43.0 mg) as a white solid; mp 135.6−137.3 °C; R_f = 0.35 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.58 (d, J = 2.0 Hz, 1H), 7.42 (d, J = 2.8 Hz, 1H), 7.28 (d, J = 8.8 Hz, 1H), 7.19−7.13 (m, 3H), 7.09−7.03 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 134.9, 132.1, 130.4, 128.9, 127.5, 126.9, 125.9, 125.1, 125.0, 123.6, 119.1, 112.8, 102.8 ppm; ν_{max} (KBr)/cm^{-1} 3388, 1653, 1556, 1498, 1470, 1410, 748; MS (EI) m/z 77, 155, 223, 259; HRMS-ESI (m/z) calcd for $C_{14}H_{11}ClNS$ [M + H]$^+$ 260.0295, found 260.0293.

3-((4-Chlorophenyl)thio)-1H-indole (**6h**).[15d] Yield of 78% (40.4 mg) as a white solid; mp 127.5−128.8 °C; R_f = 0.35 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.43 (dd, J = 11.6, 5.2 Hz, 2H), 7.26 (t, J = 7.6 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 7.10 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 136.5, 130.7, 130.6, 128.9, 128.8, 127.2, 123.2, 121.1, 119.5, 111.7, 102.5 ppm; ν_{max} (KBr)/cm^{-1} 3394, 3026, 1656, 1548, 1477, 1409, 746; MS (EI) m/z 77, 111, 148, 259; HRMS-ESI (m/z) calcd for $C_{14}H_{11}ClNS$ [M + H]$^+$ 260.0295, found 260.0291.

3-((2-Bromophenyl)thio)-1H-indole (**6i**). Yield of 72% (43.6 mg) as a white solid; mp 148.4−149.2 °C; R_f = 0.35 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.53 (dd, J =

DOI: 10.1021/acs.joc.6b01428
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8.4, 5.2 Hz, 2H), 7.40 (d, J = 7.6 Hz, 1H), 7.18−7.13 (m, 2H), 7.08 (ddd, J = 8.4, 5.6, 1.6 Hz, 3H), 7.02 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 135.2, 131.1, 130.4, 128.8, 127.3, 126.1, 125.9, 125.4, 125.1, 122.1, 119.0, 105.0, 104.6 ppm; ν_{max} (KBr)/cm^{-1} 3408, 3046, 1680, 1627, 1548, 1470, 1422, 738; MS (EI) m/z 111, 146, 224, 271, 303; HRMS-ESI (m/z) calcd for $C_{14}H_{11}BrNS$ [M + H]$^+$ 303.9790, found 303.9786.

3-((4-Bromophenyl)thio)-1H-indole (**6j**).[15d] Yield of 75% (45.5 mg) as a white solid; mp 140.0−141.3 °C; R_f = 0.35 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.75 (s, 1H), 7.44 (s, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.26 (d, J = 8.8 Hz, 1H), 7.16 (t, J = 7.6 Hz, 2H), 7.08 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 135.1, 131.9, 131.0, 128.9, 126.1, 125.9, 125.1, 122.2, 114.5, 113.1, 102.8 ppm; ν_{max} (KBr)/cm^{-1} 3404, 3046, 1637, 1546, 1445, 1400, 742; MS (EI) m/z 111, 191, 224, 271, 303; HRMS-ESI (m/z) calcd for $C_{14}H_{11}BrNS$ [M + H]$^+$ 303.9790, found 303.9791.

4-((1H-Indol-3-yl)thio)benzonitrile (**6k**). Yield of 62% (31.0 mg) as a white solid; mp 178.2−179.8 °C; R_f = 0.30 (2:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 7.95 (s, 1H), 7.61 (d, J = 2.4 Hz, 1H), 7.53−7.46 (m, 2H), 7.22−7.15 (m, 2H), 7.10 (dd, J = 7.2, 5.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 137.9, 132.7, 129.1, 128.9, 126.4, 126.0, 125.5, 125.3, 120.3, 112.7, 104.9, 104.1 ppm; ν_{max} (KBr)/cm $^{-1}$ 3406, 3028, 2249, 1657, 1626, 1553, 1454, 1412, 746; MS (EI) m/z 102, 146, 173, 218, 250; HRMS-ESI (m/z) calcd for $C_{15}H_{11}N_2S$ [M + H]$^+$ 251.0637, found 251.0637.

