Regiocontrolled Direct C4 and C2-Methyl Thiolation of Indoles under Rhodium Catalyzed Mild Conditions

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General:

All commercially available compounds were used without further purification. Solvents for elution in column were distilled. Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel 60 F<sub>254</sub>. Visualization on TLC was achieved by the use of UV light (254 nm). Column chromatography was undertaken on silica gel (230-400 mesh). <sup>1</sup>H NMR spectra were recorded on BRUKER ULTRA SHIELD (400 MHz and 600 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, m = multiplet. Coupling constants, J, were reported in hertz unit (Hz). <sup>13</sup>C NMR spectra were recorded on BRUKER (100 MHz and 150 MHz) and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the centre of a triplet at 77.16 ppm of chloroform-d. <sup>19</sup>F NMR spectra were recorded on BRUKER (376 MHz). Infrared (IR) spectra were recorded using Spectrum BX FT-IR instrument from Perkin Elmer. Frequencies are given in reciprocal centimeters (cm<sup>-1</sup>), only selected absorbance peaks are reported and KBr is used as the matrix. GC-MS were obtained from Thermo Scientific TRACE 1300. LC-MS were obtained from Agilent Technologies A6120BW (single quadruple mass analyzer). High resolution mass spectra were obtained from waters XEVO-G2QTOF by using TOF MS ES+ method. Materials were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted.

1. Synthesis of starting material:

1.1 General procedure for the synthesis of 3-acetyl indole derivatives<sup>1</sup>:

\[
\text{SnCl}_4, \text{CH}_3\text{COCl} \quad \text{toluene, } 0^\circ\text{C}-\text{rt}
\]
To a stirred solution of indole derivative (1 equiv) in dry toluene, acid chloride (2 equiv) was added. The reaction mixture was cooled to 0 °C and stirred for 10 min. Next, stannic chloride (2 equiv) was added drop wise to the reaction mixture and stirred for 12 h. After completion of reaction (as monitored by TLC), it was cooled to 0 °C, quenched by saturated NaHCO₃ solution and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to provide desired product.

1.2. General procedure for preparation of N-substituted 3-acetyl indole:

To a stirred suspension of NaH (60 wt% in mineral oil, 1.5 equiv) in dry THF, solution of 3-acetyl indole derivative (1 equiv) was added at 0 °C and stirred for 15 min. Then corresponding alkyl halide (1.1 equiv) was added drop wise to the reaction mixture and stirred overnight at rt. After completion of the reaction (as monitored by TLC), it was cooled to 0 °C and quenched by addition of water and extracted with ethyl acetate. Combined organic layers were washed with water, brine, and dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to obtain desired N-alkylated 3-acetyl indole derivatives.

1.3. Procedure for synthesis of N-phenyl indole:\n
In a flame-dried sealed tube, 3-acetyl indole (1 equiv) dissolved in CH₂Cl₂ (6 mL), phenylboronic acid (2 equiv), anhydrous copper(II) acetate (2 equiv), and triethylamine (2 equiv) were added. The mixture was stirred at room temperature for 3 days, concentrated in vacuo, diluted with chloroform and water. The organic layer was separated, washed with brine and dried...
over anhydrous Na₂SO₄, concentrated in vacuo, and purified by column chromatography (EtOAc/hexane) to obtain pure product.

1.4. General procedure for preparation of ketoximes³:

\[
\text{R}^1\text{R}^2\text{N} = \text{Me, Bn}
\]

To a 50 mL round bottom flask equipped with a stir bar was charged with ketone (1 equiv), R⁴ONH₂HCl (2.7 equiv), NaOAc (4.4 equiv), and EtOH:H₂O (1:3). The reaction mixture was heated at 70 °C. After completion of reaction (as monitored by TLC), it was cooled to rt and EtOH was removed under vacuum. The mixture was extracted with EtOAc. The combined organic layers were dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to yield the desired analytically pure ketoxime 1 in moderate to good yield.

2. General procedure for preparation of disulfides⁴:

\[
\text{ArSH} + \text{ArSH} \xrightarrow{\text{I}_2, \text{MeOH}, \text{rt}} \text{Ar}_2\text{S}_2
\]

To a stirred solution of thiol compounds (1 mmol) in methanol (5 ml) was added iodine (0.5 mmol, 0.5 equiv) at room temperature. After completion of reaction (as monitored by TLC), it was quenched with saturated sodium thiosulfate solution and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous Na₂SO₄ and concentrated under vacuum to afford pure disulfide compounds.
**Optimization Table S1.** Optimization studies for the rhodium-catalyzed C4-thiolation of indole derivatives$^a$

![Chemical reaction](image)

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>Ag salt (equiv)</th>
<th>additive (1 equiv)</th>
<th>temp (°C)</th>
<th>yield (%)$^b$</th>
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<tr>
<td>1</td>
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<td>Cu(OAc)$_2$</td>
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<td>2</td>
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<tr>
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<tr>
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</tr>
<tr>
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<td>80</td>
<td>nd</td>
</tr>
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<td>nd</td>
</tr>
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<td>Cu(OAc)$_2$</td>
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<td>trace</td>
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<td>Ag$_2$CO$_3$(1)</td>
<td>-</td>
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<td>35</td>
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</table>

$^a$Reaction conditions: 1a (0.1 mmol), 2a (0.15 mmol), [Cp*RhCl$_2$]$_2$ (2 mol%), AgSbF$_6$ (8 mol%), Ag salt, additive (0.1 mmol), solvent (0.1 M), 14-18 h. $^b$Isolated yields. $^c$[Cp*RhCl$_2$]$_2$ (2.5 mol%). $^d$[Cp*IrCl$_2$]$_2$ (2.5 mol%).
mol%). $^[Ru(p-cymene)Cl_2]_2$ (5 mol%). DCE = 1,2-dichloroethane; TCE = 1,1,2,2-tetrachlorethene; TFE = trifluoroethanol; HFIP = hexafluoroisopropanol. nd = not detected.

3.1. General procedure for the synthesis of C4-chalcogenation using Rh(III) catalyst:

![Diagram](image)

To an oven-dried 10 mL screw cap vial ketoxime 1 (0.1 mmol) was taken in HFIP (0.1 M). Followingly, $[Cp*RhCl_2]_2$ (2.5 mol%), AgSbF$_6$ (10 mol%), Ag$_2$O (0.05 mmol), Cu(OAc)$_2$ (0.1 mmol), Ph$_2$S$_2$ or Ph$_2$Se$_2$ (0.15 mmol) were added to it and stirred at 40 °C for 8-16 h. After completion of the reaction (as monitored by TLC), the solvent was evaporated under reduced pressure. The crude reaction mixture was diluted with diethyl ether and passed through a Celite bed, and repeatedly washed with diethyl ether. The combined organic layers were dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using EtOAc/hexane mixture (1:9-1:5) as eluent to obtain desired pure product 3.

3.2. General procedure for the synthesis of C2-methyl thiolation using Rh(III) catalyst:

![Diagram](image)

Compound 6 was prepared via general procedure for the synthesis of compound 3.

Control experiments:

4. Reaction in absence of oxygen atmosphere:

![Diagram](image)

To a pre-dried 10 mL round bottom flask, ketoxime 1a (27.8 mg, 0.1 mmol) was taken in deoxygenated HFIP (1 mL) under argon atmosphere. Next, $[Cp*RhCl_2]_2$ (1.5 mg, 2.5 mol%),
AgSbF₆ (3.4 mg, 10 mol%), Ag₂O (11.6 mg, 0.05 mmol), Cu(OAc)₂ (18.2 mg, 0.1 mmol), Ph₂S₂ (32.7 mg, 0.15 mmol) were added under argon atmosphere. The reaction mixture was stirred at 40 °C for 14 h. After completion of the reaction (as monitored by TLC), the solvent was evaporated under reduced pressure. The crude reaction mixture was diluted with diethyl ether and passed through a Celite bed, and repeatedly washed with diethyl ether. The combined organic layers were concentrated under reduced pressure and the crude product was purified by silica gel column chromatography (EtOAc/hexane = 1:9) to obtain pure product 3a (30.1 mg, 78% yield).

5. Reaction with thiophenol under standard condition:

In a pre-dried 10 mL screw cap vial, ketoxime 3a (27.8 mg, 0.1 mmol) was taken in HFIP (1 mL). Next, [Cp*RhCl₂]₂ (1.5 mg, 2.5 mol%), AgSbF₆ (3.4 mg, 10 mol%), Ag₂O (11.6 mg, 0.05 mmol), Cu(OAc)₂ (18.2 mg, 0.1 mmol), and PhSH (17 mg, 1.5 mmol) were added and stirred at 40 °C for 24 h. Major amount of starting material 1a remained intact without any desired product formation.

6.1. Deuterium incorporation studies in absence of 2a:

To a oven-dried 10 mL screw cap vial, ketoxime 1a (27.8 mg, 0.1 mmol) was taken in CD₃OD: HFIP (0.5 mL:0.5 mL). Next, [Cp*RhCl₂]₂ (1.5 mg, 2.5 mol%), AgSbF₆ (3.5 mg, 10 mol%), Ag₂O (11.6 mg, 0.05 mmol), Cu(OAc)₂ (18.2 mg, 1 equiv) were added and stirred at 40 °C for 14 h. The solvent was evaporated under reduced pressure. Then, the crude reaction mixture was diluted with diethyl ether and passed through a Celite bed, and repeatedly washed with diethyl ether. The combined organic layers were concentrated under reduced pressure and purified by silica gel column chromatography using EtOAc/hexane mixture as eluent. The
purified product was analyzed by $^1$H NMR which showed that 44% deuterium incorporation at C-4 position of indole 1a was happened under standard reaction conditions.

6.2. Study of deuterium incorporation in presence of 2a:

To a stirred solution of ketoxime 1a (0.1 mmol) in HFIP:CD$_3$OD (0.5 mL: 0.5 mL), [Cp*RhCl$_2$]$_2$ (2.5 mol%), AgSbF$_6$ (10 mol%), Ag$_2$O (0.05 mmol), Cu(OAc)$_2$ (1 equiv), and Ph$_2$S$_2$ (1.5 equiv) were added and stirred at 40 °C. After 1.5 h, the reaction mixture was filtered through Celite bed and washed with EtOAc. The organic layer was concentrated under vacuum and purified by silica gel column chromatography using EtOAc/hexane as eluent. The isolated starting material and product was characterized by $^1$H NMR. The $^1$H NMR analysis of the recovered starting material showed that 37% deuterium incorporation occurred at the C-4 position of 1a.
7. Reaction in presence of TEMPO:

To a oven-dried 10 mL screw cap vial, ketoxime 1a (27.8 mg, 0.1 mmol) was added in HFIP (1 mL). Then, [Cp*RhCl2]2 (1.5 mg, 2.5 mol%), AgSbF6 (3.4 mg, 10 mol%), Ag2O (11.6 mg, 0.05 mmol), Cu(OAc)2 (18.2 mg, 0.1 mmol), Ph2S2 (32.7 mg, 0.15 mmol) and TEMPO (31.2 mg, 0.2 mmol) were added to the reaction mixture and stirred at 40 °C for 6 h. After completion of the reaction (as monitored by TLC), the solvent was evaporated under reduced pressure. The crude reaction mixture was diluted with diethyl ether and passed through a Celite bed, and repeatedly washed with diethyl ether. The combined organic layers were concentrated under reduced pressure and the crude product was purified by silica gel column chromatography using EtOAc/hexane mixture as eluent to obtain pure product 3a (31 mg, 80%).

