Supporting Information for

Base promoted three-component one-pot synthesis of 3- thiomethyl indoles with paraformaldehyde under aqueous conditions

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Table of Contents

1. General information .............................. 2
2. General experimental procedure ............... 2
3. Characterization data of products .............. 2-20
4. $^1$H and $^{13}$C NMR spectra of products ...... 21-57
**General information:**

Thiolation reaction is conducted under an atmosphere of air. Flash column chromatography was performed over silica gel 48-75 μm. $^1$H NMR and $^{13}$C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to tetramethylsilane (TMS) or acetone signals. MS analyses were performed on an Agilent 5975 GC-MS instrument (EI). High-resolution mass spectra were recorded at Jiangxi University of Traditional Chinese Medicine. The structures of known compounds were further corroborated by comparing their NMR data and MS data with those of literature. Reagents were used as received or prepared by our laboratory.

**General procedure: (3aa):**

A 10 mL oven-dried reaction vessel was charged with 1-methyl-1H-indole (1a, 50 μL, 0.4 mmol), paraformaldehyde (24 mg, 0.8 mmol), 4-methylbenzenethiol (2a, 24.8 mg, 0.2 mmol), ethane-1,2-diamine (6.5 μL, 0.1 mmol) and H$_2$O (0.5 mL) was added to the sealed reaction vessel by syringe. The resulting solution was stirred at 130 °C for 4 h. The volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3aa as brown liquid; yield: 41.7 mg (78%).

**1-methyl-3-((p-tolylthio)methyl)-1H-indole (3aa)**

\[
\text{\includegraphics{structure1.png}}
\]

$^1$H NMR (CDCl$_3$, 400 MHz, ppm) $\delta$ 7.67 (d, $J = 7.9$ Hz, 1H), 7.28 – 7.20 (m, 4H), 7.14 – 7.10 (m, 1H), 7.08 – 7.06 (m, 2H), 6.91 (s, 1H), 4.30 (s, 2H), 3.69 (s, 3H), 2.30 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 137.0, 136.0, 133.6, 130.0, 129.5, 127.7, 127.2, 121.8, 119.2, 119.1, 110.2, 109.3, 32.66, 30.34, 21.00. HRMS (ESI) m/z calcd for C$_{17}$H$_{18}$NS (M+H)$^+$ 268.11545, found 268.11554.

**3-(((4-(tert-butyl)phenyl)thio)methyl)-1-methyl-1H-indole (3ab)**
The reaction was conducted with 4-(tert-butyl)benzenethiol (2b, 34.5 μL, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1-methyl-1H-indole (1a, 50 μL, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3ab as brown solid; yield: 46.4 mg (75%), mp 89 - 92 °C.

\[ \delta 7.65 (d, J = 7.9 \text{ Hz}, 1H), 7.32 - 7.28 (m, 5H), 7.25 - 7.23 (m, 1H), 7.14 - 7.10 (m, 1H), 6.96 (s, 1H), 4.33 (s, 2H), 3.73 (s, 3H), 1.30 (s, 9H). \]

\[ \delta 149.2, 137.1, 133.9, 129.5, 127.8, 127.3, 125.8, 121.8, 119.2, 119.1, 110.3, 109.3, 34.43, 32.66, 31.28, 30.11. \]

HRMS (ESI) m/z calcd for C_{20}H_{22}NS (M-H) - 308.1473, found 308.14689.

3-(((4-methoxyphenyl)thio)methyl)-1-methyl-1H-indole (3ac)

The reaction was conducted with 4-methoxybenzenethiol (2c, 24.6 μL, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1-methyl-1H-indole (1a, 50 μL, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3ac as brown liquid; yield: 47.0 mg (83%).

\[ \delta 7.65 (d, J = 7.9 \text{ Hz}, 1H), 7.32 - 7.27 (m, 3H), 7.25 - 7.21 (m, 1H), 7.12 (t, J = 7.4 \text{ Hz}, 1H), 6.84 (s, 1H), 6.82 - 6.79 (m, 2H), 4.23 (s, 2H), 3.78 (s, 3H), 3.70 (s, 3H). \]

\[ \delta 158.8, 137.0, 133.4, 127.7, 127.3, 127.2, 121.7, 119.2, 119.0, 114.3, 110.5, 109.2, 55.23, 32.55, 31.84. \]

HRMS (ESI) m/z calcd for C_{17}H_{18}NOS (M+H)^+ 284.11036, found 284.11035.

3-(((4-fluorophenyl)thio)methyl)-1-methyl-1H-indole (3ad)
The reaction was conducted with 4-fluorobenzenethiol (2d, 21.3 µL, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1-methyl-1H-indole (1a, 50 µL, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3ad as brown solid; yield: 50.4 mg (93%), mp 100 - 103 ºC.

1H NMR (CDCl₃, 400 MHz, ppm): δ 7.66 – 7.64 (m, 1H), 7.34 – 7.28 (m, 3H), 7.25 – 7.24 (m, 1H), 7.15 – 7.13 (m, 1H), 6.98 – 6.93 (m, 2H), 6.86 (s, 1H), 4.28 (s, 2H), 3.71 (s, 3H). 13C NMR (CDCl₃, 100 MHz, ppm): δ 161.8 (d, J = 244.4 Hz), 137.1, 132.7 (d, J = 7.8 Hz), 131.9, 127.8, 127.1, 121.9, 119.2, 119.1, 115.7 (d, J = 21.4 Hz), 110.0, 109.3, 32.61, 31.14. HRMS (ESI) m/z calcd for C₁₆H₁₅FNS (M+H)⁺ 272.09037, found 272.09030.

