Electronic Supplementary Information

Visible-Light-Induced Radical Cascade Reaction to Prepare Oxindoles via Alkyl Radical Addition to N-Arylacryl Amides

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Supporting Information

Table of Contents

1. General information ............................................................................................................................................. 3
2. General procedures for the preparation of substrates ......................................................................................... 4
3. General procedures for synthesis of oxindoles ..................................................................................................... 6
4. Preparation of 6 .................................................................................................................................................. 8
5. Preparation of 3ag .............................................................................................................................................. 8
6. Preparation of key intermediates 12 and 14 for the synthesis of core skeletons of physovenine, esermethole and physostigmine ............................................................................................................. 9
7. NMR titration experiments ............................................................................................................................... 11
8. Control experiments .......................................................................................................................................... 14
9. Characterization of substrates and products ...................................................................................................... 19
10. Copies of NMR Spectra .................................................................................................................................. 39
11. References ....................................................................................................................................................... 123
1. General information

Unless otherwise noted, all chemicals were purchased from commercial sources and used without further purification. All solvents for photophysical studies were used with anhydrous grade. Analytical TLC was performed on silica gel 60 F_{254} pre-coated plates. NMR spectra were recorded on Bruker Ascend™ 400 MHz and 500 MHz NMR spectrometers with tetramethylsilane (TMS) as an internal standard. Chemical shifts are reported in δ (ppm) relative to TMS. High resolution mass spectra were recorded using an Exactive Thermo Fisher Scientific mass spectrometer. Gas chromatography-mass spectrometry (GC-MS) analyses were carried out by an Agilent Technologies 7890A Network GC System. Irradiation was performed using 410 and 365 nm LEDs illumination instruments (3 W × 4) under argon atmosphere.
2. General procedures for the preparation of substrates

**Preparation of N-arylacrylamides.** Aniline (10 mmol), methyl iodide (12.0 mmol), potassium carbonate (13.0 mmol), and N,N-dimethylformamide (DMF, 25 mL) were added to a pressure vessel with a magnetic stirring bar. The vessel was then sealed and heated to 55 °C for 24 h. After being allowed to cool to room temperature, water was added into the mixture. The organic phase was collected, and the aqueous layer was extracted with ethyl acetate. The combined organic phase was washed with saturated brine and dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure by rotary evaporation. The crude product of N-methyl substituted aniline, if containing N,N-dimethyl substituted aniline and/or unreacted aniline, was purified by silica-gel flash column chromatography using petroleum ether/ethyl acetate as the eluent, or otherwise was directly used in the next step.

A round flask equipped with a magnetic stirring bar was charged with N-methyl substituted aniline (10 mmol) and trimethylamine (15.0 mmol), and dichloromethane (DCM, 50 mL). Methacryloyl chloride (15.0 mmol) in DCM solution was slowly added into the reaction at 0 °C. Then, the reaction mixture was stirred at room temperature overnight. After addition of water into the mixture, the organic phase was collected, and the aqueous layer was extracted with DCM. The combined organic phase was washed with saturated brine and dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure by rotary evaporation. The residue was purified by silica-gel flash column chromatography using petroleum ether/ethyl acetate as the eluent.
Scheme S1 Preparation of 1

2a, R = 4-OMe  2f, R = H
2b, R = 3-OMe  2g, R = 4-F
2c, R = 2-OMe  2h, R = 4-Cl
2d, R = 4-Me   2i, R = 4-CF₃
2e, R = 4-OCF₃ 2j, R = 4-CN

Fig. S2 Chemical structures of 2
Preparation of 2q. 1) To a solution of 4-acetylbenzoic acid (3.283 g, 20.0 mmol) in DCM (100 mL) at room temperature was added oxalyl chloride (5.077 g, 40.0 mmol) dropwise, followed by a catalytic amount of DMF (3 drops). The reaction mixture was stirred for 12 h at room temperature. After concentration under vacuum to remove DCM and unreacted oxalyl chloride, the crude acid chloride was re-dissolved in DCM (20 mL) and used in the next step without further purification. 2) To a solution of (-)-menthol (468.8 mg, 3.00 mmol) and Et$_3$N (607.1 mg, 6.00 mmol) in DCM (20 mL) was added the solution of the acid chloride in DCM (4 mL) dropwise at 0 °C. The resulting reaction mixture was stirred at room temperature for 24 h. Afterwards, the reaction mixture was concentrated under reduced pressure and the residue was purified by silica-gel flash column chromatography using petroleum ether/ethyl acetate as the eluent. 52% yield (menthol 4-acetylbenzoate, 470.0 mg, yellow oil). 3) To a stirred solution of menthol 4-acetylbenzoate (370.0 mg, 1.224 mmol) in MeCN (30 mL) were added $p$-TsOH·H$_2$O (349.0 mg, 1.836 mmol, 1.5 eq.) and NBS (217.8 mg, 1.224 mmol, 1.0 eq.), and the mixture was stirred for 12 h at 85 °C. After being concentrated under reduced pressure, the residue was re-dissolved in EtOAc, washed with water, dried over MgSO$_4$, filtered and evaporated under reduced pressure. The residue was purified by silica-gel flash column chromatography with DCM/pentane (2:1). 74% yield (282.0 mg, white solid).

Scheme S2 Preparation of 2q

3. General procedures for synthesis of oxindoles

Procedure A: To a dried reaction tube equipped with magnetic stirring bar were added $N$-methyl-$N$-phenylmethacrylamide 1 (0.2 mmol, 1.0 equiv), alkyl bromide 2 (0.4 mmol, 2.0 equiv), K$_3$PO$_4$ (0.4 mmol, 2.0 equiv), and MeCN (4.0 mL). The
reaction mixture was deaerated with argon for 15 min and irradiated by 410 nm LEDs for 10 h. After reaction, the mixture was filtered to remove the insoluble fraction. The filtrate was concentrated under reduced pressure by rotary evaporation. The desired product 3 was obtained by silica-gel flash column chromatography using petroleum ether/ethyl acetate as the eluent. For 1.0 mmol scale reaction, all reagents were scaled-up by ratio with 6.0 mL of MeCN were used as solvent.

![Scheme S3 Preparation of 3](image)

**Procedure B**: To a dried reaction tube equipped with magnetic stirring bar were added \(N\)-methyl-\(N\)-phenylmethacrylamide 1 (0.2 mmol, 1.0 equiv), 2,2,6,6-tetramethylpiperidine (TMP, 0.4 mmol, 2.0 equiv) and MeCN (2.0 mL). The reaction mixture was deaerated with argon for 15 min, followed by addition of alkyl iodide 4 (0.4 mmol, 2.0 equiv). The resulting mixture was irradiated by 410 nm LEDs for 10 h. After reaction, the mixture was concentrated under reduced pressure by rotary evaporation. The desired product 5 was obtained by silica-gel flash column chromatography using petroleum ether/ethyl acetate as the eluent. For 1.0 mmol scale reaction, all reagents were scaled-up by ratio with 6.0 mL of MeCN as solvent.

![Scheme S4 Preparation of 5](image)
4. Preparation of 6

1) To a round bottom flask equipped with a magnetic stirring bar, the purified oxindole 3a (97.0 mg, 0.30 mmol) and MeOH (4.0 mL) were added, followed by the addition of NH$_2$NH$_2$ (10.0 equiv., 80% w/w solution in water). After stirred at room temperature for 12 h, the resulting solution was concentrated, and the residue was extracted with ethyl acetate for 3 times. The combined organic fractions were dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The concentrated residue was directly used without further purification. By addition of freshly-distilled THF (6 mL) through a syringe under argon, the resulting solution was cooled to 0 °C and LiAlH$_4$ (113.9 mg, 3.00 mmol, 10.0 equiv) was added portionwise over 10 min under argon. Then, the suspension was stirred for 12 h at room temperature and quenched by saturated NaOH solution at 0 °C. The reaction mixture was filtered to collect the filtrate and the residue was soaked by ethyl acetate. Afterwards, the filtrate was extracted with ethyl acetate and combined with the soaking fraction. The combined fractions were dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure by rotary evaporation. The residue was purified by silica-gel flash column chromatography using petroleum ether/ethyl acetate as the eluent. 47% yield (45.3 mg, white solid).