3-((2,3-Dichlorophenyl)thio)-1H-indole (**6l**). Yield of 71% (41.6 mg) as a white solid; mp 138.5−140.3 °C; R_f = 0.32 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.43 (dd, J = 9.2, 5.6 Hz, 2H), 7.31−7.25 (m, 1H), 7.21−7.16 (m, 1H), 7.01 (t, J = 2.0 Hz, 1H), 6.92 (d, J = 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 136.6, 135.2, 131.3, 128.7, 125.4, 124.9, 123.9, 123.7, 123.5, 121.4, 119.3, 111.8, 100.9 ppm; ν_{max} (KBr)/cm^{-1} 3384, 3043, 1628, 1549, 1451, 1408, 742; MS (EI) m/z 111, 148, 223, 258, 293; HRMS-ESI (m/z) calcd for $C_{14}H_{10}Cl_2NS$ [M + H]$^+$ 293.9906, found 293.9913.

3-((2,4,5-Trichlorophenyl)thio)-1H-indole (**6m**). Yield of 73% (47.7 mg) as a yellow solid; mp 144.8−145.5 °C; R_f = 0.30 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 2.4 Hz, 1H), 7.44 (d, J = 8.4 Hz, 1H), 7.40 (s, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 6.66 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 136.6, 131.6, 131.5, 130.4, 128.8, 128.7, 128.5, 127.1, 123.6, 121.5, 119.2, 112.0, 100.0 ppm; ν_{max} (KBr)/cm^{-1} 3392, 3056, 1637, 1618, 1542, 1448, 1411, 746; MS (EI) m/z 104, 128, 195, 257, 292, 327; HRMS-ESI (m/z) calcd for $C_{14}H_9Cl_3NS$ [M + H]$^+$ 327.9516, found 327.9516.

3-(Thiophen-3-ylthio)-1H-indole (**6n**). Yield of 64% (29.6 mg) as a white solid; mp 103.6−104.8 °C; R_f = 0.40 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.78 (d, J = 7.2 Hz, 1H), 7.33 (d, J = 2.4 Hz, 1H), 7.29 (dd, J = 6.8, 1.4 Hz, 1H), 7.18 (ddd, J = 14.0, 6.8, 1.2 Hz, 2H), 7.11 (dd, J = 5.2, 1.2 Hz, 1H), 7.08 (dd, J = 3.6, 1.2 Hz, 1H), 6.87−6.80 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 136.2, 129.9, 129.3, 128.6, 127.4, 127.3, 123.0, 120.8, 119.5, 111.6, 106.7 ppm; ν_{max} (KBr)/cm^{-1} 3388, 3042, 1630, 1546, 1445, 1415, 746; MS (EI) m/z 115, 154, 186, 198, 231; HRMS-ESI (m/z) calcd for $C_{12}H_9NNaS_2$ [M + Na]$^+$ 254.0069, found 254.0068.

3-(Pyridin-4-ylthio)-1H-indole (**6o**). Yield of 53% (23.9 mg) as a yellow solid; mp 152.6−154.3 °C; R_f = 0.43 (2:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.28 (d, J = 5.6 Hz, 2H), 7.55 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 2.8 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.33−7.28 (m, 1H), 7.22−7.17 (m, 1H), 6.95 (d, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 148.7, 136.6, 131.3, 128.6, 123.5, 121.3, 120.0, 119.3, 111.9, 99.4 ppm; ν_{max} (KBr)/cm^{-1} 3406, 3048, 1650, 1573, 1506, 1445, 1412, 744; MS (EI) m/z 77, 121, 148, 199, 226; HRMS-ESI (m/z) calcd for $C_{13}H_{11}N_2S$ [M + H]$^+$ 227.0637, found 227.0645.