3-(((4-chlorophenyl)thio)methyl)-1-methyl-1H-indole (3ae)

The reaction was conducted with 4-chlorobenzenethiol (2e, 28.7 mg, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1-methyl-1H-indole (1a, 50 µL, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3ae as white solid; yield: 46.0 mg (80%), mp 89 - 92 ºC.

1H NMR (CDCl₃, 400 MHz, ppm): δ 7.66 (d, J = 7.9 Hz, 1H), 7.36 – 7.35 (m, 2H), 7.28 – 7.24 (m, 2H), 7.19 – 7.14 (m, 3H), 6.92 (s, 1H), 4.31 (s, 2H), 3.71 (s, 3H). 13C NMR (CDCl₃, 100 MHz, ppm): δ 137.1, 135.8, 131.2, 130.8, 128.8, 127.8, 127.1, 121.9, 119.2, 119.1, 109.6, 109.4, 32.64, 30.02. MS (EI) m/z (%) 331, 218, 189, 146, 115. HRMS (ESI) m/z calcd for C₁₆H₁₃ClNS (M+H)⁺ 288.06082, found 288.06052.

3-(((4-bromophenyl)thio)methyl)-1-methyl-1H-indole (3af)
The reaction was conducted with 4-bromobenzenethiol (2f, 38.4 mg, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1-methyl-1H-indole (1a, 50 μL, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3af as brown solid; yield: 53.8 mg (81%), mp 111 - 114 °C.

1H NMR (CDCl₃, 400 MHz, ppm): δ 7.66 (d, J = 7.9 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.26 – 7.20 (m, 4H), 7.16 – 7.12 (m, 1H), 6.92 (s, 1H), 4.32 (s, 2H), 3.73 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 137.1, 136.5, 131.7, 130.9, 127.8, 127.1, 121.9, 119.7, 119.2, 119.0, 109.5, 109.3, 32.63, 29.79. HRMS (ESI) m/z calcd for C₁₆H₁₅BrNS (M+H)⁺ 332.01031, found 332.01031.

1-methyl-3-(((o-tolylthio)methyl)-1H-indole (3ag)

The reaction was conducted with 2-methylbenzenethiol (2g, 24.6 μL, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1-methyl-1H-indole (1a, 50 μL, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3ag as brown liquid; yield: 40.1 mg (75%).

1H NMR (CDCl₃, 400 MHz, ppm): δ 7.68 (d, J = 7.9 Hz, 1H), 7.35 – 7.33 (m, 1H), 7.29 – 7.21 (m, 2H), 7.15 – 7.07 (m, 4H), 6.95 (s, 1H), 4.31 (s, 2H), 3.69 (s, 3H), 2.33 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 137.2, 137.1, 136.9, 129.9, 127.8, 127.1, 121.9, 119.7, 119.2, 119.0, 109.5, 109.3, 32.63, 28.70, 20.24. HRMS (ESI) m/z calcd for C₁₇H₁₅BrNS (M+H)⁺ 268.11545, found 268.11545.

3-(((2-methoxyphenyl)thio)methyl)-1-methyl-1H-indole (3ah)
The reaction was conducted with 2-methoxybenzenethiol (2h, 24.3 μL, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1-methyl-1H-indole (1a, 50 μL, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3ah as brown liquid; yield: 40.2 mg (71%).

^1^H NMR (CDCl₃, 400 MHz, ppm): δ 7.69 (d, J = 7.9 Hz, 1H), 7.31 – 7.11 (m, 5H), 6.95 (s, 1H), 6.89 – 6.82 (m, 2H), 4.31 (s, 2H), 3.86 (s, 3H), 3.66 (s, 3H). ^1^C NMR (CDCl₃, 100 MHz, ppm): δ 157.1, 136.9, 129.5, 127.8, 127.3, 126.9, 125.5, 121.7, 120.9, 119.1, 119.0, 110.3, 109.9, 109.2, 55.67, 32.58, 27.75. HRMS (ESI) m/z calcd for C₁₇H₁₈NOS (M+H)^+ 284.11036, found 284.11035.

3-(((2-fluorophenyl)thio)methyl)-1-methyl-1H-indole (3ai)

The reaction was conducted with 2-fluorobenzenethiol (2i, 22.0 μL, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1-methyl-1H-indole (1a, 50 μL, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3ai as orange liquid; yield: 52.6 mg (97%).

^1^H NMR (CDCl₃, 400 MHz, ppm): δ 7.69 (d, J = 7.9 Hz, 1H), 7.35 – 7.31 (m, 1H), 7.28 – 7.11 (m, 4H), 7.07 – 6.99 (m, 2H), 6.93 (s, 1H), 4.34 (s, 2H), 3.69 (s, 3H). ^1^C NMR (CDCl₃, 100 MHz, ppm): δ 161.3 (d, J = 243.3 Hz), 137.0, 132.3, 128.2 (d, J = 7.8 Hz), 127.9, 127.2, 124.3 (d, J = 3.6 Hz), 124.0, 123.8, 121.8, 119.2, 119.1, 115.4 (d, J = 22.4 Hz), 109.6, 109.3, 32.56, 29.19. HRMS (ESI) m/z calcd for C₁₆H₁₅FNS (M+H)^+ 272.09037, found 272.09036.