Scheme S5 Preparation of 6

5. Preparation of 3ag

To a dried reaction tube equipped with magnetic stirring bar were added acrylamide 1a (0.2 mmol, 1.0 equiv), 2q (0.4 mmol, 2.0 equiv), K$_3$PO$_4$ (0.4 mmol, 2.0 equiv), and MeCN (4.0 mL). The reaction mixture was deaerated with argon for 15 min and irradiated by 410 nm LEDs for 10 h. After reaction, the mixture was filtered to remove the insoluble fraction. The filtrate was concentrated under reduced pressure by rotary evaporation. The desired product 3ag was obtained by silica-gel flash column chromatography using petroleum ether/ethyl acetate as the eluent (60.0 mg, 63% yield).

Scheme S6 Preparation of 3ag
6. Preparation of key intermediates 12 and 14 for the synthesis of core skeletons of physovenine, esermethole and physostigmine

Preparation of diethyl 2-[(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)methyl]malonate (3ah). To a dried reaction tube equipped with magnetic stirring bar were added acrylamide 1s (41 mg, 0.20 mmol, 1.0 equiv), diethyl 2-bromomalonate 2o (96 mg, 0.40 mmol, 2.0 equiv), NaHCO₃ (34 mg, 0.40 mmol, 2.0 equiv), and MeCN (4.0 mL). The reaction mixture was deaerated with argon for 15 min and irradiated by 410 nm LEDs for 24 h. After reaction, the mixture was filtered to remove the insoluble fraction. The filtrate was concentrated under reduced pressure by rotary evaporation. The desired product 3ah was obtained by silica-gel flash column chromatography using petroleum ether/ethyl acetate as the eluent.

Preparation of 2-[(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)methyl]malonic acid (7). 3ah (1.1 g, 3.03 mmol 1.0 equiv.) was added to a solution of KOH in EtOH (15% wt, 25 mL) and stirred at 95 °C for 3 h. Upon reaction completion checked by TLC, the reaction mixture was acidified with concentrated HCl to pH < 2. After evaporating most of ethanol under reduced pressure, the aqueous residue was extracted with DCM (50 mL × 6). The combined organic phase was washed with saturated brine and dried over Na₂SO₄, filtered, and concentrated under reduced pressure by rotary evaporation.

Preparation of 3-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)propanoic acid (8). A mixture of 7 (500 mg, 1.63 mmol, 1.0 equiv.) and Cu₂O (350 mg, 2.45 mmol, 1.5 equiv.) in 40 mL of MeCN was refluxed for 30 h. Then, the mixture was acidified with concentrated HCl to pH < 2 and concentrated under reduced pressure. The residue was extracted with DCM (50 mL × 3). The combined organic phase was washed with saturated brine and dried over Na₂SO₄, filtered, and concentrated under reduced pressure by rotary evaporation. The residue was purified by silica gel flash chromatography (DCM/MeOH = 20:1 v/v).

Preparation of 1,3-dioxoisouindolin-2-yl 3-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)propanoate (9). To a mixture of 8 (100 mg, 0.38 mmol, 1.0 equiv.), N,N-dimethylpyridin-4-amine (DMAP, 5 mg, 0.04 mmol, 0.1 equiv.), and 2-hydroxyisoindoline-1,3-dione (75 mg, 0.46 mmol, 1.2 equiv.) in 4 mL of anhydrous DCM was added diisopropylmethanediimine (58 mg, 0.46 mmol, 1.2 equiv.) at 0 °C under argon. The reaction mixture was stirred at room temperature under argon for 12 h. Upon reaction completion checked by TLC, the mixture was concentrated under reduced pressure and the residue was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4:1 v/v).
Preparation of 3-(3-iodopropyl)-5-methoxy-1,3-dimethylindolin-2-one (10).

A mixture of 9 (80 mg, 0.20 mmol, 1.0 equiv.), LiI (32 mg, 0.24 mmol, 1.2 equiv.) and PPh₃ (5 mg, 0.02 mmol, 0.1 equiv.) in 4 mL of anhydrous acetone was deaerated with argon for 15 min. Then, the mixture was irradiated under 456 nm light for 24 h with stirring at room temperature. Upon reaction completion checked by TLC, the mixture was concentrated under reduced pressure and the residue was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 10:1 to 4:1 v/v).

Preparation of 2-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)ethyl acetate (11). A mixture of 10 (50 mg, 0.14 mmol, 1.0 equiv.) and NaOAc (46 mg, 0.56 mmol, 4.0 equiv.) in 10 mL of anhydrous DMF was stirred at 110 °C under argon for 12 h. Upon reaction completion checked by TLC, the mixture was diluted with water and extracted with ethyl acetate (50 mL × 3). The combined organic phase was washed with saturated brine and dried over Na₂SO₄, filtered, and concentrated under reduced pressure by rotary evaporation. The residue was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3:1 v/v).

Preparation of 3-(2-hydroxyethyl)-5-methoxy-1,3-dimethylindolin-2-one (12). A mixture of 11 (50 mg, 0.18 mmol, 1.0 equiv.) and Na₂CO₃ (50 mg, 0.36 mmol, 2.0 equiv.) in 15 mL of EtOH was refluxed for 5 h. Upon reaction completion checked by TLC, the mixture was concentrated under reduced pressure by rotary evaporation and the residue was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 1:1 v/v).

Preparation of 3-(2-isocyanatoethyl)-5-methoxy-1,3-dimethylindolin-2-one (13). To a solution of 8 (85 mg, 0.32 mmol, 1.0 equiv.) and Et₃N (36 mg, 0.35 mmol, 1.1 equiv.) in 5 mL of anhydrous THF was added DPPA (101 mg, 0.36 mmol, 1.1 equiv.) at 0 °C under argon. Then, the mixture was stirred at room temperature for 24 h. After evaporation of THF under reduced pressure, the residue was re-dissolved in 12 mL of toluene and reflux for additional 24 h. Upon reaction completion checked by TLC, the mixture was concentrated under reduced pressure by rotary evaporation and the residue was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3:1 v/v).

Preparation of 3-(2-aminoethyl)-5-methoxy-1,3-dimethylindolin-2-one (14). A suspension of 13 (50 mg, 0.19 mmol, 1.0 equiv.) in a mixture of 12 M HCl / dioxane (6 mL, 1:1) was refluxed for 12 h. Upon reaction completion checked by TLC, the mixture was acidified with KOH (15%) to pH > 12 and extracted with DCM (50 mL × 3). The combined organic phase was washed with saturated brine and dried over MgSO₄, filtered, and concentrated under reduced pressure by rotary evaporation. The residue was purified by silica gel flash chromatography (DCM/MeOH = 10:1 v/v).
7. NMR titration experiments

(1) Determination of the binding stoichiometry between N-arylacrylamide 1a and C₆F₁₃I. ¹⁹F NMR spectra of ten samples of mixtures of 1a and C₆F₁₃I in CDCl₃ were recorded at room temperature. PhCF₃ (δₐ-C = -62.76 ppm) was used as an internal standard. The total volume of the mixture was 0.5 mL, and the total amount of 1a and C₆F₁₃I was kept constant at 0.25 mmol (0.5 M), while the amount of C₆F₁₃I was varied from 0 to 0.25 mmol (0–0.5 M). The molar ratios of C₆F₁₃I/(C₆F₁₃I + 1a) (i.e. χ(C₆F₁₃I)) were increased from 0.0 to 1.0 with a step of 0.1. ¹⁹F NMR spectrum for each sample was recorded and the chemical shifts differences (Δδ) for -CF₂I of C₆F₁₃I were used to draw the Job plot. The stoichiometry was determined by plotting ratios of [C₆F₁₃I] × Δδ against χ(C₆F₁₃I), which afforded a maximum at ratio χ(C₆F₁₃I) = 0.5, suggesting a 1:1 complex ratio between 1a and C₆F₁₃I.
<table>
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<th>$\chi$(C₆F₁₃I)</th>
<th>[C₆F₁₃I] (M)</th>
<th>$\delta$ (ppm)</th>
<th>$\Delta\delta$ (ppm)</th>
<th>[C₆F₁₃I]*$\Delta\delta$ (ppm)</th>
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$y = -0.3909x^2 + 0.3929x$
$R^2 = 0.9961$

**Fig. S4** Job plot for 1a and C₆F₁₃I in CDCl₃
(2) **Determination of the association constant** \((K_a)\). \(^{19}\text{F}\) NMR spectra of five samples of mixtures of \(C_6F_{13}I\) and \(1a\) in CDCl\(_3\) were recorded at room temperature. PhCF\(_3\) (\(\delta_{C-F} = -62.76\) ppm) was used as an internal standard. The total volume of the mixture was 0.5 mL, the amount of \(C_6F_{13}I\) was kept constant at 0.02 mmol (0.04 M), while that of \(1a\) increased from 0.06 (0.12 M) to 0.23 mmol (0.46 M). \(^{19}\text{F}\) NMR spectrum for each sample was recorded and the chemical shifts differences (\(\Delta\delta\)) for -CF\(_2\)I were used to draw the plot. The association constant \((K_a)\) of \(C_6F_{13}I\) and \(1a\) was calculated by intercept/slope from the plot, which gives 2.58 M\(^{-1}\).

