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A Visible-Light-Promoted Aerobic Metal-Free C-3 Thiocyanation of Indoles

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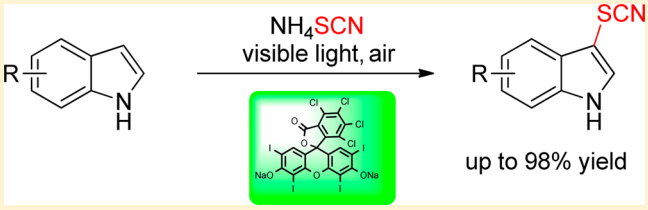
Supporting Information

ABSTRACT: A simple and efficient visible-light-promoted method for the C-3 thiocyanation of indoles has been developed. The transformation uses Rose Bengal as the photocatalyst and air as the terminal oxidant. The reaction is mild, high-yielding, and environmentally benign.

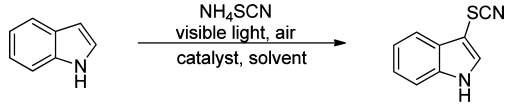


Organosulfur compounds belong to an important class of compounds due to their broad biological and pharmaceutical activity. Hence, many efforts have been devoted to the direct introduction of sulfur moieties into organic carbon skeletons.[1] Among these, thiocyanation is a convenient carbon−sulfur bond formation reaction. The products of thiocyanation, thiocyanates, are useful and versatile intermediates in the synthesis of sulfur-containing heterocycles.[2] Additionally, thiocyanates can be easily converted to other sulfur functional groups, such as thiophenols.[3] Many methods have been developed for electrophilic thiocyanation using thiocyanate salt in the presence of CAN,[4] hypervalent iodine reagents,[5] oxone,[6] $Mn(OAc)_3$,[7] or other oxidants.[8] However, these methods typically suffer from drawbacks, such as using stoichiometric oxidants or generating large amounts of heavy-metal wastes.

Molecular oxygen is the most desirable oxidant because it is abundant, low cost, and environmentally benign. Recently, visible-light-mediated aerobic oxidation has proven to be a versatile and environmentally friendly strategy.[9] In continuation of our interests in photoredox aerobic oxidations,[10] we envisioned that the thiocyanate anion would be oxidized under aerobic photoredox conditions to form a thiocyanate radical, which would participate in electrophilic thiocyanation.

We started our investigation of visible-light-mediated thiocyanation using 1*H*-indole (**1a**) as the model substrate and the thiocyanate radical trap and 3 equiv of ammonium thiocyanate as the thiocyanating agent in the presence of 1 mol % $Ru(bpy)_3Cl_2{\cdot}6H_2O$ in MeCN. The reaction was carried out open to the air, under irradiation with a 14 W compact fluorescent lamp. The desired product 3-thiocyanato-1*H*-indole was obtained in 87% yield after 24 h (Table 1, entry 1). Inspired by this result, we screened other parameters. Although the two Ru-trisbipyridyl catalysts were most effective in MeCN (87% and 94%, Table 1, entries 1 and 2), and Rose Bengal gave a lower yield (68%, Table 1, entry 4), the relatively low cost and the transition-metal-free nature of Rose Bengal motivated us to optimize the reaction conditions using Rose Bengal as the photocatalyst. Next, the reaction was investigated in several common organic solvents, such as MeOH, DMF, THF, and $CHCl_3$ (Table 1, entries 6−9). To our delight, **2a** was obtained in quantitative yield in THF after 18 h (Table 1, entry 8). Attempts to use KSCN instead of NH_4SCN gave unsatisfactory

Table 1. Optimization of Reaction Conditions[a,b]