3-(((2-chlorophenyl)thio)methyl)-1-methyl-1H-indole (3aj)
The reaction was conducted with 2-chlorobenzenethiol (2j, 22.6 μL, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1-methyl-1H-indole (1a, 50 μL, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3aj as yellow solid; yield: 50.6 mg (88%), mp 71 - 74 °C.

1H NMR (CDCl3, 400 MHz, ppm): δ 7.70 (d, J = 7.9 Hz, 1H), 7.37 – 7.29 (m, 2H), 7.27 – 7.24 (m, 2H), 7.18 – 7.12 (m, 2H), 7.10 – 7.06 (m, 1H), 7.01 (s, 1H), 4.36 (s, 2H), 3.70 (s, 3H).

13C NMR (CDCl3, 100 MHz, ppm): δ 137.0, 136.8, 133.1, 129.4, 128.6, 128.0, 127.2, 127.0, 126.3, 121.9, 119.2, 119.0, 109.3, 108.7, 32.62, 28.26. HRMS (ESI) m/z calcd for C16H15ClNS (M+H)+ 288.06082, found 288.06082.

3-(((2-bromophenyl)thio)methyl)-1-methyl-1H-indole (3ak)

The reaction was conducted with 2-bromobenzenethiol (2k, 24.0 μL, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1-methyl-1H-indole (1a, 50 μL, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3ak as brown liquid; yield: 63.1 mg (95%).

1H NMR (CDCl3, 400 MHz, ppm): δ 7.69 (d, J = 7.9 Hz, 1H), 7.53 (d, J = 7.9 Hz, 1H), 7.29 – 7.12, (m, 4H), 7.14 (t, J = 7.3 Hz, 1H), 7.00 – 6.97 (m, 2H), 4.34 (s, 2H), 3.68 (s, 3H). 13C NMR (CDCl3, 100 MHz, ppm): δ 138.8, 137.0, 132.7, 128.13, 128.07, 127.6, 127.3, 126.3, 123.1, 121.9, 119.2, 119.0, 109.3, 108.5, 32.67, 28.66. HRMS (ESI) m/z calcd for C16H15BrNS (M+H)+ 332.01031, found 332.01038.

1-methyl-3-((m-tolylthio)methyl)-1H-indole (3al)
The reaction was conducted with 3-methylbenzenethiol (2l, 24.2 μL, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1-methyl-1H-indole (1a, 50 μL, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3al as a brown solid; yield: 44.9 mg (84%), mp 58 - 60 °C.

$^{1}$H NMR (CDCl$_3$, 400 MHz, ppm): δ 7.67 (d, $J = 7.9$ Hz, 1H), 7.28 – 7.21 (m, 2H), 7.17 – 7.11 (m, 4H), 6.98 – 6.97 (m, 1H), 6.94 (s, 1H), 4.34 (s, 2H), 3.69 (s, 3H), 2.30 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): δ 138.4, 137.2, 137.0, 129.8, 128.6, 127.2, 126.7, 126.1, 121.8, 119.1, 110.0, 109.3, 32.60, 29.53, 21.28. HRMS (ESI) m/z calcd for C$_{17}$H$_{18}$NS (M+H)$^+$ 268.11545, found 268.11545.

3-(((3-methoxyphenyl)thio)methyl)-1-methyl-1H-indole (3am)

The reaction was conducted with 3-methoxybenzenethiol (2m, 24.8 μL, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1-methyl-1H-indole (1a, 50 μL, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3am as an orange liquid; yield: 27.2 mg (48%).

$^{1}$H NMR (CDCl$_3$, 400 MHz, ppm): δ 7.68 (d, $J = 7.9$ Hz, 1H), 7.30 – 7.12 (m, 4H), 6.97 – 6.94 (m, 2H), 6.88 (t, $J = 4.1$ Hz, 1H), 6.72 – 6.70 (m, 1H), 4.36 (s, 2H), 3.73 (s, 3H), 3.72 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): δ 159.7, 138.8, 137.0, 129.5, 127.8, 127.2, 126.7, 121.8, 121.2, 119.2, 119.1, 114.3, 111.7, 109.8, 109.3, 55.15, 32.62, 29.42. HRMS (ESI) m/z calcd for C$_{17}$H$_{18}$NOS (M+H)$^+$ 284.11036, found 284.11036.

3-(((2,6-dimethylphenyl)thio)methyl)-1-methyl-1H-indole (3an)
The reaction was conducted with 2,6-dimethylbenzenethiol (2n, 27.2 μL, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1-methyl-1H-indole (1a, 50 μL, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3an as brown liquid; yield: 23.6 mg (42%).

\[ 3a \]

\[ \text{\textsuperscript{1}H NMR (CDCl}_3, \text{400 MHz, ppm): } \delta 7.62 (d, J = 7.9 \text{ Hz}, 1H), 7.27 – 7.22 (m, 2H), 7.13 – 7.07 (m, 4H), 6.74 (s, 1H), 4.04 (s, 2H), 3.68 (s, 3H), 2.47 (s, 6H). \text{\textsuperscript{13}C NMR (CDCl}_3, \text{100 MHz, ppm): } \delta 143.4, 137.0, 134.1, 128.2, 127.9, 127.5, 127.3, 121.7, 119.08, 119.05, 110.9, 109.2, 32.57, 30.43, 21.94. HRMS (ESI) m/z calcd for C\textsubscript{18}H\textsubscript{20}NS (M+H\textsuperscript{+}) 282.13110, found 282.13113. \]

