Electronic Supplementary Information

Catalyst and additive-free regioselective oxidative C-H thio/selenocyanation of arenes and heteroarenes with elemental sulfur/selenium and TMSCN

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General Information

 Unless otherwise indicated, all commercial reagents and solvents were used without additional purification. $^1$H NMR spectra were recorded with a Bruker Ascend™ 600 spectrometer. Chemical shifts (in ppm) were referenced to tetramethylsilane ($\delta = 0$ ppm) in CDCl$_3$ or DMSO-$d_6$ as an internal standard. $^{13}$C NMR spectra were obtained by the same NMR spectrometer and were calibrated with CDCl$_3$ ($\delta = 77.0$ ppm) or DMSO-$d_6$ ($\delta = 39.6$ ppm). HRMS (ESI) were recorded on an AB SCIEX Triple TOF 6600 LC/MS. Melting point was recorded on a Hanon MP430 Auto Melting Point System.

Experimental Procedure

C-H Thiocyanation of Arenes or Heteroarenes

Arenes or heteroarenes (0.2 mmol), S$_8$ (2 equiv, 0.4 mmol) and DMSO (2 mL) were successively added to a 10 mL open reaction tube, followed by addition of TMSCN (2 equiv, 0.4 mmol). The mixture was stirred at 90 °C for 4 h. The solution was then cooled to room temperature, quenched by distilled water, filtered and extracted with EtOAc ($3 \times 10$ mL). The combined organic layers were dried over Na$_2$SO$_4$, filtered, and evaporated under vacuum. The residue was purified by column chromatography on silica gel to afford the desired thiocyanation products.

Gram-scale Synthesis of 2-Phenyl-3-thiocyanato-$^1$H-indole

2-Phenyl-$^1$H-indole (3b, 8 mmol, 1.54 g), S$_8$ (16 mmol, 0.51 g) and DMSO (50 mL) were successively added to a 250 mL round-bottom flask, followed by addition of TMSCN (16 mmol, 2 mL). The mixture was stirred at 90 °C for 4 h. The solution was then cooled to room temperature, quenched by distilled water, filtered and extracted with EtOAc. The combined organic layers were dried over Na$_2$SO$_4$, filtered, and evaporated under vacuum. The residue was purified by column chromatography on silica gel to afford the desired 2-phenyl-3-thiocyanato-$^1$H-indole as a white solid (4b, 1.91 g, 95% yield).

C-H Selenocyanation of Arenes or Heteroarenes

Arenes or heteroarenes (0.2 mmol), Se (2 equiv, 0.4 mmol) and DMSO (2 mL) were successively added to a 10 mL open reaction tube, followed by addition of TMSCN (2 equiv, 0.4 mmol). The mixture was stirred at 120 °C for 24 h. The solution was then cooled to room temperature, quenched by distilled water, filtered and extracted with EtOAc ($3 \times 10$ mL). The combined organic layers were dried over Na$_2$SO$_4$, filtered, and evaporated under vacuum. The residue was purified by column chromatography on silica gel to afford the desired selenocyanation products.
Characterization Data of Products

3-phenyl-1-thiocyanatoimidazo[1,5-α]pyridine (2a): 93% yield; yellowish solid; mp: 104-105 °C; \(^1\)H NMR (600 MHz, CDCl₃): \(\delta\) 8.32 (d, \(J = 7.2\) Hz, 1H), 7.77 (d, \(J = 7.8\) Hz, 2H), 7.73 (d, \(J = 9.6\) Hz, 1H), 7.57-7.53 (m, 2H), 7.52-7.48 (m, 1H), 7.11-7.07 (m, 1H), 6.80-6.77 (m, 1H); \(^1\)C NMR (150 MHz, CDCl₃): \(\delta\) 140.1, 135.3, 129.7, 129.2, 128.6, 128.3, 123.3, 122.6, 117.3, 114.4, 110.5, 108.0; HRMS (ESI): calcd for C₁₄H₁₀N₃S [M+H]⁺ 252.0590, found 252.0593.

3-(4-fluorophenyl)-1-thiocyanatoimidazo[1,5-α]pyridine (2b): 91% yield; white solid; mp: 140-142 °C; \(^1\)H NMR (600 MHz, CDCl₃): \(\delta\) 8.25 (d, \(J = 7.2\) Hz, 1H), 7.78-7.72 (m, 3H), 7.29-7.24 (m, 2H), 7.12-7.09 (m, 1H), 6.83-6.79 (m, 1H); \(^1\)C NMR (150 MHz, CDCl₃): \(\delta\) 163.4 (d, \(J = 249.3\) Hz), 139.2, 135.3, 130.4 (d, \(J = 8.6\) Hz), 124.9 (d, \(J = 3.2\) Hz), 123.3, 122.4, 117.4, 116.4 (d, \(J = 21.8\) Hz), 114.6, 110.4, 108.2; HRMS (ESI): calcd for C₁₄H₉FN₃S [M+H]⁺ 270.0496, found 270.0500.