1a **2a**

entry	catalyst	solvent	yield (%)[b]
1	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	MeCN	87
2	$Ru(bpy)_3(PF_6)_2$	MeCN	94
3	$Ir(ppy)_3$	MeCN	47
4	Rose Bengal	MeCN	68
5	Eosin Y	MeCN	33
6	Rose Bengal	MeOH	16
7	Rose Bengal	DMF	44
8[c]	Rose Bengal	THF	100
9	Rose Bengal	$CHCl_3$	trace
10[c,d]	Rose Bengal	THF	48
11[c,e]	Rose Bengal	THF	78
12[c,f]	Rose Bengal	THF	94
13		THF	28
14[g]	Rose Bengal	THF	n.r.
15[h]	Rose Bengal	THF	10

[a]Reaction conditions: 1*H*-indole (**1a**, 0.5 mmol), NH_4SCN (1.5 mmol, 3 equiv), catalyst (1 mol %), solvent (5 mL), open to the air, irradiation under a 14 W CFL at room temperature for 24 h. [b]HPLC yield. [c]For 18 h. [d]KSCN was used instead of NH_4SCN. [e]1.5 equiv of NH_4SCN was used. [f]2 equiv of NH_4SCN was used. [g]In the dark. [h]Degassed with N_2.

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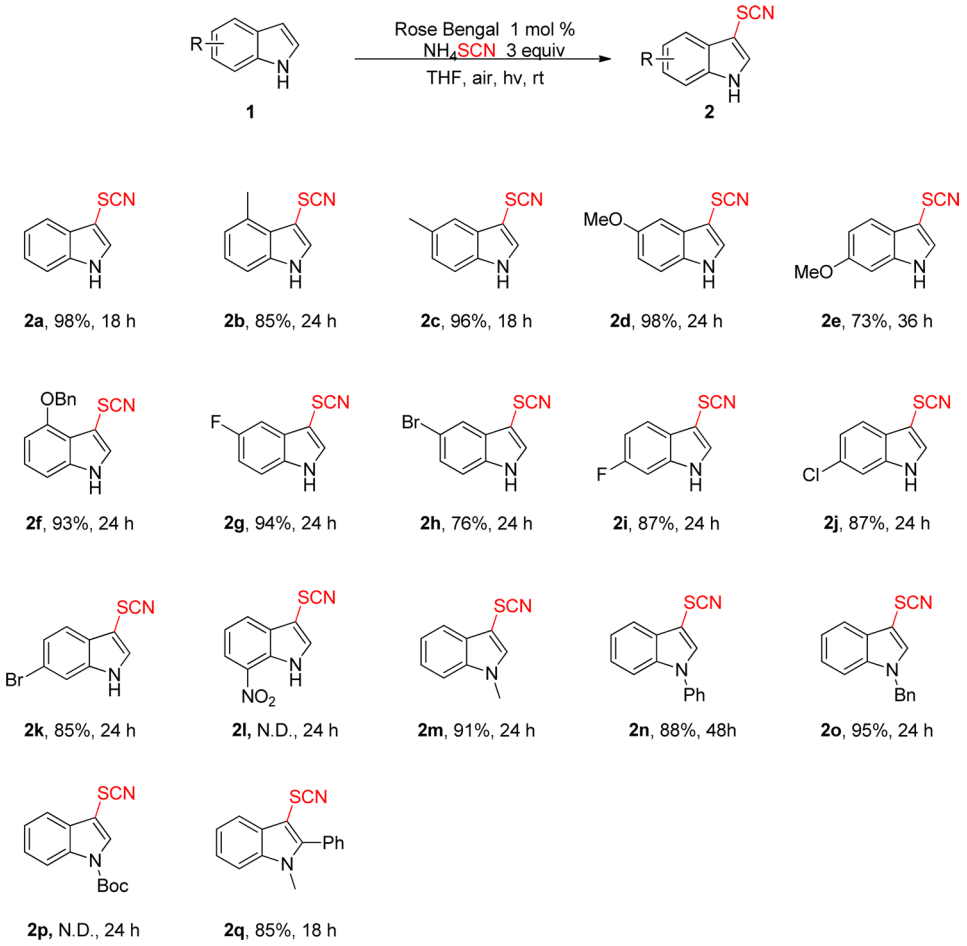
Scheme 1. Scope of Thiocyanation[a,b]