8. Large scale experiment:
To a solution of 1a (1.0 g, 3.59 mmol) in HFIP (8 mL), [Cp*RhCl2]₂ (22 mg, 1 mol%), AgSbF₆ (50 mg, 4 mol%), Ag₂O (0.42 g, 0.05 mmol), anhydrous Cu(OAc)₂ (0.65 g, 1.0 equiv), and phenyldisulfide (0.94 g, 4.31 mmol) were added. After being stirred at 40 °C (until complete consumption of starting material), the reaction mixture was filtered by short silica gel and washed with ethyl acetate. The combined organic layer was dried over Na₂SO₄ and concentrated under vaccum. The crude product was purified by short silica gel column chromatography using EtOAc/hexane as eluent to afford desired product (0.90 g, 65%) as yellow oil.

9. Product modification:

9.1. Deprotection of benzyl group:

![Chemical structure](image)

To a stirred solution of compound 3a (38.6 mg, 0.1 mmol) dissolved in dry DMSO (1.5 mL), KO'Bu (90 mg, 0.8 mmol) was added. Oxygen was then bubbled into the solution until complete consumption of starting material (as monitored by TLC). After completion, the reaction mixture was quenched by saturated solution of ammonium chloride and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to obtain pure product 7 (23 mg, 78%) as yellow oil.

9.2. Stepwise removal of oxime directing group:

![Chemical structure](image)

O-Methyl oxime compound 3a (50 mg, 0.13 mmol) was dissolved in 1,4-dioxane (4 mL) and stirred for 15 min, then 6N HCl (1.5 mL) was added. The reaction was heated at 80 °C and stirred at the same temperature for 2 h. After completion, the reaction mixture was quenched with saturated sodium bicarbonate and extracted with EtOAc. The combined organic layers were
dried over anhydrous Na$_2$SO$_4$ and concentrated under vacuum. The crude product was purified by silica gel column chromatography to obtain pure product 3ab (35 mg, 75%) as yellow oil.

Next, to a stirred solution of compound 3ab (30 mg, 0.08 mmol) in dry benzene (2 mL) ethylene glycol (0.1 mL) and $p$-toluenesulfonic acid monohydrate (20 mg, 1.1 equiv) were added and heated under reflux condition for 2 h. After completion (as monitored by TLC), the reaction mixture was cooled, quenched with saturated sodium bicarbonate solution and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na$_2$SO$_4$ and concentrated under vacuum. The crude product was purified by silica gel column chromatography to obtain pure product 8 (19 mg, 72%) as yellow oil.

9.3. One step removal of oxime directing group:

$O$-Methyl oxime compound 3a (38.6 mg, 0.1 mmol) in dry benzene was taken in a sealed tube. Next, ethylene glycol (0.4 mL) and $p$-toluenesulfonic acid monohydrate (100 mg, 5 equiv) were added consecutively. The reaction mixture was heated at 120 °C for 3 h. The reaction mixture was cooled, quenched with saturated sodium bicarbonate solution and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to obtain pure product 8 (17 mg, 55%) as yellowish liquid.
10. Characterization data

10.1. Characterization data for starting materials:

**(E)-1-(1-Benzyl-1H-indol-3-yl)ethanone O-methyl oxime (1a):** White amorphous solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.37 (dd, $J = 6.7$, 2.9 Hz, 1H), 7.49–7.18 (m, 7H), 7.11 (d, $J = 6.7$ Hz, 2H), 5.32 (s, 2H), 4.05 (s, 3H), 2.25 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 151.7, 137.4, 136.9, 128.8, 128.7, 127.8, 126.7, 125.5, 123.5, 122.9, 120.9, 113.5, 109.6, 61.8, 50.2, 13.01; FT-IR: $\tilde{\nu} = 2928, 2366, 1460, 1182, 1052$ cm$^{-1}$; GC-MS: C$_{18}$H$_{18}$N$_2$O $[M]^+$: 278.15.

**(E)-1-(1-Benzyl-5-methoxy-1H-indol-3-yl)ethanone O-methyl oxime (1b):** White amorphous solid; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$: 7.91 (d, $J = 6.9$ Hz, 1H), 7.33 – 7.25 (m, 4H), 7.10 (d, $J = 6.9$ Hz, 2H), 6.88 (dd, $J = 8.9$, 2.6 Hz, 1H), 5.28 (s, 2H), 4.05 (s, 3H), 3.89 (s, 3H), 2.24 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 155.3, 152.1, 137.1, 132.7, 129.4, 129.0, 127.9, 126.8, 126.0, 113.1, 112.9, 110.6, 105.5, 61.9, 55.9, 50.5, 13.1; FT-IR: $\tilde{\nu} = 2934, 2818, 1598, 1540, 1484, 1454, 1393, 1358, 1272, 1222, 1184, 1144, 1050$ cm$^{-1}$; GC-MS: C$_{19}$H$_{20}$N$_2$O$_2$ $[M]^+$: 308.08.
(E)-1-(1-Benzyl-5-fluoro-1H-indol-3-yl)ethanone O-methyl oxime (1c): White amorphous solid; ¹H NMR (600 MHz, CDCl₃) δ: 8.05 (dd, J = 10.1, 2.6 Hz, 1H), 7.40 – 7.27 (m, 4H), 7.14 (dd, J = 8.9, 4.3 Hz, 1H), 7.10 (d, J = 6.9 Hz, 2H), 6.96 (td, J = 9.0, 2.6 Hz, 1H), 5.30 (s, 2H), 4.04 (s, 3H), 2.23 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ: 158.9 (d, J = 235.3 Hz), 151.5, 136.8, 134.1, 130.2, 129.1, 128.1, 126.8, 126.0 (d, J = 13.2 Hz), 113.6 (d, J = 6.6 Hz), 111.4 (d, J = 26.5 Hz), 110.5 (d, J = 9.7 Hz), 108.9 (d, J = 24.6 Hz), 62.0, 50.7, 13.0; ¹⁹F NMR (376 MHz, CDCl₃) δ: -123.16; FT-IR: ν ~ = 2934, 2812, 1620, 1598, 1540, 1478, 1392, 1367, 1258, 1184, 1112, 1054 cm⁻¹; GC-MS: C₁₈H₁₇FN₂O [M⁺]: 296.09.

![Diagram of 1c](image1)

(E)-1-(1-Benzyl-6-chloro-1H-indol-3-yl)ethanone O-methyl oxime (1d): White amorphous solid; ¹H NMR (400 MHz, CDCl₃) δ: 8.29 (d, J = 8.5 Hz, 1H), 7.37 – 7.21 (m, 5H), 7.17 (dd, J = 8.5, 2.0 Hz, 1H), 7.10 (d, J = 6.4 Hz, 2H), 5.25 (s, 2H), 4.04 (s, 3H), 2.22 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 151.4, 137.9, 136.5, 129.4, 129.1, 129.0, 128.1, 126.8, 124.7, 124.1, 121.8, 113.8, 109.8, 62.0, 50.4, 13.0; FT-IR: ν = 2942, 2820, 1604, 1538, 1494, 1468, 1376, 1332, 1267, 1228, 1176, 1050 cm⁻¹; LCMS (ESI): C₁₈H₁₈Cl₃N₂O [M+H⁺]: 313.2.

![Diagram of 1d](image2)

(E)-1-(1-Benzyl-7-methyl-1H-indol-3-yl)ethanone O-methyl oxime (1e): White amorphous solid; ¹H NMR (600 MHz, CDCl₃) δ: 8.29 (d, J = 8.0 Hz, 1H), 7.31 – 7.21 (m, 4H), 7.11 (t, J = 7.6 Hz, 1H), 6.93 (dd, J = 12.4, 7.1 Hz, 3H), 5.58 (s, 2H), 4.05 (s, 3H), 2.51 (s, 3H), 2.25 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ: 151.8, 139.2, 136.3, 131.0, 129.1, 127.6, 126.7, 126.0, 125.5,
121.7, 121.4, 121.0, 113.5, 61.9, 52.7, 19.6, 13.2; FT-IR: $\tilde{\nu} = 2956, 2810, 1596, 1546, 1489, 1452, 1419, 1385, 1328, 1260, 1182, 1048 \text{ cm}^{-1}$; GC-MS: $C_{19}H_{20}N_{2}O [M]^+$: 292.13.

(E)-1-(1-Benzyl-1H-indol-3-yl)propan-1-one O-methyl oxime (1f): Yellow oil; $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$: 8.37 (m, 1H), 7.36–7.18 (m, 7H), 7.11 (dd, $J = 7.4, 1.8$ Hz, 2H), 5.33 (s, 2H), 4.04 (s, 3H), 2.72 (q, $J = 7.6$ Hz, 2H), 1.22 (t, $J = 7.6$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 157.1, 137.5, 136.9, 128.8, 128.6, 127.8, 126.7, 125.8, 123.6, 122.9, 120.9, 112.2, 109.6, 61.7, 50.2, 20.9, 12.1; FT-IR: $\tilde{\nu} = 2936, 2812, 2360, 1540, 1466, 1388, 1180, 1050 \text{ cm}^{-1}$; GC-MS: $C_{19}H_{20}N_{2}O [M]^+$: 292.09.