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<th>[1a] (M)</th>
<th>1/[1a] (M(^{-1}))</th>
<th>(\Delta\delta) (ppm)</th>
<th>1/(\Delta\delta) (ppm)</th>
<th>(\Delta) (ppm)</th>
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8. Control experiments

(1) To a dried reaction tube equipped with magnetic stirring bar were added \( N \)-methyl-\( N \)-phenylmethacrylamide 1a (0.2 mmol), alkyl bromide 2a (0.4 mmol), \( K_3 \)PO₄ (0.4 mmol), TEMPO (0.4 mmol), and MeCN (4.0 mL). The reaction mixture was deaerated with argon for 15 min and irradiated by 410 nm LEDs for 10 h. After reaction, the mixture was filtered to remove the insoluble fraction. The filtrate was analysed by high resolution mass spectroscopy (HR MS).

![Chemical structure and plots](image)

**Fig. S5** Plot of \( 1/\Delta \delta \) against \( 1/[N \text{-arylacryl amide } 1a] \) in CDCl₃

**y = 0.2976x + 0.7691**
**\( R^2 = 0.9966 \)**

\( K_a = 2.58 \text{ M}^{-1} \)
(2) To a dried reaction tube equipped with magnetic stirring bar were added N-methyl-N-phenylmethacrylamide 1a-D₅ (0.1 mmol, 1.0 equiv), 2a (0.2 mmol, 2.0 equiv), and K₃PO₄ (0.2 mmol), followed by 2 mL of MeCN. The reaction mixture was deaerated with argon for 15 min and irradiated by 410 nm LEDs for 10 h. After reaction, the mixture was filtered to remove the insoluble fraction. The filtrate was concentrated under reduced pressure by rotary evaporation. The desired product 3a-D₄ was obtained by silica-gel flash column chromatography using petroleum ether/ethyl acetate as the eluent.
(3) To a dried reaction tube equipped with magnetic stirring bar were added N-methyl-N-phenylmethacrylamide 1a (0.1 mmol), 1a-D₅ (0.1 mmol), 2a (0.4 mmol), K₃PO₄ (0.4 mmol), followed by 4 mL of MeCN. The reaction mixture was deaerated with argon for 15 min and irradiated by 410 nm LEDs. The ratio of crude product 3a and 3a-D₄ was analysed by ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard. The value of KIE is 1.08.
(4) To a dried reaction tube equipped with magnetic stirring bar were added N-methyl-N-phenylmethacrylamide 1a (0.1 mmol), alkyl iodide 4a (0.2 mmol), TMP (0.2 mmol), TEMPO (0.2 mmol), and MeCN (1.0 mL). The reaction mixture was deaerated with argon for 15 min and irradiated by 410 nm LEDs for 10 h. After reaction, the mixture was filtered to remove the insoluble fraction. The filtrate was analysed by high resolution mass spectroscopy (HR MS).

$$\text{MeCN}$$

(5) To a dried reaction tube equipped with magnetic stirring bar were added N-methyl-N-phenylmethacrylamide 1a-D$_5$ (0.1 mmol, 1.0 equiv), 2,2,6,6-tetramethylpiperidine (TMP, 0.2 mmol, 2.0 equiv) and MeCN (1.0 mL). The reaction mixture was deaerated with argon for 15 min, followed by addition of alkyl iodide 4a (0.4 mmol, 2.0 equiv). The resulting mixture was irradiated by 410 nm LEDs for 10 h. After reaction, the mixture was filtered to remove the insoluble fraction. The filtrate was concentrated under reduced pressure by rotary evaporation. The desired product 5a-D$_4$ was obtained by silica-gel flash column chromatography using petroleum ether/ethyl acetate as the eluent.
(6) To a dried reaction tube equipped with magnetic stirring bar were added N-methyl-N-phenylmethacrylamide 1a (0.1 mmol), 1a-D₅ (0.1 mmol), TMP (0.4 mmol), and 2 mL of MeCN. The reaction mixture was deaerated with argon for 15 min, followed by addition of alkyl iodide 4a (0.4 mmol, 2.0 equiv). The resulting mixture was irradiated by 410 nm LEDs. The ratio of crude product 5a and 5a-D₄ was analysed by ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard. The value of KIE is 0.82.
9. Characterization of substrates and products

N-Methyl-N-[4-(methylthio)phenyl]methacrylamide (1c)

\[
\begin{align*}
\text{MeS} & \quad \text{N} \quad \text{O} \\
\text{Me} & \quad 1c \\
\end{align*}
\]

\({}^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 7.20 (d, J = 8.6 Hz, 2H), 7.05 (d, J = 8.6 Hz, 2H), 5.04 (s, 1H), 4.99 (s, 1H), 3.28 (s, 3H), 2.45 (s, 3H), 1.73 (s, 3H). {}^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \delta 172.0, 141.6, 140.6, 137.4, 127.0, 126.9, 119.4, 37.7, 20.3, 15.8. \text{HRMS (ESI): Calcd for C}_{12}\text{H}_{16}\text{NOS ([M + H]}^+\text{)} 222.0947, \text{found 222.0944.}
\]

N-Methyl-N-[4-[(trifluoromethyl)thio]phenyl]methacrylamide (1d)

\[
\begin{align*}
\text{F}_3\text{CS} & \quad \text{N} \quad \text{O} \\
\text{Me} & \quad 1d \\
\end{align*}
\]

\({}^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 7.59 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.6 Hz, 2H), 5.07 – 5.06 (m, 1H), 4.97 – 4.96 (m, 1H), 3.33 (s, 3H), 1.77 (dd, J = 1.7, 1.1 Hz, 3H). {}^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \delta 171.8, 147.1, 140.2, 137.2, 129.4 (q, J = 308.2 Hz), 127.0, 122.4 (q, J = 2.1 Hz), 120.1, 37.5, 20.1. {}^{19}\text{F NMR (376 MHz, CDCl}_3\text{)} \delta -42.85 (s). \text{HRMS (ESI): Calcd for C}_{12}\text{H}_{13}\text{F}_3\text{NOS ([M + H]}^+\text{)} 276.0664, \text{found 276.0664.}
\]
4-Methoxy-N-methyl-N-(3-methylbut-3-en-2-yl)aniline (1s)

\[
\begin{align*}
1^1 \text{H NMR (400 MHz, CDCl}_3) & \delta 7.04 (d, J = 8.9 \text{ Hz}, 2H), 6.84 (d, J = 8.9 \text{ Hz}, 2H), 5.01 (s, 1H), 4.98 (s, 1H), 3.80 (s, 3H), 3.29 (s, 3H), 1.73 (s, 3H). \\
1^3 \text{C NMR (100 MHz, CDCl}_3) & \delta 172.2, 158.3, 140.9, 137.4, 127.8, 119.0, 114.4, 55.4, 37.9, 20.4. \\
\text{HRMS (ESI): Calcd for C}_{12}H_{16}NO_2 [M + H]^+: 206.1176; Found: 206.1174. 
\end{align*}
\]

(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl 4-acetylbenzoate (menthol 4-acetylbenzoate) (2q)

\[
\begin{align*}
1^1 \text{H NMR (400 MHz, CDCl}_3) & \delta 8.10 (d, J = 8.6 \text{ Hz}, 2H), 7.98 (d, J = 8.6 \text{ Hz}, 2H), 4.93 (td, J = 10.8, 4.4 \text{ Hz}, 1H), 2.62 (s, 3H), 2.14 – 2.06 (m, 1H), 1.99 – 1.86 (m, 1H), 1.77 – 1.69 (m, 2H), 1.62 – 1.46 (m, 2H), 1.20 – 1.02 (m, 2H), 0.98 – 0.83 (m, 7H), 0.77 (d, J = 7.0 \text{ Hz}, 3H). \\
1^3 \text{C NMR (100 MHz, CDCl}_3) & \delta 197.54, 165.20, 140.06, 134.62, 129.78, 128.17, 75.44, 47.21, 40.89, 34.25, 31.44, 26.88, 26.54, 23.61, 22.03, 20.75, 16.52. \\
\text{HRMS (ESI): Calcd for C}_{19}H_{27}O_3^+ ([M + H]^+) 303.1955, found 303.1951. 
\end{align*}
\]