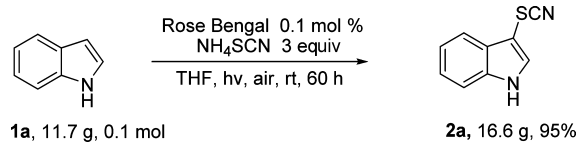
[a]Reaction conditions: indole (**1**, 0.5 mmol), NH_4SCN (1.5 mmol), Rose Bengal (1 mol %), THF (5 mL), open to the air, irradiation under a 14 W CFL at room temperature until reaction completion by HPLC or TLC. [b]Isolated yield.

results (48%, entry 10). Decreasing the amount of NH_4SCN afforded compound **3a** in lower yields (78%, and 94% respectively, Table 1, entries 11 and 12). The reactions only afforded 28, 0, or 10% yields, respectively, in the absence of catalyst, light, or O_2, indicating that all of these components are critical for the reaction (Table 1, entries 13−15).

With the optimized reaction conditions in hand, we then extended the reaction with a range of indoles. As illustrated in Scheme 1, this reaction was compatible with many functional groups. Indoles containing a methyl group at C-4 and C-5 positions reacted smoothly, affording the corresponding products in 85% and 96% yields, respectively (Scheme 1, **2b** and **2c**). Electron-donating group substituted indoles, such as 5-OMe, 6-OMe, and 4-OBn, gave the corresponding 3-thiocyanoindoles in good to excellent yields (98, 73, and 93%, Scheme 1, **2d**−**2f**). Moreover, the reaction worked very well with indoles bearing weak electron-withdrawing groups (Scheme 1, **2g**−**2k**), but was shut down by the strongly electron-withdrawing nitro group (Scheme 1, **2l**). For *N*-substituted indoles, such as *N*-methyl-, *N*-phenyl-, and *N*-benzyl indoles, the corresponding 3-thiocyano products were afforded in 91, 88, and 95% yields respectively (Scheme 1, **2m**−**2o**). Not surprisingly, the reaction of *tert*-butyl 1*H*-indole-1-carboxylate did not occur due to the electron-withdrawing effect of the Boc group (Scheme 1, **2p**). For the indole with a phenyl group at the C-2 position, **2q** was formed in 85% yield under identical conditions (Scheme 1, **2q**), indicating that the reaction was not affected by C-2 steric hindrance.

To demonstrate the utility of this visible-light-mediated protocol, several reactions were carried out. First, the reaction was performed under an oxygen balloon and the reaction time was reduced to 8 h. We also did this reaction with 100 mmol of **1a**, and the catalyst loading was reduced to 0.1 mol %. To our delight, **2a** was obtained in 95% isolated yield with a prolonged time (Scheme 2).

Scheme 2. Gram-Scale Thiocyanation of 1a



In order to better understand the mechanism of this reaction, a series of control experiments were performed, and the results are presented in Scheme 3. As expected, no desired product was obtained when 3-methylindole (Scheme 3a, **1r**) was subjected to the reaction under the optimized conditions. It is well-known that Rose Bengal is a good $^1O_2$-generating photosensitizer under visible light irradiation. To rule out the possibility of oxidation of SCN^- by $^1O_2$, the reaction was conducted using

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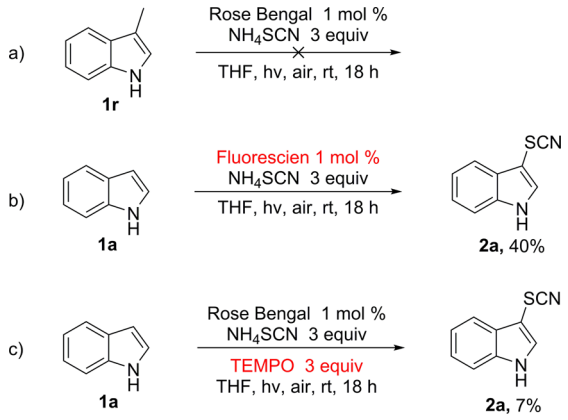
Scheme 3. Control Experiments