3,3′-Bis(phenylthio)-1H,1′H-2,2′-biindole (**8**). Yield of 41% (36.7 mg) as a white solid; mp 172.3−173.9 °C; R_f = 0.43 (2:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 8.67 (s, 1H), 7.60 (dd, J = 17.6, 8.8 Hz, 2H), 7.42 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.28 (d, J = 7.6 Hz, 2H), 7.22−7.02 (m, 11H), 6.87 (s, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 136.8, 136.2, 133.9, 131.0, 129.8, 129.2, 129.1, 127.7, 126.3, 125.6, 123.8, 123.3, 121.4, 121.4, 120.6, 120.5, 119.4, 119.3, 111.7, 111.4, 111.0, 100.5, 98.7 ppm; ν_{max} (KBr)/cm^{-1} 3404, 3056, 1675, 1626, 1583, 1526, 1443, 748; HRMS-ESI (m/z) calcd for $C_{28}H_{20}N_2NaS_2$ [M + Na]$^+$ 471.0960, found 471.0958.

3-((4-Fluorophenyl)thio)imidazo[1,2-a]pyridine (**10a**).[17f] Yield of 78% (38.1 mg) as a white solid; mp 82.3−83.5 °C; R_f = 0.40 (5:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 6.8 Hz, 1H), 7.99 (s, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.30 (d, J = 6.8 Hz, 1H), 7.10−6.99 (m, 2H), 6.95−6.83 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6 (d, J = 246.4 Hz), 148.0, 142.2, 130.0 (d, J = 3.2 Hz), 128.5 (d, J = 8.0 Hz), 126.0, 124.1, 118.2, 116.4 (d, J = 22.3 Hz), 113.2, 111.1 ppm; ν_{max} (KBr)/cm^{-1} 3046, 1640, 1616, 1508, 1483, 1426; MS (EI) m/z 78, 105, 139, 212, 244.

3-((4-Fluorophenyl)thio)-6-methylimidazo[1,2-a]pyridine (**10b**).[17f] Yield of 71% (36.6 mg) as a yellow oil; R_f = 0.40 (5:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.93 (s, 1H), 7.59 (d, J = 9.2 Hz, 1H), 7.14 (d, J = 9.2 Hz, 1H), 7.05−6.97 (m, 2H), 6.90 (t, J = 8.0 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5 (d, J = 246.1 Hz), 147.1, 142.2, 130.4 (d, J = 3.1 Hz), 129.2, 128.2 (d, J = 8.0 Hz), 123.2, 121.8, 117.3, 116.3 (d, J = 22.2 Hz), 110.4, 18.3 ppm; ν_{max} (KBr)/cm^{-1} 3054, 2923, 1638, 1610, 1522, 1415; MS (EI) m/z 78, 105, 149, 225, 258.

3-((4-Methoxyphenyl)thio)-6-methylimidazo[1,2-a]pyridine (**10c**).[17f] Yield of 65% (35.1 mg) as a yellow solid; mp 118.4−119.8 °C; R_f = 0.26 (8:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 6.4 Hz, 1H), 7.90 (s, 1H), 7.46 (s, 1H), 7.09 (t, J = 7.6 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 6.67 (d, J = 6.0 Hz, 2H), 6.36 (d, J = 7.2 Hz, 1H), 3.92 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 142.5, 137.0, 126.9, 126.1, 124.0, 123.7, 121.3, 116.5, 115.6, 110.7, 55.9, 21.3 ppm; ν_{max} (KBr)/cm $^{-1}$ 3045, 2927, 1641, 1616, 1487, 1409; MS (EI) m/z 78, 119, 139, 206, 237, 270.

6-Chloro-3-((4-chlorophenyl)thio)imidazo[1,2-a]pyridine (**10d**).[17f] Yield of 72% (42.3 mg) as a white solid; mp 118.8−120.4 °C; R_f = 0.22 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.99 (s, 1H), 7.64 (d, J = 9.2 Hz, 1H), 7.25 (d, J = 9.6 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 143.2, 133.1, 132.5, 129.5, 127.6, 127.5, 122.1, 121.9, 118.6, 111.2 ppm; ν_{max} (KBr)/cm^{-1} 3038, 1646, 1585, 1483, 1409; MS (EI) m/z 78, 105, 149, 224, 259, 294.