3-(2-chlorophenyl)-1-thiocyanatoimidazo[1,5-α]pyridine (2c): 93% yield; white solid; mp: 155-157 °C; \(^1\)H NMR (600 MHz, CDCl₃): \(\delta\) 7.77 (d, \(J = 9.0\) Hz, 1H), 7.73 (d, \(J = 7.2\) Hz, 1H), 7.63 (dd, \(J_1 = 7.6\) Hz, \(J_2 = 1.7\) Hz, 1H), 7.57 (dd, \(J_1 = 8.1\) Hz, \(J_2 = 1.1\) Hz, 1H), 7.52 (dt, \(J_1 = 1.7\) Hz, \(J_2 = 7.5\) Hz, 1H), 7.46 (dt, \(J_1 = 1.2\) Hz, \(J_2 = 7.5\) Hz, 1H), 7.17-7.14 (m, 1H), 6.83-6.80 (m, 1H); \(^1\)C NMR (150 MHz, CDCl₃): \(\delta\) 137.7, 135.0, 134.2, 133.3, 131.6, 130.1, 127.8, 127.4, 123.5, 117.0, 114.0, 110.5, 107.7; HRMS (ESI): calcd for C₁₄H₁₀ClN₃S [M+H]⁺ 286.0200, found 286.0200.
6-bromo-3-phenyl-1-thiocyanatoimidazo[1,5-a]pyridine (2d): 93% yield; yellow solid; mp: 114-115 °C; \(^1\)H NMR (600 MHz, CDCl₃): \(\delta\) 8.45 (s, 1H), 7.77-7.73 (m, 2H), 7.63 (dd, \(J_1 = 9.6\) Hz, \(J_2 = 0.6\) Hz, 1H), 7.60-7.56 (m, 2H), 7.56-7.52 (m, 1H), 7.46 (dd, \(J_1 = 9.6\) Hz, \(J_2 = 1.2\) Hz, 1H); \(^{13}\)C NMR (150 MHz, CDCl₃): \(\delta\) 140.2, 133.4, 130.1, 129.4, 128.3, 128.1, 126.7, 122.4, 117.9, 110.14, 110.06, 110.0; HRMS (ESI): calcd for C₁₅H₁₂BrN₃S [M+H]^+ 329.9695, found 329.9690.

1-phenyl-3-thiocyanatoimidazo[1,5-a]quinoline (2e): 89% yield; yellowish solid; mp: 174-175 °C; \(^1\)H NMR (600 MHz, CDCl₃): \(\delta\) 7.75-7.73 (m, 1H), 7.65 (d, \(J = 6.6\) Hz, 2H); 7.61-7.52 (m, 5H), 7.43 (t, \(J = 7.2\) Hz, 1H), 7.38 (d, \(J = 9.6\) Hz, 1H), 7.30-7.26 (m, 1H); \(^{13}\)C NMR (150 MHz, CDCl₃): \(\delta\) 143.6, 134.5, 132.2, 130.2, 129.7, 129.2, 129.0, 128.6, 126.2, 125.8, 125.2, 117.4, 114.9, 111.0, 110.3; HRMS (ESI): calcd for C₁₈H₁₂N₃S [M+H]^+ 302.0746, found 302.0744.

3-thiocyanato-1-(p-tolyl)imidazo[1,5-a]quinoline (2f): 99% yield; yellowish solid; mp: 193-195 °C; \(^1\)H NMR (600 MHz, CDCl₃): \(\delta\) 7.73 (dd, \(J_1 = 7.8\) Hz, \(J_2 = 1.2\) Hz, 1H), 7.60-7.56 (m, 2H), 7.54-7.51 (m, 2H); 7.44-7.40 (m, 1H), 7.36 (d, \(J = 8.4\) Hz, 3H), 7.31-7.27 (m, 1H), 2.50 (s, 3H); \(^{13}\)C NMR (150 MHz, CDCl₃): \(\delta\) 143.9, 140.3, 134.5, 132.3, 129.7, 129.5, 129.3, 129.2, 128.5, 126.1, 125.6, 125.2, 117.4, 114.9, 110.9, 110.4, 21.6; HRMS (ESI): calcd for C₁₉H₁₄N₃S [M+H]^+ 316.0903, found 316.0907.
1-(4-methoxyphenyl)-3-thiocyanatoimidazo[1,5-a]quinoline (2g): 97% yield; yellowish solid; mp: 180-182 °C; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.74-7.72 (m, 1H), 7.60 (d, $J = 8.4$ Hz, 1H), 7.58-7.55 (m, 3H), 7.42 (t, $J = 7.2$ Hz, 1H), 7.36 (d, $J = 9.0$ Hz, 1H), 7.32-7.29 (m, 1H), 7.07 (d, $J = 9.0$ Hz, 2H), 3.93 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 161.0, 143.7, 134.4, 132.3, 131.1, 129.2, 128.5, 126.1, 125.6, 125.2, 124.3, 117.3, 114.9, 114.4, 110.7, 110.3, 55.4; HRMS (ESI): calcd for C$_{19}$H$_{14}$N$_3$OS [M+H]$^+$ 332.0852, found 332.0852.