(E)-(1-Benzyl-1H-indol-3-yl)(cyclopropyl)methanone O-methyl oxime (1g): Colorless oil; $^1H$ NMR (600 MHz, CDCl$_3$) $\delta$: 8.05 (m, 1H), 8.00 (s, 1H), 7.32–7.27 (m, 4H), 7.22 – 7.16 (m, 2H), 7.15 (d, $J = 7.1$ Hz, 2H), 5.35 (s, 2H), 3.92 (s, 3H), 2.04 (m, 1H), 1.08 – 1.05 (m, 2H), 0.95 – 0.91 (m, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$: 152.0, 136.9, 136.1, 132.7, 129.0, 127.9, 127.1, 126.9, 122.3, 122.3, 120.6, 110.2, 109.0, 61.8, 50.6, 15.7, 7.0; FT-IR: $\tilde{\nu} = 2934, 2856, 1584, 1514, 1468, 1384, 1358, 1247, 1221, 1180, 1044 \text{ cm}^{-1}$; GC-MS: $C_{20}H_{20}N_{2}O [M]^+$: 304.13.
(E)-1-(1-Benzyl-1H-indol-3-yl)-2-methylpropan-1-one O-methyl oxime (1h): Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.62 (d, \(J = 7.9\) Hz, 1H), 7.48 (s, 1H), 7.34 – 7.23 (m, 3H), 7.20 – 7.12 (m, 5H), 5.33 (s, 2H), 3.90 (s, 3H), 3.06 (m, 1H), 1.20 (d, \(J = 6.8\) Hz, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 157.0, 137.0, 136.2, 129.6, 129.0, 127.9, 127.0, 126.9, 122.23, 122.17, 120.3, 110.1, 108.8, 61.6, 50.4, 34.5, 21.1; FT-IR: \(\tilde{\nu} = 2932, 2864, 1614, 1524, 1466, 1368, 1361, 1243, 1223, 1182, 1042\) cm\(^{-1}\); GC-MS: C\(_{20}\)H\(_{22}\)N\(_2\)O [M]\(^+\): 306.17.

(E)-1-(1-Phenyl-1H-indol-3-yl)ethanone O-methyl oxime (1i): White amorphous solid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 8.39 (m, 1H), 7.56 – 7.44 (m, 6H), 7.36 (m, 1H), 7.25 (m, 2H), 4.05 (s, 3H), 2.28 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 151.6, 139.4, 137.2, 129.8, 128.5, 127.1, 126.1, 124.8, 123.8, 123.5, 121.7, 115.2, 100.1, 62.0, 13.1; FT-IR: \(\tilde{\nu} = 2928, 2810, 1596, 1546, 1502, 1456, 1411, 1300, 1228, 1179, 1135, 1056\) cm\(^{-1}\); GC-MS: C\(_{17}\)H\(_{16}\)N\(_2\)O [M]\(^+\): 264.10.

(E)-1-(1-(4-Methoxybenzyl)-1H-indol-3-yl)ethanone O-methyl oxime (1j): Yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 8.41 (dd, \(J = 6.3, 2.9\) Hz, 1H), 7.33 – 7.20 (m, 4H), 7.08 (d, \(J = 8.7\) Hz, 2H), 6.88 – 6.81 (m, 2H), 5.23 (s, 2H), 4.07 (s, 3H), 3.79 (s, 3H), 2.27 (s, 3H); \(^{13}\)C NMR (150
MHz, CDCl$_3$) $\delta$: 159.3, 151.8, 137.4, 128.9, 128.7, 128.3, 125.6, 123.6, 122.9, 121.0, 114.3, 113.3, 109.8, 61.8, 55.3, 49.8, 13.1; FT-IR: $\tilde{\nu} = 2934, 2836, 1612, 1514, 1466, 1388, 1338, 1297, 1248, 1176, 1057$ cm$^{-1}$; GC-MS: C$_{19}$H$_{20}$N$_2$O$_2$ [M]$^+$: 308.09.

(E)-1-(1-(2,4,6-Trimethylbenzyl)-1H-indol-3-yl)ethanone O-methyl oxime (1k): Amorphous solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.36 (d, $J = 7.8$ Hz, 1H), 7.47 (d, $J = 7.8$ Hz, 1H), 7.32 (t, $J = 7.8$ Hz, 1H), 7.25 (m, 1H), 6.96 (s, 2H), 6.76 (s, 1H), 5.19 (s, 2H), 4.01 (s, 3H), 2.34 (s, 3H), 2.22 (s, 6H), 2.10 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 151.9, 138.3, 138.1, 137.6, 129.5, 128.3, 126.3, 125.6, 123.5, 122.6, 121.0, 112.8, 61.7, 43.8, 21.1, 19.7, 13.1; FT-IR: $\tilde{\nu} = 2932, 2886, 2366, 1614, 1536, 1460, 1382, 1220, 1052$ cm$^{-1}$; GC-MS: C$_{21}$H$_{24}$N$_2$O [M]$^+$: 320.17.

(E)-1-(1-Allyl-1H-indol-3-yl)ethanone O-methyl oxime (1l): Pale yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.39 (dd, $J = 7.1$, 1.6 Hz, 1H), 7.57 – 6.94 (m, 4H), 6.01 (m, 1H), 5.25 (d, $J = 10.3$ Hz, 1H), 5.12 (d, $J = 17.1$ Hz, 1H), 4.73 (d, $J = 5.2$ Hz, 2H), 4.07 (s, 3H), 2.29 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 151.8, 137.3, 133.0, 128.5, 125.5, 123.6, 122.8, 120.9, 117.8, 113.2, 109.6, 61.8, 49.0, 13.1; FT-IR: $\tilde{\nu} = 2934, 2814, 1651, 1598, 1542, 1468, 1388, 1338, 1249, 1186, 1149, 1054$ cm$^{-1}$; GC-MS: C$_{14}$H$_{16}$N$_2$O [M]$^+$: 228.10.
(E)-1-(1-Methyl-1H-indol-3-yl)ethanone O-methyl oxime (1m): Greenish oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.40 (d, $J$ = 7.7 Hz, 1H), 7.34–7.24 (m, 3H), 7.21 (s, 1H), 4.09 (s, 3H), 3.75 (s, 3H), 2.29 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 151.8, 137.8, 129.5, 125.3, 123.4, 122.7, 120.7, 112.7, 109.2, 61.8, 33.0, 13.0; FT-IR: $\tilde{\nu}$ = 2936, 2814, 1598, 1540, 1472, 1419, 1372, 1328, 1271, 1236, 1152, 1101, 1048 cm$^{-1}$; GC-MS: C$_{12}$H$_{14}$N$_2$O [M]$^+$: 202.09.

(E)-1-(1-Benzyl-1H-indol-3-yl)ethanone O-benzyl oxime (1n): Yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.29 (dd, $J$ = 6.5, 1.7 Hz, 1H), 7.49 (d, $J$ = 7.5 Hz, 2H), 7.37 (t, $J$ = 7.4 Hz, 2H), 7.33 – 7.27 (m, 5H), 7.25 – 7.16 (m, 3H), 7.11 (d, $J$ = 6.5 Hz, 2H), 5.32 (s, 2H), 5.29 (s, 2H), 2.29 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 152.2, 138.8, 137.5, 137.1, 129.0, 128.9, 128.44, 128.35, 127.9, 127.7, 126.9, 125.6, 123.7, 123.0, 121.1, 113.7, 109.7, 76.1, 50.4, 13.5; FT-IR: $\tilde{\nu}$ = 2928, 2887, 1598, 1542, 1498, 1466, 1433, 1388, 1363, 1246, 1186, 1028 cm$^{-1}$; LCMS [ESI]: C$_{24}$H$_{23}$N$_2$O [M+H]$^+$: 355.4.
\textbf{(E)-1- (1-Benzyl-2-methyl-1H-indol-3-yl)ethanone \textit{O}-methyl oxime (5a):} Greenish oil; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$: 7.78 (m, 1H), 7.33 – 7.22 (m, 4H), 7.18 – 7.16 (m, 2H), 7.04 (d, $J = 6.8$ Hz, 2H), 5.35 (s, 2H), 4.04 (s, 3H), 2.53 (s, 3H), 2.40 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 153.0, 137.4, 136.7, 135.8, 128.9, 127.5, 126.7, 126.2, 121.7, 120.4, 119.9, 110.7, 109.5, 61.8, 46.7, 16.4, 11.8; FT-IR: $\tilde{\nu} = 2934, 2814, 1604, 1548, 1468, 1416, 1360, 1328, 1218, 1154, 1109, 1056$ cm$^{-1}$; GC-MS: C$_{19}$H$_{20}$N$_2$O $[M]^{+}$: 292.10.

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\textbf{(E)-1- (1-Benzyl-2-methyl-1H-indol-3-yl)ethanone \textit{O}-benzyl oxime (5b):} Pale yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.73 (dd, $J = 7.8, 1.9$ Hz, 1H), 7.51 (d, $J = 7.5$ Hz, 2H), 7.42 (t, $J = 7.5$ Hz, 2H), 7.36 (d, $J = 7.3$ Hz, 1H), 7.34 – 7.22 (m, 4H), 7.22 – 7.12 (m, 2H), 7.03 (d, $J = 7.5$ Hz, 2H), 5.34 (s, 2H), 5.30 (s, 2H), 2.47 (s, 3H), 2.42 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 153.3, 138.8, 137.3, 136.6, 135.8, 128.8, 128.3, 128.2, 127.6, 126.4, 126.6, 126.1, 121.5, 120.3, 119.8, 110.6, 109.3, 75.7, 46.6, 16.6, 11.7; FT-IR: $\tilde{\nu} = 2940, 2882, 1590, 1542, 1462, 1446, 1420, 1388, 1363, 1246, 1186, 1154, 1050$ cm$^{-1}$; GC-MS: C$_{25}$H$_{24}$N$_2$O $[M]^{+}$: 368.11.

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\textbf{(E)-1- (1-Benzyl-2-methyl-1H-indol-3-yl)propan-1-one \textit{O}-methyl oxime (5c):} Greenish oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.66 (m, 1H), 7.34 – 7.18 (m, 4H), 7.18 – 7.09 (m, 2H), 7.02 (d, $J = 6.8$ Hz, 2H), 5.34 (s, 2H), 3.99 (s, 3H), 2.86 (q, $J = 7.5$ Hz, 2H), 2.47 (s, 3H), 1.13 (t, $J = 7.5$ Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$: 158.3, 137.5, 136.8, 136.1, 128.9, 127.5, 127.1, 126.2, 121.6, 120.3, 119.5, 109.5, 61.7, 46.8, 23.1, 11.6, 10.9; FT-IR: $\tilde{\nu} = 2936, 2814, 1606, 1556, 1468, 1454, 1415, 1380, 1352, 1214, 1156, 1114, 1050$ cm$^{-1}$; GC-MS: C$_{20}$H$_{22}$N$_2$O $[M]^{+}$: 306.09.
\[(E)-1-(1-(4\text{-Methoxybenzyl})-2\text{-methyl}-1H\text{-indol-3-yl})\text{ethanone O-methyl oxime (5k)}: \text{Yellow oil; } ^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta: 7.76 (m, 1H), 7.27 (m, 1H), 7.19 – 7.12 (m, 2H), 6.97 (d, } J = 8.2 \text{ Hz, 2H}, 6.82 (d, } J = 8.2 \text{ Hz, 2H}), 5.28 (s, 2H), 4.03 (s, 3H), 3.77 (s, 3H), 2.52 (s, 3H), 2.38 (s, 3H); ^13\text{C NMR (100 MHz, CDCl}_3\text{)} \delta: 159.0, 153.0, 136.7, 135.7, 129.4, 127.5, 126.7, 121.6, 120.3, 119.8, 114.3, 110.6, 109.5, 61.7, 55.4, 46.2, 16.4, 11.9; \text{FT-IR: } \tilde{\nu} = 2934, 2836, 1612, 1512, 1466, 1416, 1360, 1293, 1248, 1176, 1110, 1056 \text{ cm}^{-1}; \text{GC-MS: C}_{20}\text{H}_{22}\text{N}_2\text{O}_2 [M]^+: 322.07.\]