2-Methyl-3-(p-tolylthio)imidazo[1,2-a]pyridine (**10e**).[17f] Yield of 83% (42.2 mg) as a white solid; mp 102.5−103.8 °C; R_f = 0.25 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 6.8 Hz, 1H), 7.57 (d, J = 9.2 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 6.97 (d, J = 7.6 Hz, 2H), 6.85 (d, J = 7.6 Hz, 2H), 6.75 (t, J = 6.8 Hz, 1H), 2.59 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 146.8, 135.9, 131.8, 129.9, 126.0, 125.9, 124.3, 116.9, 112.5, 108.0, 20.8, 13.9 ppm; ν_{max} (KBr)/cm^{-1} 3042, 2926, 1618, 1587, 1459, 1411, 1026; MS (EI) m/z 78, 119, 163, 221, 254.

2-(tert-Butyl)-3-((4-chlorophenyl)thio)imidazo[1,2-a]pyridine (**10f**).[17f] Yield of 80% (50.6 mg) as a white solid; mp 111.2−113.0 °C; R_f = 0.24 (10:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 6.8 Hz, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.25 (t, J = 7.6 Hz, 1H), 7.13 (d, J = 8.0 Hz, 2H), 6.82−6.72 (m, 3H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 145.8, 134.6, 131.4, 129.4, 126.0, 125.9, 123.6, 117.5, 112.9, 104.1, 34.0, 30.4 ppm; ν_{max} (KBr)/cm^{-1} 3045, 2925, 2836, 1646, 1483, 1412, 1238; MS (EI) m/z 78, 105, 163, 189, 241, 283, 301, 316.

6-Methyl-2-phenyl-3-(phenylthio)imidazo[1,2-a]pyridine (**10g**).[17e] Yield of 75% (47.4 mg) as a white solid; mp 172.4−173.7 °C; R_f = 0.32 (8:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24−8.14 (m, 2H), 8.05 (s, 1H), 7.62 (d, J = 9.2 Hz, 1H), 7.44−7.38 (m, 2H), 7.37−7.31 (m, 1H), 7.22−7.17 (m, 2H), 7.15 (dd, J = 9.0, 1.6 Hz, 1H), 7.11 (dd, J = 8.4, 6.4 Hz, 1H), 7.02−6.97 (m, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 146.2, 135.6, 133.6, 129.8, 129.5, 128.5, 128.4, 128.3, 125.9, 125.5, 123.0, 122.2, 117.0, 105.7, 18.4 ppm; ν_{max} (KBr)/cm $^{-1}$ 3048, 2926, 2830, 1642, 1485, 1437, 1336, 1025; MS (EI) m/z 92, 141, 195, 239, 277, 316.

DOI: 10.1021/acs.joc.6b01428
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*3-((4-Chlorophenyl)thio)-2-(p-tolyl)imidazo[1,2-a]pyridine (**10h**).*[17e] Yield of 76% (53.2 mg) as a white solid; mp 132.2−133.9 °C; R_f = 0.30 (8:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19−8.13 (m, 2H), 8.02 (s, 1H), 7.63 (d, J = 8.8 Hz, 1H), 7.46−7.39 (m, 2H), 7.36 (ddd, J = 7.2, 3.6, 1.2 Hz, 1H), 7.21−7.15 (m, 3H), 6.94−6.88 (m, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 146.3, 134.1, 133.3, 131.9, 130.0, 129.6, 128.6, 128.5, 128.2, 126.7, 123.2, 122.0, 117.1, 105.1, 18.4 ppm; ν_{max} (KBr)/cm $^{-1}$ 3037, 2928, 1625, 1489, 1412, 1328, 1026; MS (EI) m/z 92, 195, 239, 277, 317, 350.

*5-Methyl-2-phenyl-3-(phenylthio)benzofuran (**10k**).*[27] Yield of 46% (29.1 mg) as a white solid; mp 76.3−77.5 °C; R_f = 0.35 (50:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 7.6 Hz, 2H), 7.51 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.44−7.38 (m, 2H), 7.37−7.32 (m, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.21−7.15 (m, 1H), 7.10 (d, J = 7.6 Hz, 2H), 6.98 (d, J = 7.6 Hz, 2H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 153.9, 138.2, 136.3, 130.9, 130.3, 129.7, 128.5, 126.8, 125.6, 125.2, 124.7, 123.4, 120.5, 111.3, 104.7, 21.6 ppm; ν_{max} (KBr)/cm $^{-1}$ 3038, 2930, 1633, 1484, 1410, 1028; MS (EI) m/z 119, 165, 207, 284, 301, 316.