fluorescein as the photocatalyst, which does not generate $^1O_2$, and **2a** was formed in 40% yield (Scheme 3b). A fluorescence emission quenching study also showed no interaction of RB* with air under the reaction conditions (see the Supporting Information). Hence, $^1O_2$ was unlikely a key participant in the reaction. When 3 equiv of 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO), a radical scavenger, were added to the reaction, only a 7% yield of product **2a** was obtained (Scheme 3c). Fluorescence quenching experiment showed that the addition of TEMPO did not reduce the emission intensity of RB*, showing that the reaction was not inhibited by the oxidation of TEMPO by RB*.

To prove NH_4SCN was oxidized by excited Rose Bengal (RB*), we carried out fluorescence quenching experiments (Stern–Volmer studies) of RB (Figure 1). Indeed, it was found

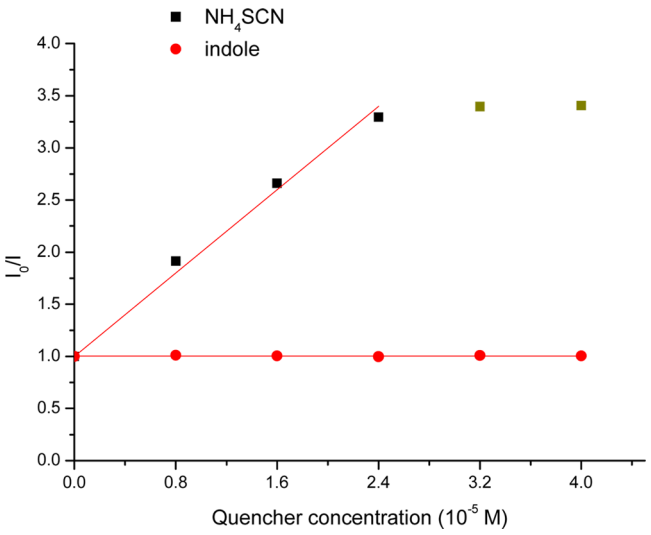


Figure 1. Plot of fluorescence intensity of Rose Bengal vs concentration of NH_4SCN or indole (for details, see the Supporting Information).

that the emission intensity of RB* was dramatically diminished in the presence of NH_4SCN. On the contrary, there is no such effect when indole was added. Although we do not understand why the emission intensity levels off at high concentration of NH_4SCN, it is very likely that NH_4SCN rather than indole was oxidized by excited RB* in the photoredox cycle.

On the basis of our observations and literature reports, a plausible mechanism is proposed in Scheme 4. Under visible-light irradiation, Rose Bengal is converted to the excited RB*. A single electron transfer between $^-$SCN and RB* affords •SCN radical **A** and generates an $RB^{\bullet-}$ radical anion. The photoredox cycle is completed by the molecular oxygen oxidation of $RB^{\bullet-}$ to the ground state Rose Bengal. After that, an electrophilic addition of radical **A** to **1a** occurs, leading to intermediate **B**. Intermediate **B** was oxidized to give cation intermediate **C**. Rearomatization of intermediate **C** by losing a proton affords the final 3-thiocyanoindole product **2a**. $(NH_4)_2SO_4$ was identified as the major byproduct. Presumably, it is formed by oxidation of $^-$SCN by a superoxide radical or the related species.[11] It explains why at least one extra equivalent of NH_4SCN is required for the completion of the reaction.

In conclusion, we have developed a simple and mild C-3 thiocyanation of indoles. The reaction uses an inexpensive and readily available organic dye, Rose Bengal, as the photocatalyst and air as the terminal oxidant. Generally, the reaction is high-yielding, efficient, and scalable. The catalyst loading could be lowered to 0.1 mol %. Moreover, no heavy-metal waste was generated during the process. It is a practical and environmentally benign protocol that could prove useful to the chemical and pharmaceutical industries.