3-(((3,5-dimethylphenyl)thio)methyl)-1-methyl-1H-indole (3ao)

\[ 3a \]

The reaction was conducted with 3,5-dimethylbenzenethiol (2o, 27.2 μL, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1-methyl-1H-indole (1a, 50 μL, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3ao as brown solid; yield: 25.3 mg (45%), mp 56 - 59 °C.

\[ \text{\textsuperscript{1}H NMR (CDCl}_3, \text{400 MHz, ppm): } \delta 7.68 (d, J = 7.9 \text{ Hz}, 1H), 7.28 (s, 1H), 7.24 (d, J = 1.0 \text{ Hz}, 1H), 7.14 (s, 1H), 6.99 (d, J = 7.0 \text{ Hz}, 3H), 6.81 (s, 1H), 4.35 (s, 2H), 3.73 (s, 3H), 2.27 (s, 6H). \text{\textsuperscript{13}C NMR (CDCl}_3, \text{100 MHz, ppm): } \delta 138.3, 137.1, 137.0, 127.8, 127.7, 127.3, 126.7, 121.8, 119.2, 119.1, 110.1, 109.3, 32.64, 29.51, 21.19. HRMS (ESI) m/z calcd for C\textsubscript{18}H\textsubscript{20}NS (M+H\textsuperscript{+}) 282.13110, found 282.13110. \]

3-(((2,3-dichlorophenyl)thio)methyl)-1-methyl-1H-indole (3ap)

\[ 3a \]
The reaction was conducted with 2,3-dichlorobenzenethiol (2p, 35.8 mg, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1-methyl-1H-indole (1a, 50 μL, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3ap as white solid; yield: 49.6 mg (77%), mp 114 - 117 °C.

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): δ 7.70 (d, $J = 7.9$ Hz, 1H), 7.30 (t, $J = 8.9$ Hz, 2H), 7.26 – 7.19 (m, 2H), 7.17 (d, $J = 7.8$ Hz, 1H), 7.11 (t, $J = 7.9$ Hz, 1H), 7.05 (s, 1H), 4.38 (s, 2H), 3.75 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): δ 139.7, 137.1, 133.2, 130.4, 128.1, 127.3, 127.20, 126.8, 125.6, 122.0, 119.3, 118.9, 109.4, 108.2, 32.68, 28.49. HRMS (ESI) m/z calcd for C$_{16}$H$_{14}$Cl$_2$NS (M+H)$^+$ 322.02185, found 322.02173.

3-((2,4-difluorophenyl)thio)methyl)-1-methyl-1H-indole (3aq)

The reaction was conducted with 2,4-difluorobenzenethiol (2q, 22.7 μL, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1-methyl-1H-indole (1a, 50 μL, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3aq as yellow liquid; yield: 53.8 mg (93%).

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): δ 7.68 – 7.66 (m, 1H), 7.29 – 7.23 (m, 3H), 7.15 – 7.13 (m, 1H), 6.87 – 6.83 (m, 2H), 6.76 – 6.74 (m, 1H), 4.27 (s, 2H), 3.70 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): δ 163.5 (q, $J = 12.8$ Hz), 161.0 (q, $J = 12.3$ Hz), 137.0, 135.0 (d, $J = 18.2$ Hz), 127.9, 127.1, 121.8, 119.2, 119.1, 118.7 (d, $J = 18.2$ Hz), 111.4 (d, $J = 21.1$ Hz), 109.6, 109.3, 104.2 (t, $J = 26.0$ Hz), 32.57, 30.21. HRMS (ESI) m/z calcd for C$_{16}$H$_{14}$F$_2$NS (M+H)$^+$ 290.08095, found 290.08084.

1-methyl-3-((pyridin-4-ylthio)methyl)-1H-indole (3ar)
The reaction was conducted with pyridine-4-thiol (2r, 22.3 mg, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1-methyl-1H-indole (1a, 50 μL, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3ar as white solid; yield: 42.7 mg (81%), mp 136 - 139 °C.

1H NMR (CDCl₃, 400 MHz, ppm): δ 8.38 (d, J = 5.1 Hz, 2H), 7.68 (d, J = 7.9 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.25 – 7.13 (m, 3H), 7.08 (s, 1H), 4.45 (s, 2H), 3.77 (s, 3H). 13C NMR (CDCl₃, 100 MHz, ppm): δ 149.8, 149.1, 137.1, 127.9, 127.0, 122.1, 120.7, 119.4, 118.8, 109.5, 108.0, 32.70, 26.67. MS (EI) m/z (%) 115, 146, 197, 225, 258. HRMS (ESI) m/z calcd for C₁₅H₁₅N₂S (M+H)⁺ 255.09505, found 255.09500.

1-methyl-3-((pyridin-2-ythio)methyl)-1H-indole (3as)

The reaction was conducted with pyridine-2-thiol (2s, 22.2 mg, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1-methyl-1H-indole (1a, 50 μL, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3as as brown liquid; yield: 26.9 mg (53%).