\[(E)-1-(1\text{-Allyl}-2\text{-methyl}-1H\text{-indol-3-yl})\text{ethanone O-methyl oxime (5l): Yellow oil; } ^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta: 7.72 (d, } J = 7.8 \text{ Hz, 1H}), 7.28 (m, 1H), 7.20-7.10 (m, 2H), 5.93 (m, 1H), 5.15 (dd, } J = 10.4, 1.2 \text{ Hz, 1H}), 4.90 (dd, } J = 17.1, 1.2 \text{ Hz, 1H}), 4.71 (m, 2H), 4.01 (s, 3H), 2.53 (s, 3H), 2.36 (s, 3H); ^13\text{C NMR (100 MHz, CDCl}_3\text{)} \delta: 152.9, 136.2, 135.4, 132.8, 126.6, 121.3, 120.1, 119.6, 116.6, 110.3, 109.2, 61.6, 45.4, 16.2, 11.4; \text{FT-IR: } \tilde{\nu} = 2930, 2810, 1596, 1542, 1472, 1382, 1249, 1179, 1149, 1054 \text{ cm}^{-1}; \text{GC-MS: C}_{15}\text{H}_{18}\text{N}_2\text{O [M]^+: 242.10.}\]
10.2. Characterization data for the final thiolated products:

\[ (E)-1-(1-Benzyl-4-(phenylthio)-1H-indol-3-yl)ethanone \text{ O-methyl oxime (3a)}: \] Pale yellow oil, 83%; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\): 7.40–7.30 (m, 3H), 7.30–7.11 (m, 11H), 5.30 (s, 2H), 3.86 (s, 3H), 2.27 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\): 152.8, 137.5, 137.3, 136.4, 129.3, 128.93, 128.91, 128.6, 127.9, 127.3, 127.2, 126.4, 125.9, 122.8, 114.5, 110.1, 61.5, 50.5, 19.2; FT-IR: \(\tilde{\nu} = \) 3060, 2932, 2814, 2362, 1724, 1550, 1432, 1358, 1248, 1176, 1050, 769 cm\(^{-1}\); HRMS (ESI): \(m/z\) calcd for C\(_{24}\)H\(_{23}\)N\(_2\)OS [M+H]\(^+\): 387.1526, found 387.1511.

\[ (E)-1-(1-Benzyl-5-methoxy-4-(phenylthio)-1H-indol-3-yl)ethanone \text{ O-methyl oxime (3b)}: \] Yellow oil, 72%; \(^1\)H NMR (CDCl\(_3\), 600 MHz) \(\delta\): 7.39–7.30 (m, 4H), 7.22 (d, \(J = 7.8\) Hz, 2H), 7.17 (s, 1H), 7.14 (d, \(J = 7.8\) Hz, 2H), 7.07–7.01 (m, 3H), 6.99 (d, \(J = 8.9\) Hz, 1H), 5.27 (s, 2H), 3.83 (s, 3H), 3.79 (s, 3H), 2.17 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 150 MHz) \(\delta\): 156.2, 153.5, 138.9, 136.6, 132.9, 130.6, 130.0, 129.0, 128.6, 128.1, 127.4, 126.4, 124.6, 114.4, 112.2, 110.1, 109.4, 61.5, 57.8, 50.7, 19.6; FT-IR: \(\tilde{\nu} = \) 2931, 2835, 1590, 1542, 1463, 1428, 1363, 1328, 1262, 1220, 1179, 1050, 772 cm\(^{-1}\); HRMS (ESI): \(m/z\) calcd for C\(_{25}\)H\(_{25}\)N\(_2\)O\(_2\)S [M+H]\(^+\): 417.1631, found 417.1623.
(E)-1-(1-Benzyl-5-fluoro-4-(phenylthio)-1H-indol-3-yl)ethanone O-methyl oxime (3c): White crystalline solid, 91%; mp = 105-107 °C; \(^1\)H NMR (CDCl\(_3\), 600 MHz) \(\delta\): 7.40–7.32 (m, 3H), 7.30 (dd, \(J = 9.0, 4.0\) Hz, 1H), 7.24–7.17 (m, 5H), 7.11 (d, \(J = 8.3\) Hz, 3H), 7.06 (m, 1H), 5.29 (s, 2H), 3.83 (s, 3H), 2.20 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 150 MHz) \(\delta\): 159.2 (d, \(J = 238.3\) Hz), 152.6, 137.6, 136.1, 133.6, 130.3, 129.43, 129.42, 128.9 (d, \(J = 29.8\) Hz), 128.1, 127.2, 127.0, 125.3, 114.9 (d, \(J = 5.1\) Hz), 112.4 (d, \(J = 9.8\) Hz), 111.2 (d, \(J = 28.6\) Hz), 109.3 (d, \(J = 21.3\) Hz), 61.4, 50.7, 19.3; \(^{19}\)F NMR (CDCl\(_3\), 376 MHz) \(\delta\): -115.8; FT-IR: \(\tilde{\nu}\) = 3064, 2932, 2814, 1582, 1459, 1434, 1226, 1160, 1052, 796 \(\text{cm}^{-1}\); HRMS (ESI): \(m/z\) calcd for C\(_{24}\)H\(_{22}\)FN\(_2\)OS [M+H]\(^+\): 405.1431, found 405.1415.

(E)-1-(1-Benzyl-6-chloro-4-(phenylthio)-1H-indol-3-yl)ethanone O-methyl oxime (3d): White amorphous solid, 74%; \(^1\)H NMR (CDCl\(_3\), 600 MHz) \(\delta\): 7.36–7.20 (m, 8H), 7.19 (d, \(J = 1.8\) Hz, 1H), 7.17–7.14 (m, 2H), 7.13 (s, 1H), 7.01 (d, \(J = 1.8\) Hz, 1H), 5.22 (s, 2H), 3.86 (s, 3H), 2.23 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 150 MHz) \(\delta\): 152.2, 137.4, 135.9, 135.6, 130.7, 129.2, 129.1, 129.0, 128.9, 128.5, 128.2, 127.1, 126.9, 125.1, 124.6, 114.8, 109.3, 61.6, 50.5, 18.9; FT-IR: \(\tilde{\nu}\) = 3062, 2932, 2814, 2364, 1546, 1426, 1220, 1050, 796 \(\text{cm}^{-1}\); HRMS (ESI): \(m/z\) calcd for C\(_{24}\)H\(_{22}\)ClN\(_2\)OS [M+H]\(^+\): 421.1136, found 421.1120.
(E)-1-(1-Benzyl-7-methyl-4-(phenylthio)-1H-indol-3-yl)ethanone O-methyl oxime (3e): Yellow oil, 83%; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$: 7.36-7.27 (m, 3H), 7.24-7.19 (m, 2H), 7.16 (d, $J = 7.3$ Hz, 1H), 7.15-7.12 (m, 3H), 7.11 (s, 1H), 7.01 (d, $J = 7.4$ Hz, 2H), 6.91 (d, $J = 7.4$ Hz, 1H), 5.58 (s, 2H), 3.80 (s, 3H), 2.56 (s, 3H), 2.24 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 153.1, 138.8, 138.7, 136.1, 130.7, 129.1, 128.9, 128.8, 128.3, 127.9, 127.7, 126.1, 125.8, 125.6, 122.6, 122.2, 114.7, 61.5, 52.5, 19.7, 19.6; FT-IR: $\tilde{\nu} = 2962, 2927, 2814, 1584, 1476, 1446, 1406, 1363, 1258, 1180, 1044$, 738 cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{25}$H$_{25}$N$_2$OS [M+H]$^+$: 401.1682, found 401.1692.

(3f) (E)-1-(1-Benzyl-4-(phenylthio)-1H-indol-3-yl)propan-1-one O-methyl oxime (3f): White amorphous solid, 79%; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$: 7.40-7.29 (m, 3H), 7.27-7.10 (m, 11H), 5.32 (s, 2H), 3.80 (s, 3H), 2.83 (q, $J = 7.6$ Hz, 2H), 0.99 (t, $J = 7.6$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$: 158.3, 137.5, 137.3, 136.7, 129.7, 129.03, 129.02, 128.0, 127.9, 127.2, 126.4, 126.2, 122.8, 112.6, 110.0, 61.5, 50.6, 25.3, 10.6; FT-IR: $\tilde{\nu} = 3070, 2932, 1552, 1476, 1466, 1406, 1363, 1258, 1180, 1044$, 738 cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{25}$H$_{25}$N$_2$OS [M+H]$^+$: 401.1682, found 401.1665.
\[(E)-(1\text{-}\text{Benzyl}-4\text{-}(\text{phenylthio})-1H\text{-}\text{indol}-3\text{-}yl)-(\text{cyclopropyl})\text{methanone} \text{ } O\text{-}\text{methyl oxime (3g)}:\n\]
White amorphous solid, 57%; \(^1\text{H} \text{NMR} \text{ (CDCl}_3, 400 \text{ MHz}) \delta: 7.37 - 7.29 \text{ (m, 3H)}, 7.28 - 7.23 \text{ (m, 4H)}, 7.22 - 7.12 \text{ (m, 4H)}, 7.12 - 7.07 \text{ (m, 2H)}, 7.01 \text{ (s, 1H)}, 5.28 \text{ (s, 2H)}, 3.80 \text{ (s, 3H)}, 2.57 \text{ (m, 1H)}, 0.86 - 0.79 \text{ (m, 2H)}, 0.52 - 0.49 \text{ (m, 2H)}; \(^{13}\text{C} \text{NMR} \text{ (CDCl}_3, 150 \text{ MHz}) \delta: 158.4, 137.6, 136.8, 136.5, 129.9, 129.3, 128.9, 128.8, 127.9, 127.1, 126.9, 126.1, 125.8, 122.8, 109.6, 108.1, 99.9, 61.6, 50.4, 11.6, 5.9; \text{FT-IR: } \tilde{\nu} = 2920, 2850, 1577, 1481, 1432, 1389, 1328, 1262, 1220, 1170, 1038, 772 \text{ cm}^{-1}; \text{HRMS (ESI): } m/z \text{ calcd for C}_{26}\text{H}_{25}\text{N}_{2}\text{OS} [\text{M+H}]^+: 413.1682, \text{found } 413.1662.\n
\[(E)-1\text{-}(1\text{-}\text{Benzyl}-4\text{-}(\text{phenylthio})-1H\text{-}\text{indol}-3\text{-}yl)-2\text{-}\text{methylpropan}-1\text{-}\text{one} \text{ } O\text{-}\text{methyl oxime (3h)}:\n\]
Pale yellow oil, 54%; \(^1\text{H} \text{NMR} \text{ (CDCl}_3, 600 \text{ MHz}) \delta: 7.35 - 7.31 \text{ (m, 2H)}, 7.30 - 7.22 \text{ (m, 5H)}, 7.18 \text{ (d, } J = 7.8 \text{ Hz, 2H}), 7.15 \text{ (d, } J = 7.8 \text{ Hz, 2H}), 7.09 - 7.04 \text{ (m, 2H)}, 6.98 \text{ (d, } J = 7.9 \text{ Hz, 1H}), 5.32 \text{ (s, 2H)}, 3.75 \text{ (s, 3H)}, 3.54 \text{ (m, 1H)}, 1.07 \text{ (d, } J = 6.9 \text{ Hz, 6H}); \(^{13}\text{C} \text{NMR} \text{ (CDCl}_3, 150 \text{ MHz}) \delta: 160.9, 136.9, 136.7, 136.6, 130.7, 128.9, 128.8, 128.4, 128.1, 127.8, 127.4, 126.9, 126.3, 124.7, 122.7, 110.3, 109.1, 61.4, 50.4, 28.9, 19.6; \text{FT-IR: } \tilde{\nu} = 2962, 2870, 1554, 1476, 1430, 1393, 1332, 1248, 1214, 1176, 1036, 736 \text{ cm}^{-1}; \text{HRMS (ESI): } m/z \text{ calcd for C}_{26}\text{H}_{27}\text{N}_{2}\text{OS} [\text{M+H}]^+: 415.1839, \text{found } 415.1823.\n
(E)-1-(1-Phenyl-4-(phenylthio)-1H-indol-3-yl)ethanone O-methyl oxime (3i): White amorphous solid, 65%; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.62–7.46 (m, 5H), 7.46–7.38 (m, 1H), 7.37(s, 1H), 7.33–7.12 (m, 7H), 3.84 (s, 3H), 2.29 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 152.8, 139.0, 137.8, 137.2, 129.9, 129.14, 129.08, 128.5, 128.1, 127.5, 127.4, 126.0, 125.9, 125.0, 123.5, 116.0, 111.1, 61.6, 19.3; FT-IR: $\tilde{v} = 2930$, 2812, 1584, 1537, 1498, 1463, 1430, 1324, 1248, 1176, 1135, 1050, 748 cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{23}$H$_{21}$N$_2$OS [M+H]$^+$: 373.1369, found 373.1355.