3-[3-(4-Methoxyphenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3a)

\[
\begin{align*}
1^1 \text{H NMR (500 MHz, CDCl}_3) & \delta 7.79 (d, J = 8.7 \text{ Hz}, 2H), 7.34 – 7.25 (m, 1H), 7.22 (d, J = 7.0 \text{ Hz}, 1H), 7.09 (t, J = 7.1 \text{ Hz}, 1H), 6.87 (d, J = 7.9 \text{ Hz}, 3H), 3.84 (s, 3H), 3.26 (s, 3H), 2.76 (ddd, J = 15.8, 11.6, 4.6 \text{ Hz}, 1H), 2.43 (ddd, J = 15.8, 11.1, 4.4 \text{ Hz}, 1H), 2.33 (td, J = 13.5, 4.5 \text{ Hz}, 1H), 2.23 (td, J = 14.1, 4.5 \text{ Hz}, 1H), 1.43 (s, 3H). \\
1^3 \text{C NMR (125 MHz, CDCl}_3) & \delta 197.9, 180.2, 163.4, 143.2, 133.4, 130.3, 129.7, 128.0, 122.8, 122.7, 113.6, 108.1, 55.4, 47.7, 33.2, 32.7, 26.2, 23.8. \\
\text{HRMS (ESI): Calcd for C}_{20}H_{22}NO_3^+ ([M + H]^+) 324.1594, found 324.1592. 
\end{align*}
\]
5-(tert-Butyl)-3-[3-(4-methoxyphenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3b)

\[ \text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3\text{) } \delta 7.79 (d, J = 8.9 \text{ Hz}, 2H), 7.31 (dd, J = 8.1, 2.0 \text{ Hz}, 1H), 7.25 (d, J = 1.9 \text{ Hz}, 1H), 6.87 (d, J = 6.8 \text{ Hz}, 2H), 6.80 (d, J = 8.1 \text{ Hz}, 1H), 3.85 (s, 3H), 3.25 (s, 3H), 2.76 (dd, J = 16.1, 11.1, 5.2 \text{ Hz}, 1H), 2.49 (ddd, J = 15.9, 10.7, 4.9 \text{ Hz}, 1H), 2.33 (ddd, J = 13.8, 10.7, 5.2 \text{ Hz}, 1H), 2.24 (ddd, J = 13.8, 11.1, 4.9 \text{ Hz}, 1H), 1.44 (s, 3H), 1.33 (s, 9H). \]

\[ \text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3\text{) } \delta 198.1, 180.4, 163.4, 146.1, 140.8, 133.2, 130.3, 129.8, 124.6, 119.8, 113.6, 107.4, 55.4, 47.9, 34.6, 33.3, 32.8, 31.6, 26.2, 23.8. \]

HRMS (ESI): Calcd for C\textsubscript{24}H\textsubscript{30}NO\textsubscript{3}+ ([M + H]^+) 380.2220, found 380.2217.

3-[3-(4-Methoxyphenyl)-3-oxopropyl]-1,3-dimethyl-5-(methylthio)indolin-2-one (3c)

\[ \text{\textsuperscript{1}H NMR (500 MHz, CDCl}_3\text{) } \delta 7.77 (d, J = 8.8 \text{ Hz}, 2H), 7.22 (dd, J = 8.1, 1.9 \text{ Hz}, 1H), 7.16 (d, J = 1.8 \text{ Hz}, 1H), 6.86 (d, J = 8.8 \text{ Hz}, 2H), 6.78 (d, J = 8.1 \text{ Hz}, 1H), 3.83 (s, 3H), 3.23 (s, 3H), 2.80 – 2.66 (m, 1H), 2.47 (s, 3H), 2.46 – 2.39 (m, 1H), 2.31 (ddd, J = 13.8, 11.0, 5.0 \text{ Hz}, 1H), 2.20 (ddd, J = 13.8, 11.2, 4.6 \text{ Hz}, 1H), 1.41 (s, 3H). \]

\[ \text{\textsuperscript{13}C NMR (125 MHz, CDCl}_3\text{) } \delta 197.8, 179.9, 163.4, 141.4, 134.4, 131.8, 130.3, 129.7, 128.0, 123.2, 113.6, 108.5, 55.5, 47.8, 33.2, 32.7, 26.3, 23.8, 17.7. \]

HRMS (ESI): Calcd for C\textsubscript{21}H\textsubscript{24}NO\textsubscript{3}S+ ([M + H]^+) 370.1471, found 370.1472.

3-[3-(4-Methoxyphenyl)-3-oxopropyl]-1,3-dimethyl-5-[(trifluoromethyl)thio]indolin-2-one (3d)

\[ \text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3\text{) } \delta 7.76 (d, J = 8.9 \text{ Hz}, 2H), 7.59 (dd, J = 8.1, 1.8 \text{ Hz}, 1H), 7.46 (d, J = 1.8 \text{ Hz}, 1H), 6.98 – 6.77 (m, 3H), 3.83 (s, 3H), 3.25 (s, 3H), 2.72 (ddd, J = 16.0, 10.8, 5.2 \text{ Hz}, 1H), 2.51 (ddd, J = 15.9, 10.8, 4.8 \text{ Hz}, 1H), 2.42 – 2.27 (m, 1H), 2.21 (ddd, J = 14.0, 11.0, 4.9 \text{ Hz}, 1H), 1.43 (s, 3H). \]

\[ \text{\textsuperscript{13}C NMR (125 MHz, CDCl}_3\text{) } \delta 197.4, 180.0, 163.5, 145.8, 137.5, 134.9, 130.9, 130.3, 129.6, 129.5 (q, J = 306.2 \text{ Hz}), 117.3 (q, J = 2.0 \text{ Hz}), 113.7, 108.9, 55.5, 47.7, 33.0, 32.6, 26.4, 23.5. \]

\[ \text{\textsuperscript{19}F NMR (376 MHz, CDCl}_3\text{) } \delta -43.7 \text{ (s). HRMS (ESI): Calcd for } C\textsubscript{21}H\textsubscript{23}F\textsubscript{3}NO\textsubscript{3}S+ ([M + H]^+) 424.1189, \text{ found 424.1190.} \]
5-Bromo-3-[3-(4-methoxyphenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3e)

\[ \text{Br} \quad \begin{array}{c}
\text{Me} \\
\text{O} \\
\text{O} \\
\text{N}
\end{array} \]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.78 (d, \( J = 8.9 \) Hz, 2H), 7.39 (dd, \( J = 8.2, 2.0 \) Hz, 1H), 7.31 (d, \( J = 1.9 \) Hz, 1H), 6.88 (d, \( J = 8.9 \) Hz, 2H), 6.73 (d, \( J = 8.2 \) Hz, 1H), 3.84 (s, 3H), 3.23 (s, 3H), 2.74 (ddd, \( J = 16.0, 11.2, 5.0 \) Hz, 1H), 2.45 (ddd, \( J = 15.9, 10.9, 4.7 \) Hz, 1H), 2.32 (ddd, \( J = 13.9, 10.9, 5.0 \) Hz, 1H), 2.19 (ddd, \( J = 13.8, 11.2, 4.7 \) Hz, 1H), 1.41 (s, 3H).

\[^{13}\text{C} \]NMR (100 MHz, CDCl\(_3\)) \( \delta \) 197.7, 179.7, 163.6, 142.3, 135.7, 131.0, 130.4, 129.8, 126.2, 115.6, 113.8, 109.6, 55.6, 48.0, 33.2, 32.8, 26.4, 23.8. HRMS (ESI): Calcd for C\(_{20}\)H\(_{21}\)BrNO\(_3\)\(^+\) ([M + H]\(^+\)) 402.0699, found 402.0696.