1-(4-chlorophenyl)-3-thiocyanatoimidazo[1,5-a]quinoline (2h): 88% yield; yellowish solid; mp: 192-194 °C; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.76 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.2$ Hz, 1H), 7.62-7.58 (m, 3H), 7.56-7.53 (m, 3H), 7.48-7.44 (m, 1H), 7.40 (d, $J = 9.0$ Hz, 1H), 7.36-7.32 (m, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 142.4, 136.3, 134.7, 132.0, 131.0, 130.7, 129.4, 129.3, 128.7, 126.4, 125.9, 125.2, 117.2, 114.9, 111.4, 110.1; HRMS (ESI): calcd for C$_{18}$H$_{11}$ClN$_3$S [M+H]$^+$ 336.0357, found 336.0358.

1-(4-bromophenyl)-3-thiocyanatoimidazo[1,5-a]quinoline (2i): 86% yield; yellowish solid; mp: 182-183 °C; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.78-7.75 (m, 1H), 7.71 (d, $J = 8.4$ Hz, 2H), 7.59 (d, $J = 9.6$ Hz, 1H), 7.55 (t, $J = 8.4$ Hz, 3H), 7.46 (t, $J = 7.2$ Hz, 1H), 7.42-7.39 (m, 1H), 7.37-7.33 (m, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 142.4, 138.2, 134.7, 132.3, 132.0, 131.2, 129.4, 128.7, 126.4, 126.0, 125.2, 124.6, 117.3, 114.9, 111.5, 110.1; HRMS (ESI): calcd for C$_{18}$H$_{11}$BrN$_3$S [M+H]$^+$ 379.9852, found 379.9853.
1-(3-fluorophenyl)-3-thiocyanatoimidazo[1,5-a]quinoline (2j): 94% yield; yellowish solid; mp: 198-199 °C; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.76 (dd, $J_1 = 7.8$ Hz, $J_2 = 0.9$ Hz, 1H), 7.66-7.63 (m, 2H), 7.59 (d, $J = 9.4$ Hz, 1H), 7.51 (d, $J = 8.4$ Hz, 1H), 7.45 (t, $J = 7.2$ Hz, 1H), 7.39 (d, $J = 9.4$ Hz, 1H), 7.34-7.30 (m, 1H), 7.27 (t, $J = 8.4$ Hz, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 163.7 (d, $J = 250.0$ Hz), 142.6, 134.5, 132.1, 131.8 (d, $J = 8.6$ Hz), 129.4, 128.7, 128.3 (d, $J = 3.3$ Hz), 126.3, 125.9, 125.2, 124.6, 117.2, 116.3 (d, $J = 21.9$ Hz), 114.9, 111.1, 110.2; HRMS (ESI): calcd for C$_{18}$H$_{11}$FN$_3$S [M+H]$^+$ 320.0652, found 320.0657.

1-(3-bromophenyl)-3-thiocyanatoimidazo[1,5-a]quinoline (2k): 93% yield; yellow solid; mp: 156-157 °C; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.84 (t, $J = 1.6$ Hz, 1H), 7.76 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.2$ Hz, 1H), 7.76 (dq, $J_1 = 8.1$ Hz, $J_2 = 0.9$ Hz, 1H), 7.61-7.57 (m, 2H), 7.55 (d, $J = 8.6$ Hz, 1H), 7.48-7.39 (m, 3H), 7.37-7.33 (m, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 141.9, 134.6, 134.1, 133.2, 132.6, 131.9, 130.4, 129.4, 128.8, 128.2, 126.5, 126.0, 125.2, 123.0, 117.3, 114.8, 111.5, 110.1; HRMS (ESI): calcd for C$_{18}$H$_{11}$BrN$_3$S [M+H]$^+$ 379.9852, found 379.9852.

1-(2-bromophenyl)-3-thiocyanatoimidazo[1,5-a]quinoline (2l): 80% yield; yellow solid; mp: 175-177 °C; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.79-7.75 (m, 2H), 7.65-7.62 (m, 2H), 7.58-7.55 (m, 1H), 7.52-7.49 (m, 1H), 7.46-7.41 (m, 2H), 7.33-7.29 (m, 1H), 7.27-7.25 (m, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 141.6, 134.09, 134.07, 133.2, 132.5, 132.2,
131.9, 129.2, 128.2, 126.3, 126.0, 124.9, 124.8, 116.1, 114.8, 110.9, 110.3; HRMS (ESI): calcd for C$_{18}$H$_{11}$BrN$_3$S [M+H]$^+$ 379.9852, found 379.9845.

7-bromo-1-phenyl-3-thiocyanatoimidazo[1,5-a]quinoline (2m): 67% yield; yellowish solid; mp: 212-214 °C; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.88 (d, $J = 1.8$ Hz, 1H), 7.65-7.61 (m, 3H), 7.61-7.54 (m, 3H), 7.42-7.35 (m, 2H), 7.29 (d, $J = 9.6$ Hz, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 143.8, 134.1, 131.8, 131.43, 131.37, 131.0, 130.5, 129.6, 129.2, 126.9, 124.5, 119.6, 118.9, 116.3, 112.0, 110.1; HRMS (ESI): calcd for C$_{18}$H$_{11}$BrN$_3$S [M+H]$^+$ 379.9852, found 379.9842.