(E)-1-(1-(4-Methoxybenzyl)-4-(phenylthio)-1H-indol-3-yl)ethanone O-methyl oxime (3j): Yellow oil, 63%; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$: 7.31 (dd, $J = 8.0$, 1.0 Hz, 1H), 7.25-7.21 (m, 2H), 7.20-7.13 (m, 8H), 6.88 (d, $J = 8.4$ Hz, 2H), 5.23 (s, 2H), 3.84 (s, 3H), 3.81(s, 3H), 2.29 (s, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$: 159.4, 152.8, 137.6, 137.3, 129.2, 128.9, 128.7, 128.4, 128.3, 127.4, 126.4, 125.9, 122.7, 114.3, 110.0, 61.4, 55.3, 49.9, 19.1; FT-IR: $\tilde{v} = 2922$, 2852, 1512, 1434, 1220, 1048, 772 cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{25}$H$_{25}$N$_2$O$_2$S [M+H]$^+$: 417.1631, found 417.1616.
(E)-1-(4-(Phenylthio)-1-(2,4,6-trimethylbenzyl)-1H-indol-3-yl)ethanone O-methyl oxime (3k): Amorphous solid, 62%; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.46 (dd, $J = 7.7$, 1.5 Hz, 1H), 7.30–7.10 (m, 7H), 6.94 (s, 2H), 6.66 (s, 1H), 5.19 (s, 2H), 3.78 (s, 3H), 2.32 (s, 3H), 2.23 (s, 6H), 2.13 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 152.9, 138.4, 138.1, 137.5, 137.4, 129.5, 129.4, 128.9, 128.1, 127.3, 126.4, 126.2, 126.0, 125.9, 122.5, 113.9, 109.4, 61.3, 43.9, 21.0, 19.8, 19.2; FT-IR: $\tilde{\nu}$ = 3064, 2924, 2845, 1542, 1424, 1228, 1178, 1050, 772 cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{27}$H$_{29}$N$_2$OS [M+H]$^+$: 429.1995, found 429.1976.

(E)-1-(1-Allyl-4-(phenylthio)-1H-indol-3-yl)ethanone O-methyl oxime (3l): Pale yellow oil, 85%; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$: 7.32 (dd, $J = 7.7$, 1.6 Hz, 1H), 7.24-7.19 (m, 4H), 7.18-7.12 (m, 4H), 6.03 (m, 1H), 5.29 (dd, $J = 10.0$, 1.6 Hz, 1H), 5.23 (dd, $J = 17.4$, 1.6 Hz, 1H), 4.73 (d, $J = 5.7$ Hz, 2H), 3.84 (s, 3H), 2.25 (s, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$: 152.8, 137.7, 137.1, 132.7, 129.0, 128.9, 128.2, 127.4, 126.6, 125.8, 125.6, 122.6, 118.3, 114.2, 110.0, 61.4, 49.2, 19.1; FT-IR: $\tilde{\nu}$ = 2920, 1446, 1220, 1050, 772 cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{20}$H$_{21}$N$_2$OS [M+H]$^+$: 337.1369, found 337.1355.

(E)-1-(1-Methyl-4-(phenylthio)-1H-indol-3-yl)ethanone O-methyl oxime (3m): Pale yellow oil, 74%; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$: 7.30 (dd, $J = 7.3$, 1.8 Hz, 1H), 7.24-7.17 (m, 4H), 7.14-7.09 (m, 4H), 3.81 (s, 3H), 3.78 (s, 3H), 2.23 (s, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$: 152.8, 137.8, 137.7, 129.3, 128.8, 127.3, 126.7, 125.7, 122.6, 113.9, 109.7, 61.4, 32.9, 19.1; FT-IR: $\tilde{\nu}$ =
3056, 2932, 1542, 1456, 1411, 1330, 1244, 1124, 1050, 769 cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{18}$H$_{19}$N$_2$OS [M+H]$^+$: 311.1213, found 311.1220.

(E)-1-(1-Benzyl-4-(phenylthio)-1H-indol-3-yl)ethanone O-benzyl oxime (3n): Yellow oil, 71%; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$: 7.42 (d, $J = 7.2$ Hz, 2H), 7.39-7.30 (m, 6H), 7.27-7.13 (m, 11H), 5.31 (s, 2H), 5.12 (s, 2H), 2.33 (s, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$: 153.5, 138.3, 137.6, 137.3, 136.5, 129.5, 128.93, 128.90, 128.7, 128.3, 127.9, 127.8, 127.5, 127.3, 127.2, 126.3, 126.1, 126.0, 122.8, 114.5, 109.9, 75.6, 50.5, 19.6; FT-IR: $\tilde{v}$ = 3030, 2922, 2858, 2362, 1550, 1432, 1362, 1220, 1024, 772 cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{30}$H$_{27}$N$_2$OS [M+H]$^+$: 463.1839, found 463.1848.

(E)-1-(1-Benzyl-4-(phenylselanyl)-1H-indol-3-yl)ethanone O-methyl oxime (3o): White amorphous solid, 94%; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.57–7.47 (m, 2H), 7.40–7.25 (m, 6H), 7.23 (s, 1H), 7.20–7.15 (m, 3H), 7.09-6.99 (m, 2H), 5.29 (s, 2H), 4.01 (s, 3H), 2.30 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 152.3, 136.9, 136.5, 133.9, 132.2, 129.2, 128.9, 128.6, 127.9, 127.3, 127.1, 126.9, 125.7, 124.6, 123.0, 115.1, 108.9, 61.6, 50.4, 18.1; FT-IR: $\tilde{v}$ = 3058, 2932, 1550, 1432, 1220, 1176, 1048, 772 cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{24}$H$_{23}$N$_2$OSe [M+H]$^+$: 435.0970, found 435.0955.
(E)-1-(1-Benzyl-5-methoxy-4-(phenylselanyl)-1H-indol-3-yl)ethanone O-methyl oxime (3p): Yellow oil, 60%; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$: 7.39-7.27 (m, 4H), 7.24-7.19 (m, 4H), 7.18 (s, 1H), 7.16-7.08 (m, 3H), 6.97 (d, $J=9.4$ Hz, 1H), 5.27 (s, 2H), 3.86 (s, 3H), 3.78 (s, 3H), 2.19 (s, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$: 155.4, 153.2, 136.5, 134.3, 132.6, 130.7, 129.8, 129.3, 128.9, 128.7, 127.9, 127.2, 125.4, 114.9, 111.9, 109.3, 107.9, 61.4, 57.8, 50.5, 19.7; FT-IR: $\tilde{\nu} = 2932, 2848, 2362, 1546, 1454, 1430, 1218, 1186, 1050, 772$ cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{25}$H$_{25}$N$_2$O$_2$Se [M+H]$^+$: 465.1076, found 465.1089.

(E)-1-(1-Benzyl-5-fluoro-4-(phenylselanyl)-1H-indol-3-yl)ethanone O-methyl oxime (3q): White amorphous solid, 93%; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$: 7.39-7.31 (m, 3H), 7.30-7.26 (m, 3H), 7.24 (s, 1H), 7.21 (d, $J=7.8$ Hz, 2H), 7.19-7.13 (m, 3H), 7.03 (t, $J=8.5$ Hz, 1H), 5.29 (s, 2H), 3.90 (s, 3H), 2.23 (s, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$: 158.8 (d, $J=235.3$ Hz), 152.7, 136.3, 133.4, 133.0, 130.3, 129.8 (d, $J=3.3$ Hz), 129.1, 128.2, 127.3, 126.2, 115.6 (d, $J=4.2$ Hz), 112.2 (d, $J=9.8$ Hz), 111.0 (d, $J=30.0$ Hz), 106.0 (d, $J=26.0$ Hz), 61.6, 50.8, 19.5; $^{19}$F NMR (CDCl$_3$, 376 MHz) $\delta$: -109.6; FT-IR: $\tilde{\nu} = 2932, 2366, 1465, 1434, 1220, 1050, 772$ cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{24}$H$_{22}$FN$_2$OSe [M+H]$^+$: 453.0876, found 453.0852.
(E)-1-(1-Benzyl-6-chloro-4-(phenylselanyl)-1H-indol-3-yl)ethanone O-methyl oxime (3r): White amorphous solid, 88%; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$: 7.59-7.54 (m, 2H), 7.39-7.30 (m, 6H), 7.21 (s, 1H), 7.16 (d, $J = 7.0$ Hz, 2H), 7.14 (d, $J = 1.8$ Hz, 1H), 6.93 (d, $J = 1.8$ Hz, 1H), 5.25 (s, 2H), 4.04 (s, 3H), 2.29 (s, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$: 151.7, 137.1, 135.9, 134.8, 130.9, 129.5, 129.2, 129.1, 128.9, 128.1, 128.0, 127.1, 126.9, 124.9, 124.5, 115.5, 108.4, 61.7, 50.5, 17.7; FT-IR: $\tilde{\nu} = 3062, 2932, 2814, 2360, 1540, 1430, 1244, 1176, 1050, 740$ cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{24}$H$_{22}$ClN$_2$OSe [M+H]$^+$: 469.0580, found 469.0559.