1H NMR (CDCl₃, 400 MHz, ppm): δ 8.53 – 8.43 (m, 1H), 7.69 (d, J = 7.9 Hz, 1H), 7.46 – 7.39 (m, 1H), 7.27 – 7.22 (m, 2H), 7.16 – 7.09 (m, 2H), 7.06 (s, 1H), 6.99 – 6.91 (m, 1H), 4.64 (s, 2H), 3.69 (s, 3H). 13C NMR (CDCl₃, 100 MHz, ppm): δ 159.6, 149.2, 136.9, 135.9, 128.0, 127.3, 122.1, 121.7, 119.3, 119.1, 109.8, 109.3, 32.62, 25.56. HRMS (ESI) m/z calcd for C₁₅H₁₅N₂S (M+H)⁺ 255.09505, found 255.09509.

1,2-dimethyl-3-((p-tolylthio)methyl)-1H-indole (3ba)
The reaction was conducted with 4-methylbenzenethiol (2a, 24.8 mg, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1,2-dimethyl-1H-indole (1b, 58.1 mg, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3ba as white solid; yield: 47.2 mg (84%), mp 117 - 119 °C.

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 7.59 (d, $J = 7.8$ Hz, 1H), 7.26 (d, $J = 8.3$ Hz, 3H), 7.19 – 7.14 (m, 1H), 7.12 – 7.06 (m, 3H), 4.28 (s, 2H), 3.62 (s, 3H), 2.32 (s, 3H), 2.22 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 136.6, 136.3, 134.9, 133.7, 131.1, 129.4, 127.1, 120.9, 119.2, 118.2, 108.6, 106.2, 30.46, 29.49, 21.03, 10.05. HRMS (ESI) m/z calcd for C$_{18}$H$_{20}$NS (M+H)$^+$ 282.13110, found 282.13113.

1-methyl-2-phenyl-3-((p-tolylthio)methyl)-1H-indole (3ca)

The reaction was conducted with 4-methylbenzenethiol (2a, 24.8 mg, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1-methyl-2-phenyl-1H-indole (1c, 82.9 mg, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3ca as yellow liquid; yield: 43.9 mg (64%).

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 7.74 (d, $J = 7.8$ Hz, 1H), 7.47 – 7.40 (m, 3H), 7.37 – 7.32 (m, 3H), 7.29 – 7.24 (m, 1H), 7.19 – 7.15 (m, 3H), 7.02 (d, $J = 7.9$ Hz, 2H), 4.24 (s, 2H), 3.58 (s, 3H), 2.30 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 139.2, 137.3, 136.0, 133.7, 131.0, 130.5, 130.4, 129.4, 128.4, 128.2, 127.2, 122.1, 119.7, 119.4, 109.4, 108.1, 30.91, 30.81, 21.00. HRMS (ESI) m/z calcd for C$_{23}$H$_{22}$NS (M+H)$^+$ 344.14675, found 344.14691.

1,4-dimethyl-3-((p-tolylthio)methyl)-1H-indole (3da)
The reaction was conducted with 4-methylbenzenethiol (2a, 24.8 mg, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1,4-dimethyl-1H-indole (1d, 58.1 mg, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3da as orange solid; yield: 37.1 mg (66%), mp 105 - 107 °C.

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 7.27 (s, 1H), 7.25 (s, 1H), 7.12 - 7.10 (m, 3H), 7.08 (s, 1H), 6.88 (s, 2H), 4.42 (s, 2H), 3.68 (s, 3H), 2.82 (s, 3H), 2.32 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 137.5, 136.0, 133.5, 131.0, 129.5, 128.4, 125.8, 121.9, 120.9, 110.4, 107.2, 32.67, 32.35, 21.00, 20.00. HRMS (ESI) m/z calcd for C$_{18}$H$_{20}$NS (M+H)$^+$ 282.13110, found 282.13095.

4-fluoro-1-methyl-3-((p-tolthio)methyl)-1H-indole (3ea)

The reaction was conducted with 4-methylbenzenethiol (2a, 24.8 mg, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 4-fluoro-1-methyl-1H-indole (1e, 59.6 mg, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3ea as white solid; yield: 33.6 mg (59%), mp 75 - 77 °C.

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 7.27 (s, 2H), 7.14 - 7.03 (m, 4H), 6.85 (s, 1H), 6.79 - 6.74 (m, 1H), 4.39 (s, 2H), 3.69 (s, 3H), 2.31 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 157.1 (d, J = 245.5 Hz), 139.7 (d, J = 11.8 Hz), 136.0, 133.3, 130.2, 129.5, 127.9, 122.3 (d, J = 7.8 Hz), 115.8 (d, J = 19.7 Hz), 109.46 (s), 105.4 (d, J = 3.6 Hz), 104.5 (d, J = 19.3 Hz), 32.99, 31.05 (d, J = 2.1 Hz), 20.99. HRMS (ESI) m/z calcd for C$_{17}$H$_{17}$FNS (M+H)$^+$ 286.10602, found 286.10690.

4-chloro-1-methyl-3-((p-tolthio)methyl)-1H-indole (3fa)
The reaction was conducted with 4-methylbenzenethiol (2a, 24.8 mg, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 4-chloro-1-methyl-1H-indole (1f, 66.2 mg, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3fa as brown solid; yield: 21.7 mg (36%), mp 87 - 89 °C.