EXPERIMENTAL SECTION

General Information. All reactions were carried out in a test tube opened to the air unless specified. Starting materials **1n**, **1o**, 1p were synthesized according to literature methods.[12] Other chemicals including solvents were purchased from commercial sources and were used without further purification. Column chromatography was generally performed on silica gel (300–400 mesh). Thin-layer chromatography (TLC) was visualized using UV light. NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a 400 MHz spectrometer. Chemical shifts were reported in parts per million (δ) relative to TMS (0.00 ppm) for ^{1}H NMR data and $CDCl_3$ (77.16 ppm) or DMSO-d_6 (39.52 ppm) for ^{13}C NMR data. The abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, and m = multiplet. Mass spectra were measured on a single quadrupole mass spectrometer with electrospray ionization. HRMS spectra were measured on a TOF mass spectrometer with chemical ionization. Melting points are uncorrected.

General Procedure. To a solution of indole **1** (0.5 mmol) and ammonium thiocyanate (1.5 mmol) in THF (5 mL) was added Rose Bengal (1 mol %). The reaction mixture was open to the air and stirred under a 14 W CFL irradiation at room temperature. After reaction completion monitored by HPLC or TLC, the reaction mixture was diluted with dichloromethane (10 mL), filtered through basic alumina powder (200–300 mesh), and rinsed with dichloromethane (30 mL) to remove precipitate (mostly $(NH_4)_2SO_4$) and most of the Rose Bengal. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography with petroleum ether/ethyl acetate (3:1–10:1) to give the desired 3-thiocyano indole product.

3-Thiocyanato-1*H*-indole (2a).[7] The general procedure was followed using 1*H*-indole (58.6 mg, 0.5 mmol) as the starting material. Purification by column chromatography yielded **2a** (85.4 mg, 98%) as a white solid. mp = 72–74 °C (lit. 73–76 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 7.78–7.73 (1H), 7.36–7.33 (2H), 7.29–7.24 (2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.1, 131.3, 127.7, 123.8, 121.9, 118.6, 112.5, 112.3, 91.5. MS (ESI) *m*/*z*: Calcd for $[M + H]^+$ $C_9H_7N_2S$ 175.03; Found 175.1.

4-Methyl-3-thiocyanato-1*H*-indole (2b).[7] The general procedure was followed using 4-methyl-1*H*-indole (65.6 mg, 0.5 mmol) as the starting material. Purification by column chromatography yielded **2b** (80.1 mg, 85%) as a white solid. mp = 129–131 °C (lit. 127–128 °C). ^{1}H NMR (400 MHz, DMSO) δ 11.99 (s, 1H), 7.95–7.94 (1H), 7.37–7.35 (1H), 7.15–7.11 (1H), 6.95–6.93 (1H), 2.85 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 136.8, 134.2, 129.4, 125.3, 123.0, 122.6,

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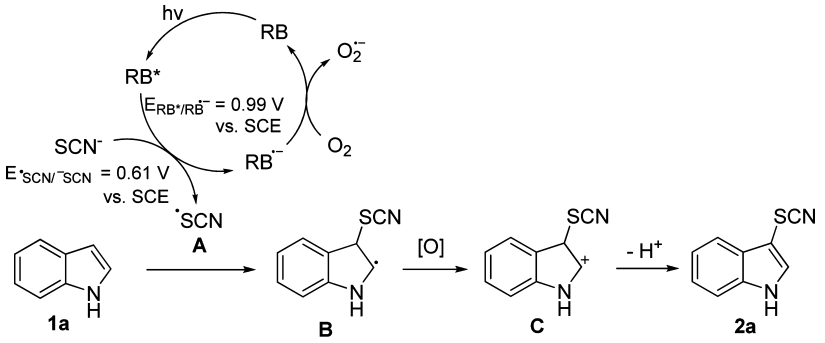
Scheme 4. Plausible Mechanism



113.9, 110.8, 89.4, 18.7. MS (ESI) *m*/*z*: Calcd for $[M + H]^+$ $C_{10}H_9N_2S$ 189.05; Found 189.1.