(E)-1-(1-Benzyl-4-(4-methoxyphenylthio)-1H-indol-3-yl)ethanone O-methyl oxime (4a): Colorless oil, 72%; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.40 – 7.28 (m, 5H), 7.23 – 7.11 (m, 4H), 7.06 (t, $J = 7.8$ Hz, 1H), 6.86 (t, $J = 8.1$ Hz, 3H), 5.28 (s, 2H), 3.95 (s, 3H), 3.80 (s, 3H), 2.33 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 159.2, 152.9, 137.1, 136.5, 133.9, 129.7, 128.9, 128.3, 127.9, 127.1, 126.0, 125.5, 122.7, 114.8, 114.4, 108.5, 61.6, 55.3, 50.4, 19.2; FT-IR: $\tilde{\nu} = 3045, 2928, 2886, 1590, 1487, 1440, 1248, 1166, 1138, 1050, 1025, 740$ cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{25}$H$_{23}$N$_2$O$_2$S [M+H]$^+$: 417.1631, found 417.1615.
(E)-1-(1-Benzyl-4-(4-tert-butylphenylthio)-1H-indol-3-yl)ethanone O-methyl oxime (4b): Colorless oil, 47%; $^1$H NMR (CDCl$_3$, 600 MHz) δ: 7.37-7.30 (m, 3H), 7.29-7.25 (m, 2H), 7.24-7.14 (m, 6H), 7.13-7.08 (m, 2H), 5.30 (s, 2H), 3.86 (s, 3H), 2.27 (s, 3H), 1.29 (s, 9H); $^{13}$C NMR (CDCl$_3$, 150 MHz) δ: 152.9, 149.4, 137.2, 136.5, 133.4, 129.9, 128.9, 128.5, 127.9, 127.2, 127.1, 126.1, 125.9, 125.3, 122.8, 114.5, 109.5, 61.4, 50.4, 34.5, 31.3, 19.2; FT-IR: $\tilde{v}$ = 3072, 2962, 2818, 1548, 1459, 1432, 1360, 1176, 1052, 772 cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{28}$H$_{31}$N$_2$OS [M+H]$^+$: 443.2152, found 443.2160.

(E)-1-(1-Benzyl-4-(m-tolylthio)-1H-indol-3-yl)ethanone O-methyl oxime (4c): Yellow oil, 61%; $^1$H NMR (CDCl$_3$, 400 MHz) δ: 7.37-7.28 (m, 3H), 7.25-7.05 (m, 8H), 6.98 (d, $J$ = 8.3 Hz, 2H), 5.23 (s, 2H), 3.86 (s, 3H), 2.27 (s, 3H), 2.25 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz) δ: 152.9, 138.6, 137.3, 136.9, 136.5, 130.4, 128.9, 128.8, 128.5, 127.9, 127.2, 127.1, 127.0, 126.9, 126.6, 125.8, 122.7, 114.5, 109.7, 61.4, 50.4, 21.3, 19.2; FT-IR: $\tilde{v}$ = 3060, 2926, 2358, 1550, 1430, 1220, 1050, 772 cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{25}$H$_{25}$N$_2$OS [M+H]$^+$: 401.1682, found 401.1693.
(E)-1-(1-Benzyl-4-(3-methoxyphenylthio)-1H-indol-3-yl)ethanone O-methyl oxime (4d):  
Pale yellow oil, 58%; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$: 7.38-7.29 (m, 3H), 7.27 (d, $J = 7.8$ Hz, 1H), 7.23-7.18 (m, 4H), 7.17-7.12 (m, 2H), 6.80-6.69 (m, 3H), 5.31 (s, 2H), 3.88 (s, 3H), 3.74 (s, 3H), 2.25 (s, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$: 159.9, 152.8, 138.9, 137.3, 136.4, 129.7, 128.9, 128.6, 127.9, 127.3, 127.2, 126.6, 125.7, 122.8, 121.7, 114.5, 111.9, 110.1, 61.4, 55.2, 50.4, 19.1; FT-IR: $\tilde{\nu} = 3064, 2928, 1592, 1494, 1450, 1248, 1176, 1138, 1050, 1030, 740$ cm$^{-1}$; HRMS (ESI): m/z calcd for C$_{25}$H$_{25}$N$_2$O$_2$S $[M+H]^+$: 417.1631, found 417.1642.

(E)-1-(1-Benzyl-4-(4-fluorophenylthio)-1H-indol-3-yl)ethanone O-methyl oxime (4e):  
Colorless oil, 68%; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$: 7.37-7.30 (m, 3H), 7.26 (dd, $J = 8.0$, 1.2 Hz, 1H), 7.23-7.19 (m, 5H), 7.16-7.09 (m, 2H), 6.96 (t, $J = 8.6$ Hz, 2H), 5.27 (s, 2H), 3.85 (s, 3H), 2.26 (s, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$: 161.8 (d, $J = 246.2$ Hz), 152.7, 137.3, 136.4, 132.1 (d, $J = 2.6$ Hz), 131.9 (d, $J = 8.3$ Hz), 128.9, 128.6, 127.9, 127.2, 126.8 (d, $J = 17.8$ Hz), 125.5, 122.8, 116.1 (d, $J = 21.9$ Hz), 114.4, 109.8, 99.9, 61.5, 50.5, 19.1; $^{19}$F NMR (CDCl$_3$, 376 MHz) $\delta$: -115.9; FT-IR: $\tilde{\nu} = 3062, 2932, 2814, 1588, 1488, 1430, 1222, 1050, 774$ cm$^{-1}$; HRMS (ESI): m/z calcd for C$_{24}$H$_{22}$FN$_2$OS $[M+H]^+$: 405.1431, found 405.1445.
(E)-1-(1-Benzyl-4-(4-bromophenylthio)-1H-indol-3-yl)ethanone O-methyl oxime (4f): White amorphous solid, 76%; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.38-7.27 (m, 6H), 7.24-7.14 (m, 5H), 6.98 (d, $J = 8.0$ Hz, 2H), 5.30 (s, 2H), 3.82 (s, 3H), 2.23 (s, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$: 152.5, 137.4, 137.3, 136.3, 131.9, 130.1, 128.9, 128.8, 128.0, 127.5, 127.2, 126.7, 124.6, 122.8, 119.4, 114.4, 110.7, 61.4, 50.5, 19.1; FT-IR: $\tilde{\nu} = 2932, 2814, 2372, 1600, 1548, 1470, 1428, 1174, 1050, 772$ cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{24}$H$_{22}$$_{79}$BrN$_2$OS [M+H]$^+$: 465.0631, found 465.0615.

(E)-1-(1-Benzyl-4-(4-chlorophenylthio)-1H-indol-3-yl)ethanone O-methyl oxime (4g): Amorphous solid, 85%; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$: 7.39-7.30 (m, 4H), 7.25 (d, $J = 7.1$ Hz, 1H), 7.23-7.16 (m, 6H), 7.08 (d, $J = 8.3$ Hz, 2H), 5.31 (s, 2H), 3.85 (s, 3H), 2.26 (s, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$: 152.6, 137.4, 136.5, 136.3, 131.7, 130.0, 129.0, 128.9, 128.0, 127.4, 127.2, 127.0, 124.9, 122.8, 114.5, 110.6, 61.4, 50.5, 19.1; FT-IR: $\tilde{\nu} = 2932, 2818, 1552, 1472, 1220, 1050, 772$ cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{24}$H$_{22}$$_{35}$ClN$_2$OS [M+H]$^+$: 421.1136, found 421.1119.
(E)-1-(1-Benzyl-4-(2-fluorophenylthio)-1H-indol-3-yl)ethanone O-methyl oxime (4h):
Yellow oil, 94%; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.39-7.27 (m, 4H), 7.23-7.12 (m, 6H), 7.06 (m, 1H), 6.98-6.88 (m, 2H), 5.30 (s, 2H), 3.83 (s, 3H), 2.26 (s, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$: 160.1 (d, $J$ = 245.6 Hz), 152.7, 137.5, 136.5, 131.4, 129.0, 128.9, 128.1, 127.7 (d, $J$ = 7.3 Hz), 127.4, 127.3, 126.7, 124.9 (d, $J$ = 17.0 Hz), 124.7 (d, $J$ = 3.4 Hz), 124.1, 122.9, 115.5 (d, $J$ = 21.5 Hz), 114.6, 110.5, 61.5, 50.6, 19.1; $^{19}$F NMR (CDCl$_3$, 376 MHz) $\delta$: -110.8; FT-IR: $\tilde{\nu}$ = 3064, 2934, 2814, 1550, 1472, 1439, 1220, 1171, 1050, 772 cm$^{-1}$; HRMS (ESI): $m/z$ calcld for C$_{24}$H$_{22}$FN$_2$OS [M+H]$^+$: 405.1431, found 405.1442.