7-methyl-1-phenyl-3-thiocyanatoimidazo[1,5-a]quinoline (2n): 94% yield; yellowish solid; mp: 200-202 °C; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.66-7.62 (m, 2H), 7.59-7.51 (m, 5H), 7.40 (d, $J = 8.7$ Hz, 1H), 7.31 (d, $J = 9.4$ Hz, 1H), 7.09 (dd, $J_1 = 8.7$ Hz, $J_2 = 1.5$ Hz, 1H), 2.43 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 143.4, 136.1, 134.4, 132.3, 130.14, 130.06, 129.7, 129.6, 128.99, 128.97, 125.7, 125.2, 117.2, 114.8, 110.7, 110.4, 20.9; HRMS (ESI): calcd for C$_{19}$H$_{14}$N$_3$S [M+H]$^+$ 316.0903, found 316.0909.

7-nitro-1-phenyl-3-thiocyanatoimidazo[1,5-a]quinoline (2o): 93% yield; yellow solid; mp: 177-178 °C; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.63 (d, $J = 2.5$ Hz, 1H), 8.12 (dd, $J_1 = 9.4$ Hz, $J_2 = 2.5$ Hz, 1H), 7.74 (d, $J = 9.4$ Hz, 1H), 7.68 (d, $J = 9.4$ Hz, 1H), 7.67-7.59 (m, 5H), 7.46 (d, $J = 9.4$ Hz, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 144.9, 144.6, 135.6, 134.1, 131.3, 130.9, 129.5, 125.7, 124.8, 124.4, 123.0, 118.3, 117.5, 113.4, 109.6; HRMS (ESI): calcd for C$_{19}$H$_{14}$N$_3$O$_2$S [M+H]$^+$ 347.0597, found 347.0600.
1-methyl-3-thiocyanatoimidazo[1,5-α]quinoline (2p): 65% yield; yellowish solid; mp: 171-172 °C; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.26 (d, $J = 8.4$ Hz, 1H), 7.75 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.2$ Hz, 1H), 7.65-7.61 (m, 1H), 7.53-7.47 (m, 2H), 7.28 (d, $J = 9.6$ Hz, 1H), 3.11 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 141.7, 134.5, 132.9, 129.3, 129.0, 126.0, 125.2, 125.1, 116.2, 115.0, 110.3, 108.9, 19.6; HRMS (ESI): calcd for C$_{13}$H$_{10}$N$_3$S [M+H]$^+$ 240.0590, found 240.0596.

1-propyl-3-thiocyanatoimidazo[1,5-α]quinoline (2q): 80% yield; yellowish solid; mp: 153-155 °C; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.18 (d, $J = 8.4$ Hz, 1H), 7.77-7.74 (m, 1H), 7.65-7.61 (m, 1H), 7.53-7.47 (m, 2H), 7.28 (d, $J = 9.6$ Hz, 1H), 3.36 (t, $J = 7.4$ Hz, 2H), 2.05 (sextet, $J = 7.4$ Hz, 2H), 1.16 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 145.7, 134.5, 132.9, 129.3, 129.0, 125.3, 125.1, 116.6, 115.1, 110.5, 109.0, 34.3, 20.4, 13.9; HRMS (ESI): calcd for C$_{15}$H$_{14}$N$_3$S [M+H]$^+$ 268.0903, found 268.0903.

1-isobutyl-3-thiocyanatoimidazo[1,5-α]quinoline (2r): 87% yield; yellowish solid; mp: 162-163 °C; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.16 (d, $J = 8.4$ Hz, 1H), 7.77-7.74 (m, 1H), 7.65-7.61 (m, 1H), 7.52-7.48 (m, 2H), 7.28 (d, $J = 9.6$ Hz, 1H), 3.27 (d, $J = 7.0$ Hz, 2H), 2.46-2.38 (m, 1H), 1.11 (d, $J = 6.6$ Hz, 6H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 145.1, 134.5, 132.8, 129.3, 129.0, 125.9, 125.4, 125.0, 116.6, 115.1, 110.5, 109.1, 41.0, 26.4, 22.5; HRMS (ESI): calcd for C$_{16}$H$_{16}$N$_3$S [M+H]$^+$ 282.1059, found 282.1065.
2-phenyl-3-thiocyanatoimidazo[1,2-\(a\)]pyridine (2s)\(^1\): 77% yield; yellowish solid; mp: 118-119 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 8.47 (d, \(J = 6.8\) Hz, 1H), 8.08-8.05 (m, 2H), 7.79 (d, \(J = 9.0\) Hz, 1H), 7.56-7.53 (m, 2H), 7.51-7.47 (m, 2H), 7.15 (t, \(J = 6.8\) Hz, 1H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 153.0, 147.9, 131.9, 129.5, 128.8, 128.7, 128.0, 124.4, 118.3, 114.4, 108.1, 94.7.