3-[3-(4-Methoxyphenyl)-3-oxopropyl]-1,3-dimethyl-2-oxoindoline-5-carbonitrile (3f)

\[ \text{NC} \quad \begin{array}{c}
\text{Me} \\
\text{O} \\
\text{O} \\
\text{N}
\end{array} \]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.76 (d, \( J = 8.9 \) Hz, 2H), 7.59 (dd, \( J = 8.1, 1.5 \) Hz, 1H), 7.43 (d, \( J = 1.4 \) Hz, 1H), 6.89 (dd, \( J = 13.4, 8.5 \) Hz, 3H), 3.84 (s, 3H), 3.26 (s, 3H), 2.74 (ddd, \( J = 16.0, 10.6, 5.3 \) Hz, 1H), 2.49 (ddd, \( J = 16.0, 10.3, 5.1 \) Hz, 1H), 2.33 (ddd, \( J = 14.1, 10.3, 5.3 \) Hz, 1H), 2.22 (ddd, \( J = 14.1, 10.6, 5.2 \) Hz, 1H), 1.43 (s, 3H).

\[^{13}\text{C} \]NMR (100 MHz, CDCl\(_3\)) \( \delta \) 197.1, 179.9, 163.5, 147.0, 134.6, 133.5, 130.3, 129.5, 126.2, 119.1, 113.7, 108.5, 105.9, 55.5, 47.5, 32.9, 32.5, 26.5, 23.5. HRMS (ESI): Calcd for C\(_{21}\)H\(_{21}\)N\(_2\)O\(_3\)\(^+\) ([M + H]\(^+\)) 349.1547, found 349.1543.

Methyl 3-[3-(4-methoxyphenyl)-3-oxopropyl]-1,3-dimethyl-2-oxoindoline-5-carboxylate (3g)

\[ \text{MeO}_2\text{C} \quad \begin{array}{c}
\text{Me} \\
\text{O} \\
\text{O} \\
\text{N}
\end{array} \]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.03 (dd, \( J = 8.2, 1.7 \) Hz, 1H), 7.87 (d, \( J = 1.4 \) Hz, 1H), 7.80 – 7.69 (m, 2H), 6.89 (d, \( J = 8.2 \) Hz, 1H), 6.88 – 6.83 (m, 2H), 3.90 (s, 3H), 3.83 (s, 3H), 3.27 (s, 3H), 2.73 (ddd, \( J = 15.8, 11.3, 4.8 \) Hz, 1H), 2.45 (ddd, \( J = 15.6, 11.0, 4.5 \) Hz, 1H), 2.34 (ddd, \( J = 13.8, 10.9, 4.8 \) Hz, 1H), 2.23 (ddd, \( J = 13.8, 11.3, 4.5 \) Hz, 1H), 1.44 (s, 3H).

\[^{13}\text{C} \]NMR (100 MHz, CDCl\(_3\)) \( \delta \) 197.5, 180.5, 166.8, 163.4, 147.3, 133.5, 130.9, 130.3, 129.6, 124.7, 124.0, 113.6, 107.7, 55.4, 52.1, 47.5, 33.1, 32.6, 26.4, 23.7. HRMS (ESI): Calcd for C\(_{22}\)H\(_{24}\)NO\(_5\)\(^+\) ([M + H]\(^+\)) 382.1649, found 382.1650.

5-Acetyl-3-[3-(4-methoxyphenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3h)

\[ \text{Ac} \quad \begin{array}{c}
\text{Me} \\
\text{O} \\
\text{O} \\
\text{N}
\end{array} \]

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.95 (dd, \( J = 8.2, 1.6 \) Hz, 1H), 7.83 (d, \( J = 1.5 \) Hz, 1H), 7.78 – 7.74 (m, 2H), 6.91 (d, \( J = 8.2 \) Hz, 1H), 6.89 – 6.84 (m, 2H), 3.84 (s, 3H), 3.29 (s, 3H), 2.74 (ddd, \( J = 16.1, 11.0, 5.1 \) Hz,
1H), 2.59 (s, 3H), 2.48 (ddd, J = 16.0, 10.8, 4.9 Hz, 1H), 2.36 (ddd, J = 15.8, 10.8, 5.1 Hz, 1H), 2.26 (ddd, J = 14.0, 11.1, 4.8 Hz, 1H), 1.45 (s, 3H). 13C NMR (125 MHz, CDCl3) δ 197.5, 196.9, 180.6, 163.4, 147.5, 133.7, 132.3, 130.3, 130.1, 129.6, 122.8, 113.6, 107.6, 55.5, 47.5, 33.1, 32.6, 26.5, 26.5, 23.6. HRMS (ESI): Calcd for C22H24NO4+ ([M + H]+) 366.1700, found 366.1697.

5-Benzoyl-3-[3-(4-methoxyphenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3i)

1H NMR (500 MHz, CDCl3) δ 7.81 – 7.75 (m, 6H), 7.60 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 6.91 (d, J = 8.1 Hz, 1H), 6.87 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H), 3.30 (s, 3H), 2.77 (ddd, J = 16.0, 10.5, 5.0 Hz, 1H), 2.56 (ddd, J = 16.0, 10.5, 5.0 Hz, 1H), 2.38 – 2.32 (m, 1H), 1.46 (s, 3H). 13C NMR (125 MHz, CDCl3) δ 197.5, 195.7, 180.6, 163.5, 147.2, 138.1, 133.7, 132.2, 132.1, 130.3, 129.8, 129.6, 128.3, 124.7, 113.7, 107.4, 55.5, 47.6, 33.1, 32.6, 26.5, 23.6. HRMS (ESI): Calcd for C27H26NO4+ ([M + H]+) 428.1856, found 428.1858.

4,5,6-Trimethoxy-3-[3-(4-methoxyphenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3j)

1H NMR (400 MHz, CDCl3) δ 7.83 – 7.76 (m, 2H), 6.91 – 6.83 (m, 2H), 6.21 (s, 1H), 3.97 (s, 3H), 3.90 (s, 3H), 3.84 (s, 3H), 3.82 (s, 3H), 3.20 (s, 3H), 2.67 (ddd, J = 16.8, 11.1, 5.1 Hz, 1H), 2.52 – 2.39 (m, 2H), 2.29 (ddd, J = 13.0, 11.7, 5.1 Hz, 1H), 1.47 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 198.1, 180.7, 163.3, 154.2, 150.8, 139.3, 137.6, 130.3, 129.8, 115.6, 113.6, 89.5, 61.0, 60.8, 56.4, 55.4, 48.5, 33.7, 31.8, 26.3, 22.6. HRMS (ESI): Calcd for C23H28NO6+ ([M + H]+) 414.1911, found 414.1907.

3-[3-(4-Methoxyphenyl)-3-oxopropyl]-1,3-dimethyl-1,3-dihydro-2H-benzo[g]indol-2-one (3k)

1H NMR (500 MHz, CDCl3) δ 7.81 – 7.67 (m, 3H), 7.59 – 7.50 (m, 2H), 7.50 – 7.42 (m, 2H), 6.98 (d, J = 7.6 Hz, 1H), 6.82 (d, J = 8.9 Hz, 2H), 3.82 (s, 3H), 3.57 (s, 3H), 2.87 (ddd, J = 16.1, 11.6, 4.9 Hz, 1H), 2.76 (ddd, J = 13.8, 11.4, 4.9 Hz, 1H), 2.49 (ddd, J = 15.7, 11.4, 4.1 Hz, 1H), 2.40 (ddd, J = 13.7, 11.6, 4.1 Hz, 1H), 1.70 (s, 3H). 13C NMR (125 MHz, CDCl3) δ 198.2, 173.0, 163.3, 137.5, 136.7, 133.4, 130.3, 129.7, 127.3, 126.4, 126.3, 122.8, 122.6, 119.7, 113.5, 108.5, 55.4, 47.1, 37.6, 34.5, 31.4, 29.8. HRMS (ESI): Calcd for C24H24NO3+ ([M + H]+) 374.1751, found 374.1751.
3-[3-(4-Methoxyphenyl)-3-oxopropyl]-3-methyl-1-phenylindolin-2-one (3l)

\[
\text{H NMR (400 MHz, CDCl}_3\) \delta 7.80 (d, } J = 8.8 \text{ Hz, 2H), } 7.55 (dd, } J = 8.5, 7.1 \text{ Hz, 2H), } 7.48 - 7.37 \text{ (m, 3H), } 7.28 (d, } J = 7.3 \text{ Hz, 1H), } 7.20 (t, } J = 7.7 \text{ Hz, 1H), } 7.11 (t, } J = 7.4 \text{ Hz, 1H), } 6.86 (dd, } J = 8.4, 3.1 \text{ Hz, 3H), } 3.83 (s, 3H), 2.91 (ddd, } J = 16.1, 11.3, 5.0 \text{ Hz, 1H), 2.57 (ddd, } J = 15.8, 11.0, 4.6 \text{ Hz, 1H), 2.42 (ddd, } J = 16.0, 11.3, 5.0 \text{ Hz, 1H), 2.31 (ddd, } J = 13.8, 11.5, 4.6 \text{ Hz, 1H), 1.55 (s, 3H).}
\]

13C NMR (101 MHz, CDCl3) δ 197.8, 179.7, 163.4, 143.0, 134.5, 133.3, 130.3, 129.7, 129.7, 128.1, 128.0, 126.5, 123.3, 123.1, 113.7, 109.4, 55.5, 47.8, 33.3, 33.3, 24.0.