(E)-1-(1-Benzyl-4-(3-fluorophenylthio)-1H-indol-3-yl)ethanone O-methyl oxime (4i):
Pale yellow oil, 64%; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$: 7.38-7.29 (m, 5H), 7.21 (d, $J$ = 7.7 Hz, 3H), 7.19 (s, 1H), 7.16 (m, 1H), 6.89 (d, $J$ = 8.0 Hz, 1H), 6.83-6.78 (m, 2H), 5.32 (s, 2H), 3.83 (s, 3H), 2.23 (s, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$: 163.1 (d, $J$ = 247.4 Hz), 152.7, 140.9 (d, $J$ = 7.8 Hz), 137.6, 136.5, 130.1 (d, $J$ = 8.2 Hz), 129.1, 128.9, 128.2, 128.1, 128.0, 127.3, 124.0, 123.8 (d, $J$ = 2.4 Hz), 122.9, 115.1 (d, $J$ = 23.6 Hz), 114.6, 112.6 (d, $J$ = 21.7 Hz), 111.1, 61.5, 50.6, 19.2; $^{19}$F NMR (CDCl$_3$, 376 MHz) $\delta$: -112.7; FT-IR: $\tilde{\nu}$ = 3064, 2934, 2814, 2358, 1598, 1472, 1430, 1176, 1050, 774 cm$^{-1}$; HRMS (ESI): $m/z$ calcld for C$_{24}$H$_{22}$FN$_2$OS [M+H]$^+$: 405.1431, found 405.1445.
(E)-1-(1-Benzyl-4-(3-chlorophenylthio)-1H-indol-3-yl)ethanone O-methyl oxime (4j):
Yellow oil, 90%; \(^1\)H NMR (CDCl\(_3\), 600 MHz) \(\delta\): 7.39-7.27 (m, 5H), 7.23-7.18 (m, 4H), 7.17-7.07 (m, 3H), 6.97 (dt, \(J = 7.8, 1.8\) Hz, 1H), 5.32 (s, 2H), 3.85 (s, 3H), 2.23 (s, 3H); \(^13\)C NMR (CDCl\(_3\), 150 MHz) \(\delta\): 152.5, 140.4, 137.4, 136.3, 134.6, 132.9, 129.8, 128.9, 128.0, 127.9, 127.7, 127.2, 126.4, 125.7, 124.0, 122.8, 114.4, 110.9, 61.4, 50.5, 19.1; FT-IR: \(\tilde{\nu}\) = 3060, 2932, 2814, 1574, 1456, 1433, 1176, 1050, 774 cm\(^{-1}\); HRMS (ESI): \(m/z\) calcd for C\(_{24}\)H\(_{22}\)ClN\(_2\)O\(_3\) [M+H]\(^+\): 421.1136, found 421.1136.

(E)-1-(1-Benzyl-4-(naphthalen-2-ylthio)-1H-indol-3-yl)ethanone O-methyl oxime (4k):
Amorphous solid, 62%; \(^1\)H NMR (CDCl\(_3\), 600 MHz) \(\delta\): 7.78 (d, \(J = 8.4\) Hz, 1H), 7.75 (s, 1H), 7.72-7.68 (m, 2H), 7.47-7.40 (m, 2H), 7.39-7.25 (m, 5H), 7.23 (t, \(J = 7.8\) Hz, 3H), 7.19 (s, 1H), 7.16 (m, 1H), 5.32 (s, 2H), 3.71 (s, 3H), 2.29 (s, 3H); \(^13\)C NMR (CDCl\(_3\), 150 MHz) \(\delta\): 152.9, 137.5, 136.6, 134.9, 133.9, 132.0, 129.0, 128.8, 128.6, 128.1, 128.0, 127.8, 127.7, 127.4, 127.3, 126.42, 126.40, 126.3, 125.7, 122.9, 114.7, 110.1, 61.4, 50.6, 19.3; FT-IR: \(\tilde{\nu}\) = 3054, 2932, 2362, 1550, 1430, 1356, 1174, 1050, 742 cm\(^{-1}\); HRMS (ESI): \(m/z\) calcd for C\(_{28}\)H\(_{25}\)N\(_2\)O\(_3\) [M+H]\(^+\): 437.1682, found 437.1692.
(E)-1-(1-Benzyl-4-(benzylthio)-1H-indol-3-yl)ethanone O-methyl oxime (4l): Colorless oil, 26%; $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 7.34-7.28 (m, 3H), 7.25-7.19 (m, 5H), 7.19-7.14 (m, 4H), 7.13-7.05 (m, 2H), 5.28 (s, 2H), 4.09 (s, 2H), 3.99 (s, 3H), 2.34 (s, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$: 154.0, 137.9, 137.1, 136.7, 129.2, 129.0, 128.5, 128.27, 128.25, 128.0, 127.2, 127.12, 127.09, 124.1, 122.7, 114.5, 109.4, 61.7, 50.5, 40.7, 19.8; FT-IR: $\tilde{\nu}$ = 2930, 2852, 1650, 1540, 1454, 1428, 1359, 1339, 1248, 1176, 1050, 769 cm$^{-1}$; HRMS (ESI): m/z calcd for C$_{25}$H$_{25}$N$_2$OS [M+H]$^+$: 401.1682, found 401.1699.

(6a)

(E)-1-(1-Benzyl-2-(phenylthiomethyl)-1H-indol-3-yl)ethanone O-methyl oxime (6a): Yellow oil, 65%; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$: 7.69 (d, $J$ = 7.8 Hz, 1H), 7.34-7.31 (m, 2H), 7.30-7.22 (m, 7H), 7.21-7.13 (m, 2H), 7.01 (d, $J$ = 7.8 Hz, 2H), 5.52 (s, 2H), 4.48 (s, 2H), 3.98 (s, 3H), 2.19 (s, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$: 152.5, 137.2, 137.1, 134.9, 133.5, 131.4, 128.9, 128.8, 127.5, 127.1, 126.2, 126.1, 122.5, 120.5, 120.2, 112.7, 109.8, 61.7, 46.9, 29.5, 15.9; FT-IR: $\tilde{\nu}$ = 2932, 2814, 1585, 1546, 1466, 1433, 1360, 1234, 1197, 1160, 1052, 742 cm$^{-1}$; HRMS (ESI): m/z calcd for C$_{25}$H$_{25}$N$_2$OS [M+H]$^+$: 401.1682, found 401.1688.

(6b)

(E)-1-(1-Benzyl-2-(phenylthiomethyl)-1H-indol-3-yl)ethanone O-benzyl oxime (6b): Yellow oil, 63%; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$: 7.62 (d, $J$ = 7.8 Hz, 1H), 7.44 (d, $J$ = 7.8 Hz, 2H), 7.36
[(E)-1-(1-Benzyl-2-(phenylthiomethyl)-1H-indol-3-yl)propan-1-one O-methyl oxime (6c): Yellow oil, 67%; 1H NMR (CDCl3, 600 MHz) δ: 7.70 (d, J = 7.5 Hz, 1H), 7.35 (d, J = 9.0 Hz, 2H), 7.32-7.23 (m, 7H), 7.22-7.14 (m, 2H), 6.99 (d, J = 8.2 Hz, 2H), 5.40 (s, 2H), 4.47 (s, 2H), 3.97 (s, 3H), 2.81 (q, J = 7.5 Hz, 2H), 1.13 (t, J = 7.5 Hz, 3H); 13C NMR (CDCl3, 150 MHz) δ: 157.7, 137.4, 137.2, 137.1, 133.8, 132.2, 131.1, 129.7, 128.8, 127.0, 126.8, 126.6, 126.1, 122.5, 120.1, 111.5, 109.9, 61.6, 46.9, 29.6, 23.0, 10.8; FT-IR: ν = 2932, 2848, 1581, 1537, 1464, 1411, 1352, 1284, 1220, 1192, 1158, 772 cm⁻¹; HRMS (ESI): m/z calcd for C₂₆H₂₇N₂OS [M+H]⁺: 415.1839, found 415.1838.

(E)-1-(1-Benzyl-2-(p-tolylthiomethyl)-1H-indol-3-yl)ethanone O-methyl oxime (6d): Pale yellow oil, 49%; 1H NMR (CDCl3, 600 MHz) δ: 7.70 (d, J = 7.8 Hz, 1H), 7.30-7.24 (m, 4H), 7.23-7.14 (m, 4H), 7.08 (d, J = 7.8 Hz, 2H), 7.02 (d, J = 7.8 Hz, 2H), 5.53 (s, 2H), 4.43 (s, 2H), 3.99 (s, 3H), 2.34 (s, 3H), 2.18 (s, 3H); 13C NMR (CDCl3, 150 MHz) δ: 152.5, 137.4, 137.2, 137.1, 133.8, 132.2, 131.1, 129.7, 128.8, 127.0, 126.8, 126.1, 122.5, 120.4, 120.2, 112.7, 109.8, 99.9,
61.7, 46.9, 30.1, 21.1, 15.9; FT-IR: $\tilde{\nu} = 3028, 2932, 2814, 2362, 1548, 1464, 1356, 1220, 1052, 772$ cm$^{-1}$; HRMS (ESI): $m/z$ calcd for $C_{26}H_{27}N_{2}OS$ $[M+H]^+$: 415.1839, found 415.1840.

(E)-1-(1-Benzyl-2-((4-tert-butyllphenylthio)methyl)-1H-indol-3-yl)ethanone O-methyl oxime (6e):

Yellow oil, 55%; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.66 (d, $J = 7.8$ Hz, 1H), 7.31-7.22 (m, 8H), 7.21-7.10 (m, 2H), 7.00 (dd, $J = 7.8, 1.8$ Hz, 2H), 5.51 (s, 2H), 4.42 (s, 2H), 3.97 (s, 3H), 2.12 (s, 3H), 1.30 (s, 9H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$: 152.5, 150.5, 137.2, 137.1, 133.8, 131.9, 131.2, 128.8, 127.4, 126.2, 126.1, 125.9, 122.4, 120.4, 120.2, 112.7, 109.8, 61.6, 46.9, 34.5, 31.2, 29.9, 15.9; FT-IR: $\tilde{\nu} = 2960, 2904, 2859, 1462, 1416, 1360, 1220, 1160, 1052, 772$ cm$^{-1}$; HRMS (ESI): $m/z$ calcd for $C_{29}H_{33}N_{2}OS$ $[M+H]^+$: 457.2308, found 457.2317.

(E)-1-(1-Benzyl-2-((m-tolylthiomethyl)-1H-indol-3-yl)ethanone O-methyl oxime (6f):

Yellowish liquid, 62%; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$: 7.70 (d, $J = 8.0$ Hz, 1H), 7.29-7.23 (m, 4H), 7.20 (dt, $J = 8.0, 1.1$ Hz, 1H), 7.18-7.11 (m, 4H), 7.04 (d, $J = 8.0$ Hz, 1H), 7.02 (d, $J = 8.0$ Hz, 2H), 5.32 (s, 2H), 4.48 (s, 2H), 4.00 (s, 3H), 2.30 (s, 3H), 2.20 (s, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$: 152.5, 138.7, 137.2, 137.1, 134.7, 133.7, 131.9, 128.8, 128.7, 128.3, 127.9, 127.5, 126.2, 122.5, 120.4, 120.2, 112.7, 109.8, 61.7, 46.9, 29.4, 21.2, 15.9; FT-IR: $\tilde{\nu} = 3030, 2930, 1540, 1460, 1413, 1220, 1160, 1052, 772$ cm$^{-1}$; HRMS (ESI): $m/z$ calcd for $C_{26}H_{27}N_{2}OS$ $[M+H]^+$: 415.1839, found 415.1838.
(E)-1-(1-Benzyl-2-((4-chlorophenylthio)methyl)-1H-indol-3-yl)ethanone O-methyl oxime (6g): Yellow oil, 51%; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$: 7.68 (d, $J = 7.8$ Hz, 1H), 7.27-7.24 (m, 4H), 7.23-7.19 (m, 5H), 7.16 (m, 1H), 7.01 (d, $J = 7.8$ Hz, 2H), 5.52 (s, 2H), 4.46 (s, 2H), 3.97 (s, 3H), 2.20 (s, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$: 152.3, 137.2, 137.1, 133.3, 133.1, 132.9, 129.0, 128.8, 127.5, 126.1, 126.0, 122.6, 120.6, 120.3, 112.9, 109.9, 61.7, 46.9, 29.7, 15.9; FT-IR: $\tilde{\nu}$ = 3060, 2932, 2841, 1604, 1470, 1420, 1356, 1160, 1089, 1052, 742 cm$^{-1}$; HRMS (ESI): m/z calcd for C$_{25}$H$_{24}$ClN$_2$OS $[\text{M+H}]^+$: 435.1292, found 435.1299.