![2-phenyl-3-thiocyanatoimidazo[1,2-\(a\)]pyridine](image)

2-(4-(methylsulfonyl)phenyl)-3-thiocyanatoimidazo[1,2-\(a\)]pyridine (2t)\(^1\): 72% yield; yellowish solid; mp: 190-192 °C; \(^1\)H NMR (600 MHz, DMSO-d\(_6\)): \(\delta\) 8.80-8.78 (m, 1H), 8.39-8.36 (m, 2H), 8.16-8.12 (m, 2H), 7.90-7.87 (m, 1H), 7.67-7.63 (m, 1H), 7.36-7.33 (m, 1H), 3.32 (s, 3H); \(^{13}\)C NMR (150 MHz, DMSO-d\(_6\)): \(\delta\) 148.4, 146.9, 141.0, 137.1, 129.0, 128.9, 127.6, 125.6, 117.8, 115.1, 110.2, 99.4, 43.5.

![2-(4-(methylsulfonyl)phenyl)-3-thiocyanatoimidazo[1,2-\(a\)]pyridine](image)

2-phenyl-3-thiocyanatobenzo[\(d\)]imidazo[2,1-\(b\)]thiazole (2u)\(^1\): 55% yield; white solid; mp: 197-198 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 8.49 (d, \(J = 7.8\) Hz, 1H), 7.98 (d, \(J = 7.8\) Hz, 2H), 7.79 (d, \(J = 7.8\) Hz, 1H), 7.59 (t, \(J = 7.8\) Hz, 1H), 7.52 (t, \(J = 7.5\) Hz, 2H), 7.46 (t, \(J = 7.5\) Hz, 2H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 155.4, 152.7, 132.8, 131.6, 130.2, 129.3, 128.7, 128.4, 127.0, 124.5, 113.9, 108.8, 99.1.

![2-phenyl-3-thiocyanatobenzo[\(d\)]imidazo[2,1-\(b\)]thiazole](image)

1-methyl-3-thiocyanato-\(1H\)-indole (4a)\(^2\): 82% yield; brown solid; mp: 82-84 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.80-7.78 (m, 1H), 7.39 (s, 1H), 7.38-7.31 (m, 3H), 3.81 (s, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 137.1, 135.0, 128.5, 123.4, 121.6, 118.9, 111.8, 110.2, 89.9, 33.4.
2-phenyl-3-thiocyanato-1H-indole (4b): 97% yield; white solid; mp: 169-171 °C; ¹H NMR (600 MHz, CDCl₃): δ 8.73 (bs, 1H), 7.84-7.82 (m, 1H), 7.73-7.70 (m, 2H), 7.55-7.51 (m, 2H), 7.50-7.47 (m, 1H), 7.43-7.42 (m, 1H), 7.34-7.31 (m, 2H); ¹³C NMR (150 MHz, CDCl₃): δ 143.1, 135.4, 130.0, 129.7, 129.6, 129.1, 128.6, 124.1, 122.1, 119.0, 111.9, 111.6, 89.1.

5-methoxy-3-thiocyanato-1H-indole (4f): 75% yield; brown solid; mp: 89-91 °C; ¹H NMR (600 MHz, CDCl₃): δ 8.60 (bs, 1H), 7.48 (d, J = 2.4 Hz, 1H), 7.31 (d, J = 8.9 Hz, 1H), 7.19 (d, J = 2.4 Hz, 1H), 6.96 (dd, J₁ = 8.9 Hz, J₂ = 2.4 Hz, 1H), 3.92 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 156.8, 131.3, 130.8, 128.5, 114.6, 112.9, 111.8, 99.8, 91.7, 55.8.

2-(pyridin-2-yl)-3-thiocyanato-1H-indole (4c): 94% yield; white solid; mp: 165-167 °C; ¹H NMR (600 MHz, CDCl₃): δ 10.48 (bs, 1H), 8.66 (d, J = 4.2 Hz, 1H), 8.58 (d, J = 7.8 Hz, 1H), 7.90 (dt, J₁ = 1.2 Hz, J₂ = 7.8 Hz, 1H), 7.85 (d, J = 7.2 Hz, 1H), 7.43 (d, J = 7.2 Hz, 1H), 7.35-7.29 (m, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 149.4, 147.8, 139.2, 137.4, 134.9, 130.5, 124.9, 123.8, 122.6, 122.1, 119.3, 112.1, 110.9, 89.1; HRMS (ESI): calcd for C₁₄H₁₀N₃S [M+H]⁺ 252.0590, found 252.0590.

ethyl 3-thiocyanato-1H-indole-2-carboxylate (4d): 97% yield; white solid; mp: 130-131 °C; ¹H NMR (600 MHz, DMSO-d₆): δ 12.8 (bs, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.59 (d, J = 8.2 Hz, 1H), 7.46-7.42 (m, 1H), 7.35-7.31 (m, 1H), 4.45 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H); ¹³C NMR (150 MHz, DMSO-d₆): δ 159.8, 136.1, 128.9, 127.5, 126.2, 122.2, 119.6, 113.8, 111.4, 96.8, 61.6, 14.2.
5-bromo-3-thiocyanato-1H-indole (4g): 89% yield; offwhite solid; mp: 140-142 °C; $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ 12.21 (bs, 1H), 8.07 (s, 1H), 7.81 (d, $J = 1.8$ Hz, 1H), 7.51 (d, $J = 8.6$ Hz, 1H), 7.40 (dd, $J_1 = 8.6$ Hz, $J_2 = 1.8$ Hz, 1H); $^{13}$C NMR (150 MHz, DMSO-$d_6$): $\delta$ 135.2, 134.8, 129.3, 125.7, 120.1, 115.0, 113.9, 112.3, 89.5.