HRMS (ESI): Calcd for C_{25}H_{24}NO_{3}+ ([M + H]^+) 386.1751, found 386.1745.

3-[3-[3-(4-Methoxyphenyl)-3-oxopropyl]-3-methyl-2-oxoindolin-1-yl]propanenitrile (3m)

\[
\text{H NMR (400 MHz, CDCl}_3\) \delta 7.91 – 7.74 (m, 2H), 7.37 – 7.19 (m, 2H), 7.13 (td, } J = 7.5, 1.0 \text{ Hz, 1H), 6.95 (d, } J = 7.8 \text{ Hz, 1H), 6.91 – 6.82 (m, 2H), 4.15 (dt, } J = 14.2, 6.6 \text{ Hz, 1H), 4.00 (dt, } J = 14.1, 6.8 \text{ Hz, 1H), 3.84 (s, 3H), 2.99 – 2.73 (m, 3H), 2.46 (ddd, } J = 16.0, 10.6, 4.7 \text{ Hz, 1H), 2.40 – 2.22 (m, 2H), 1.46 (s, 3H).}
\]

13C NMR (100 MHz, CDCl3) δ 197.7, 180.4, 163.4, 141.2, 133.3, 130.3, 129.7, 128.2, 123.4, 123.3, 117.2, 113.6, 108.0, 55.4, 47.6, 35.9, 33.2, 32.6, 24.1, 16.4. HRMS (ESI): Calcd for C_{22}H_{23}N_{2}O_{3}+ ([M + H]^+) 363.1703, found 363.1703.

1-Benzyl-3-[3-(4-methoxyphenyl)-3-oxopropyl]-3-methylindolin-2-one (3n)

\[
\text{H NMR (400 MHz, CDCl}_3\) \delta 7.75 – 7.61 (m, 2H), 7.43 – 7.29 (m, 5H), 7.25 – 7.16 (m, 2H), 7.05 (td, } J = 7.5, 1.0 \text{ Hz, 1H), 6.89 – 6.80 (m, 3H), 5.11 (d, } J = 15.4 \text{ Hz, 1H), 4.84 (d, } J = 15.4 \text{ Hz, 1H), 3.86 (s, 3H), 2.88 – 2.65 (m, 1H), 2.49 – 2.18 (m, 3H), 1.50 (s, 3H).}
\]

13C NMR (100 MHz, CDCl3) δ 197.7, 180.4, 163.4, 142.3, 136.3, 133.4, 130.2, 129.7, 128.9, 128.0, 127.7, 127.6, 122.9, 122.8, 113.6, 109.0, 55.4, 47.7, 43.7, 33.3, 32.7, 24.0. HRMS (ESI): Calcd for C_{26}H_{26}NO_{3}+ ([M + H]^+) 400.1907, found 400.1909.

1-[3-(4-Methoxyphenyl)-3-oxopropyl]-1-methyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one (3o)

\[
\text{H NMR (400 MHz, CDCl}_3\) \delta 7.83 – 7.74 (m, 2H), 7.02 (dd, } J = 9.9, 7.1 \text{ Hz, 2H), 6.98 – 6.92 (m, 1H), 6.90 – 6.83 (m, 2H), 3.83 (s, 3H), 3.74 (t, } J = 5.9 \text{ Hz, 2H), 2.86 – 2.72 (m, 3H), 2.48 (ddd, } J = 15.9, 10.8, 4.9 \text{ Hz, 1H), 2.35 – 2.15 (m, 2H), 2.07 – 1.96 (m, 2H), 1.42 (s, 3H).}
\]

13C NMR
(100 MHz, CDCl$_3$) $\delta$ 198.0, 179.1, 163.4, 138.9, 132.0, 130.3, 129.8, 126.8, 122.2, 120.6, 120.1, 113.6, 55.4, 49.1, 38.8, 33.4, 32.7, 24.6, 23.5, 21.4. HRMS (ESI): Calcd for C$_{22}$H$_{24}$NO$_3$ $^{+}$ ([M + H]$^+$) 350.1752, found 350.1752.

8-[3-(4-Methoxyphenyl)-3-oxopropyl]-6,8-dimethyl-6,8-dihydro-7H-thiazolo[4,5-e]indol-7-one (3p)

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.03 (s, 1H), 7.88 (d, $J = 8.4$ Hz, 1H), 7.77 – 7.63 (m, 2H), 7.05 (d, $J = 8.3$ Hz, 1H), 6.88 – 6.72 (m, 2H), 3.82 (s, 3H), 3.33 (s, 3H), 2.84 – 2.64 (m, 2H), 2.55 – 2.45 (m, 2H), 1.67 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 197.9, 180.3, 163.2, 156.2, 149.0, 142.0, 130.3, 129.8, 129.0, 125.7, 121.4, 113.5, 107.2, 55.4, 49.2, 33.9, 32.2, 26.7, 22.7. HRMS (ESI): Calcd for C$_{21}$H$_{21}$N$_2$O$_3$S $^{+}$ ([M + H]$^+$) 381.1267, found 381.1267.

7-[3-(4-Methoxyphenyl)-3-oxopropyl]-5,7-dimethyl-5,7-dihydro-6H-thiazolo[5,4-f]indol-6-one (3p$'$)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.98 (s, 1H), 7.80 – 7.68 (m, 3H), 7.55 (s, 1H), 6.86 – 6.80 (m, 2H), 3.83 (s, 3H), 3.35 (s, 3H), 2.95 – 2.61 (m, 1H), 2.46 – 2.36 (m, 2H), 2.30 (td, $J = 10.6$, 1.6 Hz, 1H), 1.49 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 197.7, 179.7, 163.4, 154.3, 153.2, 142.7, 133.2, 130.2, 129.6, 128.1, 116.2, 113.6, 102.5, 55.4, 47.7, 33.1, 33.1, 26.6, 24.4. HRMS (ESI): Calcd for C$_{21}$H$_{21}$N$_2$O$_3$S $^{+}$ ([M + H]$^+$) 381.1267, found 381.1267.

4-Methoxy-3-[3-(4-methoxyphenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3q)

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.84 – 7.75 (m, 2H), 7.26 (t, $J = 8.1$ Hz, 1H), 6.88 (d, $J = 8.9$ Hz, 2H), 6.63 (d, $J = 8.4$ Hz, 1H), 6.53 (d, $J = 7.7$ Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.24 (s, 3H), 2.73 – 2.61 (m, 1H), 2.57 – 2.40 (m, 2H), 2.31 (ddd, $J = 12.7$, 11.1, 4.7 Hz, 1H), 1.50 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 198.3, 180.6, 163.3, 156.1, 144.4, 130.4, 129.8, 129.2, 118.5, 113.5, 105.9, 101.4, 55.4, 55.4, 48.4, 33.9, 30.7, 26.4, 21.6. HRMS (ESI): Calcd for C$_{21}$H$_{24}$NO$_4^+$ ([M + H]$^+$) 354.1700, found 354.1700.

6-Methoxy-3-[3-(4-methoxyphenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3q$'$)

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.79 (d, $J = 8.9$ Hz, 2H), 7.11 (d, $J = 8.1$ Hz, 1H), 6.88 (d, $J = 8.9$ Hz, 2H), 6.59 (dd, $J = 8.1$, 2.3 Hz, 1H), 6.45 (d, $J = 2.3$ Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.25 (s, 3H), 2.73 (ddd, $J = 16.2$, 11.3, 5.0 Hz, 1H), 2.44 (ddd, $J = 15.9$, 11.0, 4.7 Hz, 1H), 2.31
(dd, $J = 13.7, 10.9, 5.0$ Hz, 1H), 2.21 (dd, $J = 13.8, 11.3, 4.7$ Hz, 1H), 1.41 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 198.0, 180.9, 163.4, 160.1, 144.4, 130.3, 129.8, 125.3, 123.3, 113.6, 106.4, 96.2, 55.5, 55.5, 47.3, 33.3, 32.9, 26.3, 24.1. HRMS (ESI): Calcd for C$_{21}$H$_{24}$NO$_4^+$ ([M + H]$^+$) 354.1700, found 354.1700.