(6h): Yellow oil, 46%; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$: 7.68 (d, $J = 8.0$ Hz, 1H), 7.32-7.23 (m, 6H), 7.21 (t, $J = 8.0$ Hz, 1H), 7.16 (t, $J = 8.0$ Hz, 1H), 7.02 (d, $J = 7.6$ Hz, 2H), 6.95 (t, $J = 8.6$ Hz, 2H), 5.52 (s, 2H), 4.43 (s, 2H), 3.97 (s, 3H), 2.16 (s, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$: 162.6 (d, $J = 247.9$ Hz), 152.5, 137.3 (d, $J = 4.3$ Hz), 134.8 (d, $J = 7.9$ Hz), 133.6, 129.7, 128.9, 127.7, 126.3, 126.2, 122.7, 120.7, 120.4, 116.1 (d, $J = 21.9$ Hz), 113.1, 109.9, 61.8, 47.0, 30.6, 16.1; $^{19}$F NMR (CDCl$_3$, 376 MHz) $\delta$: -113.9; FT-IR: $\tilde{\nu}$ = 3021, 2948, 2856, 1605, 1542, 1427, 1218, 1160, 1052, 772 cm$^{-1}$; HRMS (ESI): m/z calcd for C$_{25}$H$_{24}$FN$_2$OS $[\text{M+H}]^+$: 419.1588, found 419.1590.
(E)-1-(1-Benzyl-2-((2-fluorophenylthio)methyl)-1H-indol-3-yl)ethanone O-methyl oxime (6i): Yellow oil, 74%; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$: 7.69 (d, $J = 8.0$ Hz, 1H), 7.34-7.24 (m, 6H), 7.21 (dt, $J = 8.0$, 1.1 Hz, 1H), 7.16 (dt, $J = 8.0$, 1.1 Hz, 1H), 7.09 (m, 1H), 7.06-7.00 (m, 3H), 5.62 (s, 2H), 4.48 (s, 2H), 3.99 (s, 3H), 2.16 (s, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$: 162.5 (d, $J = 246.4$ Hz), 152.3, 137.3 (d, $J = 2.2$ Hz), 135.0, 133.4, 130.1 (d, $J = 8.0$ Hz), 128.9, 127.6, 126.30, 126.28, 124.5 (d, $J = 3.8$ Hz), 122.7, 121.4, 120.5 (d, $J = 29.9$ Hz), 115.9 (d, $J = 23.0$ Hz), 113.1, 110.0, 61.8, 47.0, 28.9, 15.9; $^{19}$F NMR (CDCl$_3$, 376 MHz) $\delta$: -107.6; FT-IR: $\tilde{\nu} = 3062, 2930, 2856, 1542, 1470, 1358, 1220, 1160, 1052, 772$ cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{25}$H$_{24}$FN$_2$OS [M+H]$^+$: 419.1588, found 419.1596.

(E)-1-(1-Benzyl-2-((3-fluorophenylthio)methyl)-1H-indol-3-yl)ethanone O-methyl oxime (6j): Yellow oil, 59%; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.69 (d, $J = 7.6$ Hz, 1H), 7.32 – 7.11 (m, 7H), 7.11 – 6.96 (m, 4H), 6.91 (m, 1H), 5.32 (s, 2H), 4.51 (s, 2H), 4.38 (s, 3H), 3.98 (s, 3H), 2.26 (s, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$: 162.8 (d, $J = 249.0$ Hz), 152.6, 137.7, 137.3 (d, $J = 20.8$ Hz), 133.0, 130.3 (d, $J = 8.7$ Hz), 129.0, 127.7, 126.33, 126.30 (d, $J = 2.9$ Hz), 126.25, 122.8, 120.7, 120.4, 117.5 (d, $J = 22.5$ Hz), 113.9 (d, $J = 21.5$ Hz), 113.1, 110.1, 61.9, 47.1, 29.2, 16.1; $^{19}$F NMR (CDCl$_3$, 376 MHz) $\delta$: -112.07; FT-IR: $\tilde{\nu} = 2974, 2908, 1700, 1540, 1472, 1218, 1050, 772$ cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{25}$H$_{24}$FN$_2$OS [M+H]$^+$: 419.1588, found 419.1598.
(E)-1-(1-(4-Methoxybenzyl)-2-(phenylthiomethyl)-1H-indol-3-yl)ethanone O-methyl oxime (6k): Pale yellow oil, 56%; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$: 7.68 (d, $J$ = 8.0 Hz, 1H), 7.35-7.30 (m, 2H), 7.27-7.22 (m, 4H), 7.21-7.11 (m, 2H), 6.95 (d, $J$ = 8.0 Hz, 2H), 6.81 (d, $J$ = 8.0 Hz, 2H), 5.45 (s, 2H), 4.48 (s, 2H), 3.98 (s, 3H), 3.78 (s, 3H), 2.19 (s, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$: 158.9, 152.5, 137.1, 133.5, 131.4, 129.2, 128.9, 127.4, 127.1, 126.2, 122.5, 120.4, 120.2, 114.2, 112.7, 109.9, 99.9, 61.7, 55.3, 46.4, 29.5, 15.9; FT-IR: $\tilde{\nu}$ = 2941, 2893, 1612, 1512, 1462, 1253, 1220, 1050, 772 cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{26}$H$_{27}$N$_2$O$_2$S [M+H]$^+$: 431.1788, found 431.1786.

(E)-1-(1-Allyl-2-(phenylthiomethyl)-1H-indol-3-yl)ethanone O-methyl oxime (6l): Yellow oil, 57%; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$: 7.65 (d, $J$ = 8.0 Hz, 1H), 7.37-7.33 (m, 2H), 7.31-7.21 (m, 5H), 7.14 (t, $J$ = 8.0 Hz, 1H), 5.98 (m, 1H), 5.17 (dd, $J$ = 10.2, 1.1 Hz, 1H), 4.97 (dd, $J$ = 17.2, 1.1 Hz, 1H), 4.92-4.87 (m, 2H), 4.55 (s, 2H), 3.98 (s, 3H), 2.16 (s, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$: 152.5, 136.7, 135.0, 133.3, 133.1, 131.4, 128.9, 127.1, 126.2, 122.3, 120.3, 120.1, 116.8, 112.5, 109.8, 61.6, 45.8, 29.3, 15.9; FT-IR: $\tilde{\nu}$ = 3067, 2930, 2362, 1464, 1362, 1220, 1160, 772 cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{21}$H$_{23}$N$_2$OS [M+H]$^+$: 351.1526, found 351.1527.
1-(1-Benzyl-4-(phenylthio)-1H-indol-3-yl)ethanone (3ab): Yellow oil, 75%; \(^1H\) NMR (CDCl\(_3\), 600 MHz) \(\delta\): 7.73 (s, 1H), 7.51 (dd, \(J = 8.0, 1.2\) Hz, 2H), 7.40-7.30 (m, 6H), 7.16 (d, \(J = 8.0\) Hz, 2H), 7.10-7.03 (m, 2H), 6.81 (d, \(J = 7.8\) Hz, 1H), 5.36 (s, 2H), 2.55 (s, 3H); \(^13C\) NMR (CDCl\(_3\), 150 MHz) \(\delta\): 192.6, 138.0, 135.6, 135.0, 134.0, 133.1, 129.3, 129.1, 128.3, 127.8, 126.9, 123.9, 123.6, 122.8, 119.7, 110.7, 107.6, 50.8, 28.7; FT-IR: \(\tilde{\nu} = 3058, 2926, 2360, 1656, 1524, 1436, 1388\) cm\(^{-1}\); HRMS (ESI): \(m/z\) calcd for C\(_{23}\)H\(_{20}\)NOS \([M+H]^+\): 358.1260, found 358.1265.

![Image of 1-Benzyl-4-(phenylthio)-1H-indole (8)]

1-Benzyl-4-(phenylthio)-1H-indole (8): White amorphous solid, 72%; \(^1H\) NMR (CDCl\(_3\), 600 MHz) \(\delta\): 7.38-7.22 (m, 9H), 7.22-7.13 (m, 5H), 6.61 (d, \(J = 3.3\) Hz, 1H), 5.35 (s, 2H); \(^13C\) NMR (CDCl\(_3\), 150 MHz) \(\delta\): 137.2, 136.8, 136.5, 130.4, 129.4, 128.9, 128.84, 128.82, 127.8, 126.9, 126.0, 125.5, 124.4, 122.2, 109.9, 101.4, 50.4; FT-IR: \(\tilde{\nu} = 3058, 2922, 1548, 1464, 1360, 1220, 1174, 1026, 772\) cm\(^{-1}\); HRMS (ESI): \(m/z\) calcd for C\(_{21}\)H\(_{18}\)NS \([M+H]^+\): 316.1154, found 316.1147.

![Image of (E)-1-(4-(Phenylthio)-1H-indol-3-yl)ethanone O-methyl oxime (7)]

(E)-1-(4-(Phenylthio)-1H-indol-3-yl)ethanone O-methyl oxime (7): Yellow oil, 78%; \(^1H\) NMR (CDCl\(_3\), 400 MHz) \(\delta\): 8.53 (br s, 1H), 7.35 – 7.25 (m, 1H), 7.23 – 7.06 (m, 8H), 3.83 (s, 3H), 2.23 (s, 3H); \(^13C\) NMR (CDCl\(_3\), 100 MHz) \(\delta\): 153.2, 137.8, 136.9, 129.1, 129.0, 127.0, 126.8, 125.9, 125.5, 124.8, 123.2, 115.4, 111.7, 61.5, 19.2; FT-IR: \(\tilde{\nu} = 3056, 2928, 2370, 1584, 1438, 1220, 1158, 1050, 772\) cm\(^{-1}\); HRMS (ESI): \(m/z\) calcd for C\(_{17}\)H\(_{17}\)N\(_2\)OS \([M+H]^+\): 297.1056, found 297.1053.

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Reference:
Table 1: Crystal data and structure refinement for (E)-1-(1-Benzyl-5-fluoro-4-(phenylthio)-1H-indol-3-yl)ethanone O-methyl oxime (3c, CCDC: 1570067):

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S = 0.932    Npar = 268
Fig 1. ORTEP diagram of compound 3c.