3-thiocyanato-1H-indole-5-carbonitrile (4h): 42% yield; yellowish solid; mp: 212-214 °C; $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ 12.52 (bs, 1H), 8.23 (s, 1H), 8.22 (s, 1H), 7.72 (d, $J = 8.5$ Hz, 1H), 7.65 (d, $J = 8.5$ Hz, 1H); $^{13}$C NMR (150 MHz, DMSO-$d_6$): $\delta$ 138.3, 136.0, 127.4, 125.8, 123.5, 120.0, 114.4, 112.1, 103.5, 91.6.

5-nitro-3-thiocyanato-1H-indole (4i): 52% yield; yellow solid; mp: 207-209 °C; $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ 12.66 (bs, 1H), 8.56 (s, 1H), 8.30 (d, $J = 1.7$ Hz, 1H), 8.18-8.14 (m, 1H), 7.74 (dd, $J_1 = 9.0$ Hz, $J_2 = 1.7$ Hz, 1H); $^{13}$C NMR (150 MHz, DMSO-$d_6$): $\delta$ 142.3, 139.6, 137.2, 127.0, 118.3, 114.5, 113.8, 112.1, 93.3.

methyl 3-thiocyanato-1H-indole-6-carboxylate (4j): 98% yield; yellowish solid; mp: 202-204 °C; $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ 12.38 (bs, 1H), 8.24 (s, 1H), 8.17 (d, $J = 0.6$ Hz, 1H), 7.86 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.2$ Hz, 1H), 7.78 (d, $J = 8.4$ Hz, 1H), 3.89 (s, 3H); $^{13}$C NMR (150 MHz, DMSO-$d_6$): $\delta$ 166.8, 136.7, 135.8, 131.1, 124.2, 121.7, 117.9, 114.7, 112.2, 90.6, 52.2; HRMS (ESI): calcd for C$_{13}$H$_6$N$_2$O$_2$S [M+H]$^+$ 233.0379, found 233.0372.
4-chloro-3-thiocyanato-1H-pyrrolo[2,3-b]pyridine (4k): 65% yield; yellowish solid; mp: 215-217 °C; \(^1\)H NMR (600 MHz, DMSO-\(d^6\)): \(\delta\) 12.97 (bs, 1H), 8.32 (d, \(J = 5.2\) Hz, 1H), 8.28 (s, 1H), 7.38 (d, \(J = 5.2\) Hz, 1H); \(^{13}\)C NMR (150 MHz, DMSO-\(d^6\)): \(\delta\) 149.5, 145.3, 136.4, 134.7, 118.3, 116.6, 113.1, 89.2; HRMS (ESI): calcd for C\(_8\)H\(_5\)ClN\(_3\)S [M+H]\(^+\) 209.9887, found 209.9872.

![ethyl 2-phenyl-1-thiocyanatopyrrolo[1,2-a]quinoline-3-carboxylate (4l)](image)

ethyl 2-phenyl-1-thiocyanatopyrrolo[1,2-a]quinoline-3-carboxylate (4l): 64% yield; white solid; mp: 207-208 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 9.58 (d, \(J = 8.8\) Hz, 1H), 8.43 (d, \(J = 9.4\) Hz, 1H), 7.85 (dd, \(J_1 = 7.8\) Hz, \(J_2 = 1.2\) Hz, 1H), 7.75-7.71 (m, 1H), 7.60 (d, \(J = 9.4\) Hz, 1H), 7.55 (t, \(J = 7.4\) Hz, 1H), 7.51-7.39 (m, 3H), 4.14 (q, \(J = 7.1\) Hz, 2H), 1.02 (t, \(J = 7.1\) Hz, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 163.7, 143.7, 139.2, 134.5, 133.8, 130.2, 129.6, 129.2, 128.0, 127.8, 127.4, 125.6, 125.5, 118.2, 117.1, 110.2, 107.9, 102.4, 59.9, 13.7; HRMS (ESI): calcd for C\(_{22}\)H\(_{17}\)N\(_2\)O\(_2\)S [M+H]\(^+\) 373.1005, found 373.1006.

![1,3,5-trimethoxy-2-thiocyanatobenzene (6a)](image)

1,3,5-trimethoxy-2-thiocyanatobenzene (6a): 83% yield; white solid; mp: 151-152 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 6.16 (s, 2H), 3.92 (s, 6H), 3.84 (s, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 164.2, 161.4, 111.8, 91.3, 89.7, 56.3, 55.6.