5-Methyl-3-thiocyanato-1*H*-indole (2c). The general procedure was followed using 5-methyl-1*H*-indole (65.6 mg, 0.5 mmol) as the starting material. Purification by column chromatography yielded **2c** (90.6 mg, 96%) as a white solid. mp = 88−90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.53 (s, 1H), 7.30 (1H), 7.24−7.22 (1H), 7.08−7.06 (1H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.4, 131.5, 131.3, 127.9, 125.5, 118.1, 112.6, 112.0, 90.7, 21.6. MS (ESI) *m*/*z*: Calcd for $[M + H]^+$ $C_{10}H_9N_2S$ 189.05; Found 189.1. HRMS (CI-TOF) *m*/*z*: Calcd for $[M]^+$ $C_{10}H_8N_2S$ 188.0408; Found 188.0415.

5-Methoxy-3-thiocyanato-1*H*-indole (2d).[8g] The general procedure was followed using 5-methoxy-1*H*-indole (73.5 mg, 0.5 mmol) as the starting material. Purification by column chromatography yielded **2c** (100.0 mg, 98%) as a pale yellow solid. mp = 123−125 °C (lit. 121−122 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.44−7.43 (1H), 7.30−7.27 (1H), 7.18−7.17 (1H), 6.95−6.92 (1H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 131.6, 131.0, 128.6, 114.6, 113.2, 112.2, 99.9, 91.5, 56.0. MS (ESI) *m*/*z*: Calcd for $[M + H]^+$ $C_{10}H_9N_2OS$ 205.04; Found 205.1.

6-Methoxy-3-thiocyanato-1*H*-indole (2e). The general procedure was followed using 6-methoxy-1*H*-indole (73.5 mg, 0.5 mmol) as the starting material. Purification by column chromatography yielded **2e** (75.2 mg, 73%) as a pale yellow solid. mp = 107−109 °C. ^{1}H NMR (400 MHz, DMSO) δ 11.79 (s, 1H), 7.84 (1H), 7.55−7.53 (1H), 7.02 (1H), 6.92−6.89 (1H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 156.7, 137.2, 131.9, 121.5, 118.4, 112.3, 111.5, 95.5, 89.2, 55.4. HRMS (CI-TOF) *m*/*z*: Calcd for $[M]^+$ $C_{10}H_8N_2OS$ 204.0357; Found 204.0367.

4-(Benzyloxy)-3-thiocyanato-1*H*-indole (2f).[7] The general procedure was followed using 4-(benzyloxy)-1*H*-indole (111.6 mg, 0.5 mmol) as the starting material. Purification by column chromatography yielded **2f** (131.0 mg, 93%) as a pale yellow solid. mp = 109−112 °C (lit. 106−107 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.57−7.55 (2H), 7.37−7.35 (2H), 7.29 (1H), 7.14−7.13 (1H), 7.06 (1H), 6.88−6.86 (1H), 6.61−6.59 (1H), 5.18 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 138.1, 137.0, 129.7, 128.6, 127.9, 127.4, 124.7, 117.1, 113.6, 105.6, 102.9, 91.4, 70.2. MS (ESI) *m*/*z*: Calcd for $[M + Na]^+$ $C_{16}H_{12}N_2NaOS$ 303.06; Found 303.0.

5-Fluoro-3-thiocyanato-1*H*-indole (2g).[13] The general procedure was followed using 5-fluoro-1*H*-indole (67.6 mg, 0.5 mmol) as the starting material. Purification by column chromatography yielded **2f** (89.8 mg, 94%) as white solid. mp = 108−110 °C (lit. 110−112 °C). ^{1}H NMR (400 MHz, DMSO) δ 12.15 (s, 1H), 8.08 (1H), 7.59−7.56 (1H), 7.44−7.41 (1H), 7.17−7.12 (1H). ^{13}C NMR (101 MHz, DMSO) δ 158.1 (d, *J* = 235.4 Hz), 135.1, 133.0, 128.2 (d, *J* = 10.5 Hz), 114.3 (d, *J* = 9.8 Hz), 112.2, 111.3 (d, *J* = 26.2 Hz), 102.7 (d, *J* = 24.5 Hz), 89.7 (d, *J* = 4.7 Hz). MS (ESI) *m*/*z*: Calcd for $[M + Na]^+$ $C_9H_5FN_2NaS$ 215.01; Found 215.0.