3-[3-(3-Methoxyphenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3r)

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.40 – 7.33 (m, 2H), 7.33 – 7.27 (m, 2H), 7.22 (d, $J = 7.2$ Hz, 1H), 7.12 – 7.04 (m, 2H), 6.88 (d, $J = 7.8$ Hz, 1H), 3.84 (s, 3H), 3.27 (s, 3H), 2.79 (ddd, $J = 16.3, 11.3, 5.0$ Hz, 1H), 2.49 (ddd, $J = 16.2, 11.0, 4.6$ Hz, 1H), 2.35 (ddd, $J = 13.9, 10.9, 5.0$ Hz, 1H), 2.25 (ddd, $J = 13.8, 11.2, 4.6$ Hz, 1H), 1.44 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 199.2, 180.2, 159.7, 143.2, 138.0, 133.4, 129.5, 128.1, 122.8, 122.7, 120.7, 119.4, 112.3, 108.1, 55.4, 47.6, 33.7, 32.5, 26.3, 23.9. HRMS (ESI): Calcd for C$_{20}$H$_{22}$NO$_3^+$ ([M + H]$^+$) 324.1594, found 324.1592.

3-[3-(2-Methoxyphenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3s)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.54 (dd, $J = 7.7, 1.8$ Hz, 1H), 7.41 (ddd, $J = 8.3, 7.3, 1.8$ Hz, 1H), 7.32 – 7.26 (m, 1H), 7.25 – 7.20 (m, 1H), 7.09 (td, $J = 7.5, 1.0$ Hz, 1H), 6.95 (td, $J = 7.5, 1.0$ Hz, 1H), 6.88 (ddd, $J = 13.1, 8.1$ Hz, 2H), 3.77 (s, 3H), 3.24 (s, 3H), 2.80 (ddd, $J = 16.6, 11.3, 5.2$ Hz, 1H), 2.51 (ddd, $J = 16.8, 10.9, 4.8$ Hz, 1H), 2.37 – 2.13 (m, 2H), 1.43 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 201.9, 180.4, 158.4, 143.4, 133.8, 133.4, 130.2, 128.3, 128.0, 122.9, 122.7, 120.7, 111.6, 108.0, 55.4, 47.8, 38.9, 32.9, 26.2, 23.5. HRMS (ESI): Calcd for C$_{20}$H$_{22}$NO$_3^+$ ([M + H]$^+$) 324.1594, found 324.1591.

1,3-Dimethyl-3-(3-oxo-3-(p-tolyl)propyl)indolin-2-one (3t)$^2$

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.68 (d, $J = 8.2$ Hz, 2H), 7.27 (td, $J = 7.7, 1.2$ Hz, 1H), 7.24 – 7.15 (m, 3H), 7.07 (td, $J = 7.5, 0.8$ Hz, 1H), 6.86 (d, $J = 7.8$ Hz, 1H), 3.25 (s, 3H), 2.77 (ddd, $J = 16.2, 11.3, 5.0$ Hz, 1H), 2.46 (ddd, $J = 16.0, 11.0, 4.6$ Hz, 1H), 2.37 (s, 3H), 2.36 – 2.28 (m, 1H), 2.22 (ddd, $J = 13.8, 11.3, 4.6$ Hz, 1H), 1.42 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 199.0, 180.2, 143.7, 143.2, 134.2, 133.5, 129.2, 128.1, 128.0, 122.8, 122.7, 108.1, 47.7, 33.5, 32.6, 26.2, 23.8, 21.6. HRMS (ESI): Calcd for C$_{20}$H$_{22}$NO$_2^+$ ([M + H]$^+$) 308.1645, found 308.1643.

26
1,3-Dimethyl-3-[3-oxo-3-[4-(trifluoromethoxy)phenyl]propyl]indolin-2-one (3u)

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.91 – 7.79 (m, 2H), 7.31 – 7.26 (m, 1H), 7.25 – 7.17 (m, 3H), 7.08 (t, J = 7.8 Hz, 1H), 6.86 (d, J = 7.8 Hz, 1H), 3.25 (s, 3H), 2.77 (ddd, J = 16.3, 11.1, 5.0 Hz, 1H), 2.58 – 2.40 (m, 1H), 2.34 (dd, J = 13.9, 10.8, 5.0 Hz, 1H), 2.23 (dd, J = 14.0, 11.1, 4.7 Hz, 1H), 1.43 (s, 3H). 13C NMR (125 MHz, CDCl$_3$) δ 197.8, 180.1, 152.5, 143.1, 134.8, 133.3, 130.0, 128.2, 122.9, 122.7, 120.3, 120.2 (q, J = 257.5 Hz), 108.2, 47.6, 33.6, 32.4, 26.3, 23.8. 19F NMR (376 MHz, CDCl$_3$) δ −57.64 (s). HRMS (ESI): Calcd for C$_{20}$H$_{19}$F$_3$NO$_3$+ ([M + H]$^+$) 378.1312, found 378.1310.

1,3-Dimethyl-3-[3-oxo-3-phenylpropyl]indolin-2-one (3v)$^2$

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.85 – 7.73 (m, 2H), 7.60 – 7.48 (m, 1H), 7.47 – 7.35 (m, 2H), 7.29 (td, J = 7.7, 1.2 Hz, 1H), 7.23 (d, J = 7.3 Hz, 1H), 7.09 (td, J = 7.5, 1.0 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 3.27 (s, 3H), 2.82 (ddd, J = 16.3, 11.2, 5.0 Hz, 1H), 2.51 (ddd, J = 16.5, 10.9, 4.7 Hz, 1H), 2.36 (ddd, J = 13.8, 10.9, 5.0 Hz, 1H), 2.25 (ddd, J = 13.9, 11.2, 4.7 Hz, 1H), 1.45 (s, 3H). 13C NMR (100 MHz, CDCl$_3$) δ 199.3, 180.2, 143.2, 136.7, 133.4, 133.0, 128.5, 128.1, 128.0, 122.8, 122.7, 108.1, 47.6, 33.6, 32.5, 26.2, 23.8. HRMS (ESI): Calcd for C$_{19}$H$_{20}$NO$_2$+ ([M + H]$^+$) 294.1489, found 294.1485.

3-[3-(4-Fluorophenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3w)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.89 – 7.73 (m, 2H), 7.28 (td, J = 7.7, 1.3 Hz, 1H), 7.25 – 7.16 (m, 1H), 7.15 – 6.99 (m, 3H), 6.86 (d, J = 7.7 Hz, 1H), 3.25 (s, 3H), 2.76 (ddd, J = 16.2, 11.2, 5.0 Hz, 1H), 2.47 (ddd, J = 16.3, 10.8, 4.7 Hz, 1H), 2.33 (ddd, J = 13.8, 10.8, 5.0 Hz, 1H), 2.22 (ddd, J = 13.8, 11.2, 4.7 Hz, 1H), 1.42 (s, 3H). 13C NMR (100 MHz, CDCl$_3$) δ 197.8, 180.3, 167.0, 164.5, 143.3, 133.5, 133.2 (d, J = 3.0 Hz), 130.8, 129.5 (d, J = 250.9 Hz), 122.9 (d, J = 10.7 Hz), 115.7 (d, J = 21.7 Hz), 108.2, 47.7, 33.6, 32.6, 26.4, 23.9. 19F NMR (376 MHz, CDCl$_3$) δ −105.39 (tt, J = 8.6, 5.4 Hz). HRMS (ESI): Calcd for C$_{19}$H$_{19}$FNO$_2$+ ([M + H]$^+$) 312.1394, found 312.1391.

3-[3-(4-Chlorophenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3x)$^2$

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.78 – 7.71 (m, 2H), 7.40 – 7.35 (m, 2H), 7.30 (td, J = 7.7, 1.2 Hz, 1H), 7.22 (d, J = 7.3 Hz, 1H), 7.09 (td, J = 7.5, 0.9 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 3.27 (s, 3H), 2.77 (ddd, J = 16.3, 11.1, 5.1 Hz, 1H), 2.50 (ddd, J = 16.4, 10.7, 4.8 Hz, 1H), 2.34 (ddd, J = 13.9, 10.8, 5.0 Hz, 1H), 2.23
(dd, J = 13.9, 11.1, 4.8 Hz, 1H), 1.44 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 198.1, 180.1, 143.1, 139.4, 134.9, 133.3, 129.4, 128.8, 128.1, 122.8, 122.7, 108.1, 47.6, 33.6, 32.4, 26.3, 23.8. HRMS (ESI): Calcd for C$_{19}$H$_{19}$ClNO$_2$ $^+$ ([M + H]$^+$) 328.1099, found 328.1097.