General Procedure for the Synthesis of 11. Following a reported procedure,[18] a mixture of 3-phenylthioindole (**3aw**, 0.1 mmol), benzyl bromide (0.15 mmol), KOH (0.2 mmol), and DMSO (1 mL) was reacted at room temperature for 24 h. After the reaction was finished, the reaction mixture was quenched with water, extracted with ethyl acetate, washed with brine, dried over $MgSO_4$, and concentrated. Column chromatography on silica (50:1 petroleum ether/ethyl acetate) gave desired product **11**.

*1-Benzyl-5-chloro-2-methyl-3-(phenylthio)-1H-indole (**11**).* Yield of 83% (30.1 mg) as a yellow oil; R_f = 0.34 (50:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 2.0 Hz, 1H), 7.60−7.56 (m, 3H), 7.17 (t, J = 8.4 Hz, 3H), 7.11 (dd, J = 8.8, 2.0 Hz, 1H), 7.06 (d, J = 7.2 Hz, 1H), 7.01 (d, J = 7.6 Hz, 2H), 6.97 (d, J = 7.2 Hz, 2H), 5.37 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 139.1, 136.6, 135.4, 131.2, 129.0, 128.8, 127.8, 126.7, 125.9, 125.4, 124.7, 122.4, 118.6, 110.7, 99.1, 47.6, 11.0 ppm; ν_{max} (KBr)/cm^{-1} 3048, 2937, 1630, 1458, 1407, 1034, 744; MS (EI) m/z 91, 152, 237, 363; HRMS-ESI (m/z) calcd for $C_{22}H_{19}ClNS$ $[M + H]^+$ 364.0921, found 364.0915.

General Procedure for the Synthesis of 12. Following a reported procedure,[19] a mixture of 3-phenylthioindole (**3aw**, 0.1 mmol), iodobenzene (0.15 mmol), Cu_2O (0.01 mmol), KOH (0.2 mmol) and DMSO (1 mL) was stirred at 120 °C under N_2 atmosphere for 18 h. After cooling the reaction to room temperature, the mixture was quenched by water and extracted with CH_2Cl_2 three times. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The residue was purified by flash column chromatography on silica gel (50:1 hexanes/ethyl acetate) to afford desired product **12**.

*5-Chloro-2-methyl-1-phenyl-3-(phenylthio)-1H-indole (**12**).* Yield of 76% (26.5 mg) as a yellow solid; mp 143.4−144.6 °C; R_f = 0.30 (50:1 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63−7.53 (m, 3H), 7.50 (d, J = 6.8 Hz, 1H), 7.35 (d, J = 7.2 Hz, 2H), 7.19 (t, J = 7.2 Hz, 2H), 7.10−7.01 (m, 5H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 138.8, 137.2, 136.4, 131.0, 129.8, 128.9, 128.7, 127.8, 127.1, 125.7, 124.8, 122.6, 118.4, 111.5, 100.0, 11.8 ppm; ν_{max} (KBr)/cm $^{-1}$ 3038, 2926, 1653, 1624, 1538, 1446, 1034, 748; MS (EI) m/z 118, 157, 204, 238, 281, 314, 349; HRMS-ESI (m/z) calcd for $C_{21}H_{16}ClNNaS$ $[M + Na]^+$ 372.0584, found 372.0589.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01428.

Copies of ^{1}H and ^{13}C NMR spectra data for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank the National Program on Key Research Project (2016YFA0602900), the National Natural Science Foundation of China (21490572, 21502055, and 21420102003), Pearl River S&T Nova Program of Guangzhou (201610010160), and the China Postdoctoral Science Foundation (2016T90779 and 2015M572303) for financial support.

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DOI: 10.1021/acs.joc.6b01428
J. Org. Chem. 2016, 81, 7771−7783