5-Bromo-3-thiocyanato-1*H*-indole (2h).[8h] The general procedure was followed using 5-bromo-1*H*-indole (98.0 mg, 0.5 mmol) as the starting material. Purification by column chromatography yielded **2h** (95.8 mg, 76%) as a white solid. mp = 138−141 °C (lit. 125−127 °C). ^{1}H NMR (400 MHz, DMSO) δ 12.23 (s, 1H), 8.07−8.06 (1H), 7.84−7.83 (1H), 7.55−7.52 (1H), 7.43−7.40 (1H). ^{13}C NMR (101 MHz, DMSO) δ 135.1, 134.6, 129.3, 125.6, 120.0, 114.9, 113.8, 112.1, 89.4. MS (ESI) *m*/*z*: Calcd for $[M + Na]^+$ $C_9H_5BrN_2NaS$ 274.93; Found 274.9.

6-Fluoro-3-thiocyanato-1*H*-indole (2i).[14] The general procedure was followed using 6-fluoro-1*H*-indole (67.6 mg, 0.5 mmol) as the starting material. Purification by column chromatography yielded **2i** (83.0 mg, 87%) as a white solid. mp = 104−106 °C. ^{1}H NMR (400 MHz, DMSO) δ 12.07 (s, 1H), 8.01 (s, 1H), 7.69−7.66 (1H), 7.37−7.34 (1H), 7.16−7.11 (1H). ^{13}C NMR (101 MHz, DMSO) δ 159.6 (d, *J* = 237.0 Hz), 136.3 (d, *J* = 12.9 Hz), 133.9 (d, *J* = 2.9 Hz), 124.1, 119.0 (d, *J* = 10.4 Hz), 112.1, 109.8 (d, *J* = 24.9 Hz), 99.0 (d, *J* = 26.1 Hz), 89.9. MS (ESI) *m*/*z*: Calcd for $[M + Na]^+$ $C_9H_5FN_2NaS$ 215.01; Found 215.0.

6-Chloro-3-thiocyanato-1*H*-indole (2j). The general procedure was followed using 6-chloro-1*H*-indole (75.8 mg, 0.5 mmol) as the starting material. Purification by column chromatography yielded **2j** (90.8 mg, 87%) as a white solid. mp = 124−126 °C. ^{1}H NMR (400 MHz, DMSO) δ 12.13 (s, 1H), 8.05 (s, 1H), 7.69−7.68 (1H), 7.61 (1H), 7.29−7.27 (1H). ^{13}C NMR (101 MHz, DMSO) δ 136.7, 134.3, 127.7, 126.2, 121.5, 119.2, 112.5, 112.1, 90.2. MS (ESI) *m*/*z*: Calcd for $[M + Na]^+$ $C_9H_5ClN_2NaS$ 230.98; Found 230.9. HRMS (CI-TOF) *m*/*z*: Calcd for $[M]^+$ $C_9H_5ClN_2S$ 207.9862; Found 207.9866.

6-Bromo-3-thiocyanato-1*H*-indole (2k). The general procedure was followed using 6-bromo-1*H*-indole (98.0 mg, 0.5 mmol) as the starting material. Purification by column chromatography yielded **2k** (107.6 mg, 85%) as a white solid. mp = 139−142 °C. ^{1}H NMR (400 MHz, DMSO) δ 12.14 (s, 1H), 8.04−8.03 (1H), 7.76−7.75 (1H), 7.64−7.62 (1H), 7.41−7.38 (1H). ^{13}C NMR (101 MHz, DMSO) δ 137.2, 134.2, 126.5, 124.1, 119.6, 115.6, 115.4, 112.1, 90.2. MS (ESI) *m*/*z*: Calcd for $[M + Na]^+$ $C_9H_5BrN_2NaS$ 274.93; Found 275.0. HRMS (CI-TOF) *m*/*z*: Calcd for $[M]^+$ $C_9H_5BrN_2S$ 251.9357; Found 251.9361.