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\text{1H NMR (CDCl}_3, 400 MHz, ppm): \delta 7.27 (d, J = 1.8 Hz, 2H), 7.18 – 7.16 (m, 1H), 7.13 – 7.07 (m, 4H), 6.92 (s, 1H), 4.55 (s, 2H), 3.69 (s, 3H), 2.32 (s, 3H). \]

\[
\text{13C NMR (CDCl}_3, 100 MHz, ppm): \delta 138.5, 136.0, 133.4, 130.2, 129.5, 129.3, 126.4, 123.9, 122.3, 120.3, 110.9, 108.1, 33.93, 31.09, 21.00. HRMS (ESI) m/z calcd for C\textsubscript{17}H\textsubscript{17}ClNS (M+H)\textsuperscript{+} 302.07647, found 302.07617.
\]

\[3fa\]

1,5-dimethyl-3-((p-tolylthio)methyl)-1H-indole (3ga)

The reaction was conducted with 4-methylbenzenethiol (2a, 24.8 mg, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1,5-dimethyl-1H-indole (1g, 58 mg, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3ga as brown liquid; yield: 41.6 mg (74%).

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\text{1H NMR (CDCl}_3, 400 MHz, ppm): \delta 7.41 (s, 1H), 7.25 (d, J = 4.6 Hz, 2H), 7.17 (d, J = 8.3 Hz, 1H), 7.09 – 7.03 (m, 3H), 6.88 (s, 1H), 4.28 (s, 2H), 3.68 (s, 3H), 2.45 (s, 3H), 2.32 (s, 3H). \]

\[
\text{13C NMR (CDCl}_3, 100 MHz, ppm): \delta 136.0, 135.5, 133.7, 130.1, 129.5, 128.4, 127.8, 127.4, 123.4, 118.8, 109.6, 109.0, 32.66, 30.45, 21.45, 20.99. HRMS (ESI) m/z calcd for C\textsubscript{18}H\textsubscript{20}NS (M+H)\textsuperscript{+} 282.13110, found 282.13107.
\]

5-methoxy-1-methyl-3-((p-tolylthio)methyl)-1H-indole (3ha)
The reaction was conducted with 4-methylbenzenethiol (2a, 24.8 mg, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 5-methoxy-1-methyl-1H-indole (1h, 64.4 mg, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3ha as brown solid; yield: 42.2 mg (71%), mp 66 - 69 °C.

^1^H NMR (CDCl₃, 400 MHz, ppm): δ 7.27 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 8.8 Hz, 1H), 7.10 – 7.05 (m, 3H), 6.90 – 6.87 (m, 2H), 4.28 (s, 2H), 3.84 (s, 3H), 3.69 (s, 3H), 2.32 (s, 3H). \(^{13}\)C NMR (CDCl₃, 100 MHz, ppm): δ 153.9, 136.0, 133.7, 132.4, 130.1, 129.5, 128.3, 127.5, 112.1, 110.1, 109.7, 100.8, 55.81, 32.77, 30.51, 20.97. HRMS (ESI) m/z calcd for C₁₈H₂₀NOS (M+H)^+ 298.12601, found 298.12592.

5-fluoro-1-methyl-3-(((p-tolylthio)methyl)-1H-indole (3ia)

The reaction was conducted with 4-methylbenzenethiol (2a, 24.8 mg, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 5-fluoro-1-methyl-1H-indole (1i, 59.6 mg, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3ia as brown solid; yield: 38.2 mg (67%), mp 64 - 67 °C.

^1^H NMR (CDCl₃, 400 MHz, ppm): δ 7.29 (d, J = 2.4 Hz, 2H), 7.25 (s, 1H), 7.20 – 7.17 (m, 1H), 7.08 (d, J = 8.1 Hz, 2H), 7.00 – 6.93 (m, 2H), 4.24 (s, 2H), 3.71 (s, 3H), 2.32 (s, 3H). \(^{13}\)C NMR (CDCl₃, 100 MHz, ppm): δ 157.7 (d, J = 233.0 Hz), 136.3, 133.7, 133.2, 130.4, 129.6, 129.3, 127.5 (d, J = 9.8 Hz), 110.3, 110.0 (d, J = 43.3 Hz), 109.9, 104.2 (d, J = 23.5 Hz), 32.96, 30.45, 21.02. HRMS (ESI) m/z calcd for C₁₇H₁₇FNS (M+H)^+ 286.10602, found 286.10596.

5-chloro-1-methyl-3-(((p-tolylthio)methyl)-1H-indole (3ja)
The reaction was conducted with 4-methylbenzenethiol (2a, 24.8 mg, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 5-chloro-1-methyl-1H-indole (1j, 66.2 mg, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3ja as brown solid; yield: 25.9 mg (43%), mp 98 - 100 °C.

1H NMR (CDCl₃, 400 MHz, ppm): δ 7.57 – 7.54 (m, 1H), 7.24 (s, 2H), 7.17 – 7.16 (m, 2H), 7.08 (d, J = 7.9 Hz, 2H), 6.93 (s, 1H), 4.23 (s, 2H), 3.70 (s, 3H), 2.32 (s, 3H). 13C NMR (CDCl₃, 100 MHz, ppm): δ 136.4, 135.4, 133.1, 130.5, 129.6, 129.0, 128.2, 125.0, 122.1, 118.7, 110.3, 110.2, 32.83, 30.38, 21.01. HRMS (ESI) m/z calcd for C₁₇H₁₇ClNS (M+H)+ 302.07647, found 302.07626.