![N,N-dimethyl-4-thiocyanatoaniline (6b)](image)

N,N-dimethyl-4-thiocyanatoaniline (6b): 80% yield; yellowish solid; mp: 72-73 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.42 (d, \(J = 9.0\) Hz, 2H), 6.69 (d, \(J = 9.0\) Hz, 2H), 3.00 (s, 6H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 151.5, 134.4, 113.3, 112.5, 106.8, 40.2.
2-methyl-4-thiocyanatoaniline (6c): 96% yield; yellow solid; mp: 67-68 °C; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.27 (d, $J = 1.6$ Hz, 1H), 7.24 (dd, $J_1 = 8.3$ Hz, $J_2 = 2.2$ Hz, 1H), 6.66 (d, $J = 8.3$ Hz, 1H), 3.89 (bs, 2H), 2.16 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 147.0, 135.0, 132.1, 123.9, 115.7, 112.5, 109.4, 17.2.

![2-methyl-4-thiocyanatoaniline](image)

2-bromo-4-thiocyanatoaniline (6d): 71% yield; yellow solid; mp: 58-59 °C; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.63 (d, $J = 1.9$ Hz, 1H), 7.30 (dd, $J_1 = 8.5$ Hz, $J_2 = 2.1$ Hz, 1H), 6.75 (d, $J = 8.5$ Hz, 1H), 4.26 (bs, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 146.4, 136.8, 133.2, 116.1, 111.7, 110.0, 109.1.

![2-bromo-4-thiocyanatoaniline](image)

5-fluoro-2-methyl-4-thiocyanatoaniline (6e): 73% yield; tawny solid; mp: 49-51 °C; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.23 (d, $J = 7.7$ Hz, 1H), 6.46 (d, $J = 10.4$ Hz, 1H), 4.05 (bs, 2H), 2.11 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 161.4 (d, $J = 246.0$ Hz), 149.4 (d, $J = 10.8$ Hz), 136.3, 119.2 (d, $J = 2.3$ Hz), 111.2, 102.0 (d, $J = 25.0$ Hz), 95.3 (d, $J = 18.6$ Hz), 16.4; HRMS (ESI): calcd for C$_8$H$_7$FN$_2$NaS $[M+Na]^+$ 205.0206, found 205.0197.

![5-fluoro-2-methyl-4-thiocyanatoaniline](image)

5-thiocyanatoquinolin-8-amine (6f): 45% yield; brown solid; mp: 89-90 °C; $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ 8.86 (dd, $J_1 = 4.1$ Hz, $J_2 = 1.5$ Hz, 1H), 8.57 (dd, $J_1 = 8.5$ Hz, $J_2 = 1.5$ Hz, 1H), 7.82 (d, $J = 8.2$ Hz, 1H), 7.76 (dd, $J_1 = 8.5$ Hz, $J_2 = 4.1$ Hz, 1H), 6.91 (d, $J = 8.2$ Hz, 1H), 6.79 (bs, 2H); $^{13}$C NMR (150 MHz, DMSO-$d_6$): $\delta$ 149.7, 147.7, 138.0, 137.8, 132.9, 129.3, 123.7, 112.7, 108.2, 99.6.

![5-thiocyanatoquinolin-8-amine](image)

6-bromobenzo[d]thiazol-2-amine (6g): 36% yield; yellowish solid; mp: 214-216 °C; $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ 7.90 (d, $J = 2.1$ Hz, 1H), 7.67 (s, 2H), 7.34 (dd, $J_1 = 8.5$ Hz, $J_2 = 2.1$ Hz, 1H), 7.25 (d, $J = 8.5$ Hz, 1H); $^{13}$C NMR (150 MHz, DMSO-$d_6$): $\delta$ 167.3, 151.8, 133.0, 128.4, 123.4, 119.1, 112.2.
3-phenyl-1-selenocyanatoimidazo[1,5-a]pyridine (7a): 91% yield; green solid; mp: 106-108 °C; $^1$H NMR (600 MHz, CDCl$_3$): δ 8.32 (d, J = 7.2 Hz, 1H), 7.77 (d, J = 7.2 Hz, 2H), 7.70 (d, J = 9.2 Hz, 1H), 7.57-7.53 (m, 2H), 7.52-7.48 (m, 1H), 7.11-7.07 (m, 1H), 6.79-6.76 (m, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$): δ 140.5, 136.2, 129.6, 129.2, 128.7, 128.3, 123.0, 122.5, 118.0, 114.3, 106.3, 100.9; HRMS (ESI): calcd for C$_{14}$H$_{10}$N$_3$Se [M+H]$^+$ 300.0034, found 300.0023.

7-methyl-1-phenyl-3-selenocyanatoimidazo[1,5-a]quinoline (7b): 75% yield; yellow solid; mp: 213-215 °C; $^1$H NMR (600 MHz, CDCl$_3$): δ 7.66-7.62 (m, 2H), 7.59-7.52 (m, 5H), 7.40 (d, J = 8.7 Hz, 1H), 7.30 (d, J = 9.4 Hz, 1H), 7.09 (dd, $J_1 = 8.7$ Hz, $J_2 = 1.6$ Hz, 1H), 2.43 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): δ 143.7, 136.0, 135.2, 132.3, 130.1, 130.0, 129.63, 129.62, 129.0, 128.97, 125.4, 125.2, 117.2, 115.6, 109.0, 100.9, 20.9; HRMS (ESI): calcd for C$_{19}$H$_{14}$N$_3$Se [M+H]$^+$ 364.0347, found 364.0347.