1-Methyl-3-thiocyanato-1*H*-indole (2m).[8h] The general procedure was followed using 1-methyl-1*H*-indole (62.4 mg, 0.5 mmol) as the starting material. Purification by column chromatography yielded **2m** (85.3 mg, 91%) as a white solid. mp = 76−78 °C (lit. 79−81 °C). ^{1}H NMR (400 MHz, DMSO) δ 7.98 (s, 1H), 7.69−7.68 (1H), 7.60−7.58 (1H), 7.36−7.29 (2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 136.9, 136.6, 127.8, 122.9, 121.3, 117.9, 111.2, 88.0, 33.1. MS (ESI) *m*/*z*: Calcd for $[M + H]^+$ $C_{10}H_9N_2S$ 189.05; Found 189.0.

1-Phenyl-3-thiocyanato-1*H*-indole (2n).[15] The general procedure was followed using 1-phenyl-1*H*-indole (94.2 mg, 0.488 mmol) as the starting material. Purification by column chromatography yielded **2n** (107.3 mg, 88%) as a pale yellow oil. ^{1}H NMR (400 MHz, DMSO) δ 8.34 (s, 1H), 7.81−7.79 (1H), 7.64−7.59 (5H), 7.52−7.50 (1H), 7.41−7.38 (2H). ^{13}C NMR (101 MHz, DMSO) δ 137.7, 135.9, 135.3, 130.0, 128.2, 127.8, 124.5, 124.2, 122.3, 118.5, 111.9, 111.6, 92.5. MS (ESI) *m*/*z*: Calcd for $[M + Na]^+$ $C_{15}H_{10}N_2NaS$ 273.05; Found 273.0.

1-Benzyl-3-thiocyanato-1*H*-indole (2o).[5c] The general procedure was followed using 1-benzyl-1*H*-indole (103.6 mg, 0.5 mmol) as the starting material. Purification by column chromatography yielded **2o** (140.8 mg, 95%) as a white solid. mp = 84−86 °C (lit. 83−85 °C).

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^{1}H NMR (400 MHz, DMSO) δ 8.19 (s, 1H), 7.71−7.62 (2H), 7.34−7.26 (7H), 5.49 (s, 2H). ^{13}C NMR (101 MHz, DMSO) δ 137.1, 136.2, 136.0, 128.7, 128.0, 127.7, 127.3, 123.1, 121.5, 118.1, 112.2, 111.6, 89.3, 49.7. MS (ESI) *m*/*z*: Calcd for $[M + Na]^+$ $C_{16}H_{12}N_2NaS$ 287.06; Found 287.0.

Methyl-2-phenyl-3-thiocyanato-1*H*-indole (2q). The general procedure was followed using 1-methyl-2-phenyl-1*H*-indole (103.6 mg, 0.5 mmol) as the starting material. Purification by column chromatography yielded **2q** (112.5 mg, 85%) as a white solid. mp = 83−84 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.77−7.75 (1H), 7.70−7.68 (1H), 7.64−7.60 (5H), 7.40−7.35 (2H), 3.71 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 146.1 136.9, 130.6, 129.6, 128.7, 128.7, 127.7, 123.4, 121.8, 118.0, 112.2, 111.4, 88.4, 31.8. MS (ESI) *m*/*z*: Calcd for $[M + Na]^+$ $C_{16}H_{12}N_2NaS$ 287.06; Found 287.1. HRMS (CI-TOF) *m*/*z*: Calcd for $[M]^+$ $C_{16}H_{12}N_2S$ 264.0721; Found 264.0728.

■ ASSOCIATED CONTENT

Supporting Information

Results of fluorescence quenching and electrochemical studies, and ^{1}H and ^{13}C NMR spectra of all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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