5-bromo-1-methyl-3-((p-tolylthio)methyl)-1H-indole (3ka)

The reaction was conducted with 4-methylbenzenethiol (2a, 24.8 mg, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 5-bromo-1-methyl-1H-indole (1k, 84.0 mg, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3ka as brown solid; yield: 34.6 mg (50%), mp 101 - 104 °C.

1H NMR (CDCl₃, 400 MHz, ppm): δ 7.69 (d, J = 1.8 Hz, 1H), 7.30 – 7.25 (m, 2H), 7.24 (d, J = 1.8 Hz, 1H), 7.15 – 7.07 (m, 3H), 6.91 (s, 1H), 4.22 (s, 2H), 3.69 (s, 3H), 2.32 (s, 3H). 13C NMR (CDCl₃, 100 MHz, ppm): δ 136.4, 135.7, 133.1, 130.6, 129.6, 128.9, 128.8, 124.6, 121.8, 112.6, 110.7, 110.2, 32.81, 30.37, 21.03. HRMS (ESI) m/z calcd for C₁₇H₁₇BrNS (M+H)+ 346.02596, found 346.02600.

1,6-dimethyl-3-((p-tolylthio)methyl)-1H-indole (3la)
The reaction was conducted with 4-methylbenzenethiol (2a, 24.8 mg, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1,6-dimethyl-1H-indole (1l, 58.0 mg, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3la as brown liquid; yield: 45.0 mg (80%).

^1^H NMR (CDCl_3, 400 MHz, ppm): δ 7.55 (d, J = 8.1 Hz, 1H), 7.25 (d, J = 8.1 Hz, 2H), 7.09 – 7.05 (m, 3H), 6.98 – 6.94 (m, 1H), 6.84 (s, 1H), 4.28 (s, 2H), 3.65 (s, 3H), 2.49 (s, 3H), 2.31 (s, 3H).

^13^C NMR (CDCl_3, 100 MHz, ppm): δ 137.4, 135.8, 133.7, 131.5, 129.9, 129.4, 127.1, 125.1, 120.8, 118.8, 109.9, 109.2, 32.46, 30.35, 21.81, 20.95. HRMS (ESI) m/z calcd for C_{18}H_{20}NS (M+H)^+ 282.13110, found 282.13098.

6-fluoro-1-methyl-3-((p-tolylthio)methyl)-1H-indole (3ma)

The reaction was conducted with 4-methylbenzenethiol (2a, 24.8 mg, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 6-fluoro-1-methyl-1H-indole (1m, 59.6 mg, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3ma as brown solid; yield: 34.4mg (60%), mp 59 - 61 °C.

^1^H NMR (CDCl_3, 400 MHz, ppm): δ 7.57 – 7.53 (m, 1H), 7.26 – 7.23 (m, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.95 – 6.85 (m, 3H), 4.26 (s, 2H), 3.64 (s, 3H), 2.31 (s, 3H). ^13^C NMR (CDCl_3, 100 MHz, ppm): δ 160.0 (d, J = 233.8 Hz), 137.1 (d, J = 11.4 Hz), 136.2, 133.3, 130.2, 129.5, 128.0, 123.7, 120.0 (d, J = 10.1 Hz), 110.6, 107.8 (d, J = 24.9 Hz), 95.69 (d, J = 26.0 Hz), 32.76, 30.38, 21.01. HRMS (ESI) m/z calcd for C_{17}H_{17}FNS (M+H)^+ 286.10602, found 286.10580.

methyl 1-methyl-3-((p-tolylthio)methyl)-1H-indole-6-carboxylate (3na)
The reaction was conducted with 4-methylbenzenethiol (2a, 24.8 mg, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and methyl 1-methyl-1H-indole-6-carboxylate (1n, 75.6 mg, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3na as brown solid; yield: 32.5 mg (50%), mp 108 - 111 °C.

\[ \text{1H NMR (CDCl}_3, 400 MHz, ppm): } \delta 8.06 (s, 1H), 7.82 - 7.79 (m, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.24 (s, 2H), 7.08 (d, J = 7.4 Hz, 3H), 4.28 (s, 2H), 3.95 (s, 3H), 3.78 (s, 3H), 2.32 (s, 3H). \]

\[ \text{13C NMR (CDCl}_3, 100 MHz, ppm): } \delta 168.1, 136.4, 136.3, 133.1, 131.0, 130.7, 130.4, 129.6, 123.4, 120.2, 118.8, 111.8, 111.0, 51.93, 32.87, 30.23, 21.00. \]

HRMS (ESI) m/z calcd for C_{19}H_{20}NO_2S (M+H)^+ 326.12093, found 326.12097.

1,7-dimethyl-3-((p-tolylthio)methyl)-1H-indole (3oa)

The reaction was conducted with 4-methylbenzenethiol (2a, 24.8 mg, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1,7-dimethyl-1H-indole (1o, 58.0 mg, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3oa as brown solid; yield: 39.3 mg (70%), mp 78 - 81 °C.

\[ \text{1H NMR (CDCl}_3, 400 MHz, ppm): } \delta 7.50 (d, J = 7.9 Hz, 1H), 7.27 (s, 2H), 7.08 (d, J = 8.1 Hz, 2H), 6.99 (t, J = 7.5 Hz, 1H), 6.91 (d, J = 7.1 Hz, 1H), 6.82 (s, 1H), 4.27 (s, 2H), 3.98 (s, 3H), 2.74 (s, 3H), 2.32 (s, 3H). \]

\[ \text{13C NMR (CDCl}_3, 100 MHz, ppm): } \delta 135.9, 135.8, 133.7, 129.9, 129.5, 129.4, 128.3, 124.4, 121.3, 119.4, 117.2, 109.8, 36.55, 30.18, 20.97, 19.60. \]

HRMS (ESI) m/z calcd for C_{18}H_{20}NS (M+H)^+ 282.13110, found 282.13110.