2-phenyl-3-selenocyanatoimidazo[1,2-a]pyridine (7c): 72% yield; yellow solid; mp: 157-159 °C; $^1$H NMR (600 MHz, CDCl$_3$): δ 8.45 (d, J = 6.8 Hz, 1H), 7.98 (d, J = 7.6 Hz, 2H), 7.75 (d, J = 9.0 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.48-7.43 (m, 2H), 7.11 (t, J = 6.8 Hz, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$): δ 153.5, 148.4, 132.3, 129.2, 129.1, 128.6, 127.8, 125.4, 118.0, 114.3, 98.9, 93.4; HRMS (ESI): calcd for C$_{14}$H$_{10}$N$_3$Se [M+H]$^+$ 300.0034, found 300.0024.
2-(pyridin-2-yl)-3-selenocyanato-1H-indole (7d): 99% yield; yellow solid; mp: 161-163 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 10.38 (bs, 1H), 8.68-8.66 (m, 1H), 8.58 (d, \(J = 7.8\) Hz, 1H), 7.90 (dt, \(J_1 = 1.8\) Hz, \(J_2 = 7.8\) Hz, 1H), 7.86-7.84 (m, 1H), 7.45-7.43 (m, 1H), 7.35-7.29 (m, 3H); \(^13\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 149.5, 147.8, 139.4, 137.3, 134.9, 130.6, 124.8, 123.8, 122.5, 122.1, 119.3, 112.0, 110.9, 89.0; HRMS (ESI): calcd for C\(_{14}\)H\(_{10}\)N\(_3\)Se [M+H]\(^+\) 300.0034, found 300.0025.

![Image of 2-(pyridin-2-yl)-3-selenocyanato-1H-indole](image)

1,3,5-trimethoxy-2-selenocyanatobenzene (7e): 57% yield; white solid; mp: 152-153 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 6.17 (s, 2H), 3.90 (s, 6H), 3.85 (s, 3H); \(^13\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 164.1, 160.8, 111.9, 91.3, 89.8, 56.3, 55.6.

![Image of 1,3,5-trimethoxy-2-selenocyanatobenzene](image)

\(N,N\)-dimethyl-4-selenocyanatoaniline (7f): 63% yield; yellow solid; mp: 94-95 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.52 (d, \(J = 8.6\) Hz, 2H), 6.54 (d, \(J = 8.6\) Hz, 2H), 2.99 (s, 6H); \(^13\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 151.5, 136.4, 113.3, 104.4, 102.8, 40.1; HRMS (ESI): calcd for C\(_9\)H\(_{11}\)N\(_2\)Se [M+H]\(^+\) 227.0082, found 227.0078.

![Image of \(N,N\)-dimethyl-4-selenocyanatoaniline](image)

2-bromo-4-selenocyanatoaniline (7g): 71% yield; yellow solid; mp: 104-106 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.75 (d, \(J = 1.9\) Hz, 1H), 7.42 (dd, \(J_1 = 8.4\) Hz, \(J_2 = 1.9\) Hz, 1H), 6.74 (d, \(J = 8.4\) Hz, 1H), 4.42 (bs, 2H); \(^13\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 146.3, 138.7, 135.2, 116.4, 109.3, 107.3, 102.1; HRMS (ESI): calcd for C\(_7\)H\(_8\)BrN\(_2\)Se [M+H]\(^+\) 276.8874, found 276.8868.
Intermediate Experiment

1a (0.2 mmol), S₈ (2 equiv, 0.4 mmol) and DMSO (2 mL) were successively added to a 10 mL open reaction tube, and the mixture was stirred at 90 °C for 24 h. The solution was then cooled to room temperature, filtered and extracted with EtOAc (3×10 mL). The combined organic layers were dried over Na₂SO₄, filtered, and evaporated under vacuum. The residue was purified by column chromatography on silica gel to afford the intermediate 8 in a 42% yield. In addition, the reaction mixture was also directly analyzed by LC-MS and trace amount of the intermediate 11 could be detected.

bis(3-phenylimidazo[1,5-a]pyridin-1-yl)sulfane (8): 42% yield; yellowish solid; mp: 203-205 °C; ¹H NMR (600 MHz, CDCl₃): δ 8.17 (d, J = 7.0 Hz, 2H), 8.04 (d, J = 9.1 Hz, 2H), 7.75 (d, J = 7.5 Hz, 4H), 7.48 (t, J = 7.5 Hz, 4H), 7.40 (t, J = 7.3 Hz, 2H), 6.84-6.80 (m, 2H), 6.56 (t, J = 6.6 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃): δ 137.8, 133.6, 129.8, 128.9, 128.8, 128.2, 123.1, 121.5, 120.1, 119.4, 113.6; HRMS (ESI): calcd for C₂₆H₁₉N₄S [M+H]+ 419.1325, found 419.1308.
References

$^1$H NMR and $^{13}$C NMR Spectra