3-((p-tolylthio)methyl)-1H-indole (3pa)
The reaction was conducted with 4-methylbenzenethiol (2a, 24.8 mg, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1H-indole (1p, 46.8 mg, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3pa as brown solid; yield: 19.7 mg (39%), mp 102 - 104 °C.

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\text{1H NMR (CDCl}_3, 400 MHz, ppm): \delta \ 7.95 \ (s, 1H), \ 7.70 \ (d, J = 7.8 \ Hz, 1H), \ 7.35 \ (d, J = 8.0 \ Hz, 1H), \ 7.26 \sim 7.18 \ (m, 3H), \ 7.17 \sim 7.12 \ (m, 1H), \ 7.08 \sim 7.03 \ (m, 3H), \ 4.30 \ (s, 2H), \ 2.31 \ (s, 3H). \n\]

\[
\text{13C NMR (CDCl}_3, 100 MHz, ppm): \delta \ 136.3, \ 136.2, \ 133.3, \ 130.4, \ 129.5, \ 126.7, \ 123.1, \ 122.2, \ 119.6, \ 119.1, \ 112.0, \ 111.2, \ 30.49, \ 21.00. \ HRMS (ESI) m/z calcd for C_{16}H_{16}NS (M+H)^+ 254.09980, found 254.09972. \n\]

1-ethyl-3-((p-tolylthio)methyl)-1H-indole (3qa)

The reaction was conducted with 4-methylbenzenethiol (2a, 24.8 mg, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1-ethyl-1H-indole (1q, 58 μL, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3qa as orange liquid; yield: 34.8 mg (62%).

\[
\text{1H NMR (CDCl}_3, 400 MHz, ppm): \delta \ 7.71 \sim 7.66 \ (m, 1H), \ 7.31 \ (d, J = 8.2 \ Hz, 1H), \ 7.26 \sim 7.20 \ (m, 3H), \ 7.15 \sim 7.05 \ (m, 3H), \ 6.95 \ (s, 1H), \ 4.30 \ (d, J = 1.7 \ Hz, 2H), \ 4.11 \sim 4.05 \ (m, 2H), \ 2.31 \ (s, 3H), \ 1.39 \ (t, J = 5.3 \ Hz, 3H). \n\]

\[
\text{13C NMR (CDCl}_3, 100 MHz, ppm): \delta \ 136.1, \ 133.5, \ 130.4, \ 129.5, \ 127.3, \ 126.0, \ 121.6, \ 119.3, \ 119.0, \ 110.2, \ 109.3, \ 40.75, \ 30.61, \ 21.00, \ 15.40. \ HRMS (ESI) m/z calcd for C_{18}H_{20}NS (M+H)^+ 282.13110, found 282.13120. \n\]

1-isopropyl-3-((p-tolylthio)methyl)-1H-indole (3ra)
The reaction was conducted with 4-methylbenzenethiol (2a, 24.8 mg, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1-isopropyl-1H-indole (1r, 63.6 mg, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3ra as orange liquid; yield: 37.2 mg (63%).

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 7.69 (d, $J = 7.9$ Hz, 1H), 7.34 (d, $J = 8.2$ Hz, 1H), 7.25 - 7.19 (m, 3H), 7.14 - 7.10 (m, 1H), 7.07 (d, $J = 7.9$ Hz, 2H), 7.01 (s, 1H), 4.64 - 4.57 (m, 1H), 4.30 (s, 2H), 2.31 (s, 3H), 1.45 (d, $J = 6.7$ Hz, 6H).

$^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 136.2, 135.9, 133.4, 130.8, 129.4, 127.2, 122.7, 121.5, 119.3, 119.1, 110.2, 109.5, 46.84, 30.99, 22.72, 21.02.

HRMS (ESI) m/z calcd for C$_{19}$H$_{22}$NS (M+H)$^+$ 296.14675, found 296.14679.

1-methyl-3-((p-tolylthio)methyl)-1H-pyrrolo[2,3-b]pyridine (3sa)

The reaction was conducted with 4-methylbenzenethiol (2a, 24.8 mg, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), and 1-methyl-1H-pyrrolo[2,3-b]pyridine (1s, 52.9 mg, 0.4 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3sa as brown liquid; yield: 18.8 mg (35%).

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 8.34 - 8.32 (m, 1H), 7.95 - 7.92 (m, 1H), 7.25 - 7.21 (m, 2H), 7.08 - 7.03 (m, 3H), 7.02 (s, 1H), 4.25 (s, 2H), 3.82 (s, 3H), 2.31 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 147.9, 143.0, 136.5, 132.9, 130.7, 129.6, 127.7, 127.6, 119.7, 115.2, 109.1, 31.08, 30.70, 21.00.

HRMS (ESI) m/z calcd for C$_{16}$H$_{17}$N$_2$S (M+H)$^+$ 269.11070, found 269.11081.
$^1$H and $^{13}$C NMR spectra of products