1,3-Dimethyl-3-[3-oxo-3-[4-(trifluoromethyl)phenyl]propyl]indolin-2-one (3y)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.90 (d, J = 8.1 Hz, 2H), 7.67 (d, J = 8.2 Hz, 2H), 7.30 (td, J = 7.7, 1.2 Hz, 1H), 7.22 (d, J = 6.8 Hz, 1H), 7.10 (td, J = 7.5, 0.8 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 3.27 (s, 3H), 2.82 – 2.66 (m, 1H), 2.66 – 2.46 (m, 1H), 2.42 – 2.31 (m, 1H), 2.30 – 2.20 (m, 1H), 1.45 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 198.4, 180.1, 143.1, 139.3, 134.3 (q, J = 32.7 Hz), 133.2, 128.3, 128.2, 125.6 (q, J = 3.7 Hz), 123.6 (q, J = 272.6 Hz), 122.9, 122.7, 108.2, 47.5, 33.9, 32.2, 26.3, 23.8. 19F NMR (376 MHz, CDCl$_3$) $\delta$ –63.1 (s). HRMS (ESI): Calcd for C$_{20}$H$_{19}$F$_3$NO$_2$ $^+$ ([M + H]$^+$) 362.1362, found 362.1359.

4-[3-(1,3-Dimethyl-2-oxoindolin-3-yl)propanoyl]benzonitrile (3z)$^2$

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 – 7.79 (m, 2H), 7.73 – 7.66 (m, 2H), 7.33 – 7.25 (m, 1H), 7.20 (dd, J = 7.4, 0.7 Hz, 1H), 7.08 (td, J = 7.5, 1.0 Hz, 1H), 6.87 (d, J = 7.8 Hz, 1H), 3.25 (s, 3H), 2.79 (ddd, J = 16.8, 10.8, 5.1 Hz, 1H), 2.56 (ddd, J = 13.9, 10.5, 4.9 Hz, 1H), 2.34 (ddd, J = 13.9, 10.5, 5.2 Hz, 1H), 2.23 (ddd, J = 13.9, 10.8, 4.9 Hz, 1H), 1.43 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 198.0, 180.0, 143.1, 139.6, 133.2, 132.4, 128.4, 128.2, 122.9, 122.7, 117.9, 116.3, 108.2, 47.5, 33.9, 32.1, 26.3, 23.8. HRMS (ESI): Calcd for C$_{20}$H$_{19}$N$_2$O$_2$ $^+$ ([M + H]$^+$) 319.1441, found 319.1440.

3-[3-(2,5-Dimethoxyphenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3aa)

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.31 – 7.26 (m, 1H), 7.22 (d, J = 7.2 Hz, 1H), 7.13 – 7.06 (m, 2H), 6.97 (dd, J = 9.0, 3.2 Hz, 1H), 6.85 (dd, J = 14.4, 8.4 Hz, 2H), 3.77 (s, 3H), 3.72 (s, 3H), 3.24 (s, 3H), 2.83 – 2.77 (m, 1H), 2.56 – 2.49 (m, 1H), 2.30 – 2.17 (m, 2H), 1.43 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 201.3, 180.3, 153.4, 152.9, 143.3, 133.6, 128.3, 127.9, 122.9, 122.6, 119.9, 113.7, 113.1, 107.8, 55.9, 55.8, 47.7, 38.8, 32.8, 26.1, 23.3. HRMS (ESI): Calcd for C$_{21}$H$_{24}$NO$_4$ $^+$ ([M + H]$^+$) 354.1700, found 354.1697.
3-[3-(3,4-Dimethoxyphenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3ab)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.41 – 7.36 (m, 2H), 7.26 (td, $J = 7.7$, 1.2 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.07 (td, $J = 7.5$, 0.8 Hz, 1H), 6.82 (dd, $J = 15.5$, 7.9 Hz, 2H), 3.90 (s, 3H), 3.89 (s, 3H), 3.24 (s, 3H), 2.75 (ddd, $J = 15.8$, 11.3, 4.8 Hz, 1H), 2.43 (ddd, $J = 15.5$, 11.0, 4.6 Hz, 1H), 2.32 (ddd, $J = 13.8$, 11.0, 4.8 Hz, 1H), 2.20 (ddd, $J = 13.7$, 11.3, 4.6 Hz, 1H), 1.41 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 198.0, 180.2, 153.2, 148.9, 143.2, 133.4, 129.9, 128.0, 122.8, 122.7, 110.1, 109.9, 108.1, 56.0, 56.0, 47.7, 33.2, 33.0, 26.2, 23.8. HRMS (ESI): Calcd for C$_{21}$H$_{24}$NO$_4$ + ([M + H]$^+$) 354.1700, found 354.1698.

3-[3-(3,4-Dichlorophenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3ac)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.85 (d, $J = 2.0$ Hz, 1H), 7.62 (dd, $J = 8.4$, 2.0 Hz, 1H), 7.48 (d, $J = 8.3$ Hz, 1H), 7.30 (td, $J = 7.7$, 1.3 Hz, 1H), 7.21 (ddd, $J = 7.4$, 1.3, 0.6 Hz, 1H), 7.09 (td, $J = 7.5$, 1.0 Hz, 1H), 6.88 (d, $J = 7.8$ Hz, 1H), 3.27 (s, 3H), 2.74 (ddd, $J = 16.6$, 10.7, 5.2 Hz, 1H), 2.52 (ddd, $J = 16.7$, 10.3, 5.0 Hz, 1H), 2.34 (ddd, $J = 13.9$, 10.4, 5.3 Hz, 1H), 2.24 (ddd, $J = 13.9$, 10.7, 5.0 Hz, 1H), 1.44 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 197.1, 180.1, 143.1, 137.5, 136.2, 133.2, 130.6, 130.0, 128.2, 127.1, 122.9, 122.8, 108.2, 47.5, 33.6, 32.2, 26.3, 23.9. HRMS (ESI): Calcd for C$_{19}$H$_{18}$Cl$_2$NO$_2$ + ([M + H]$^+$) 362.0709, found 362.0708.

3-[3-(Benzofuran-2-yl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3ad)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.65 (d, $J = 7.6$ Hz, 1H), 7.52 (d, $J = 8.4$ Hz, 1H), 7.48 – 7.41 (m, 1H), 7.36 (d, $J = 0.8$ Hz, 1H), 7.32 – 7.20 (m, 3H), 7.08 (td, $J = 7.5$, 1.0 Hz, 1H), 6.83 (d, $J = 7.7$ Hz, 1H), 3.27 (s, 3H), 2.77 (ddd, $J = 16.1$, 10.7, 5.4 Hz, 1H), 2.53 (ddd, $J = 16.1$, 10.2, 5.4 Hz, 1H), 2.45 – 2.22 (m, 2H), 1.44 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 190.3, 180.1, 155.5, 152.1, 143.2, 133.1, 128.2, 128.1, 127.0, 123.9, 123.3, 122.9, 122.8, 112.9, 112.4, 108.1, 47.7, 34.0, 32.3, 26.3, 23.8. HRMS (ESI): Calcd for C$_{21}$H$_{20}$NO$_3$ + ([M + H]$^+$) 334.1438, found 334.1429.

Diethyl 2-[(1,3-dimethyl-2-oxindolin-3-yl)methyl]malonate (3ae)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.25 (td, $J = 7.7$, 1.2 Hz, 1H), 7.18 – 7.12 (m, 1H), 7.03 (td, $J = 7.5$, 0.8 Hz, 1H), 6.83 (d, $J = 7.8$ Hz, 1H), 4.11 (q, $J = 7.2$ Hz, 2H), 3.82 (dq, $J = 10.8$, 7.1 Hz, 1H), 3.65 (dq, $J = 10.8$, 7.1 Hz, 1H), 3.20 (s, 3H), 3.01 (dd, $J = 8.1$, 5.4 Hz, 1H), 2.63 – 2.40 (m, 2H), 1.37 (s, 3H), 1.20 (t, $J = 7.1$ Hz, 3H), 1.05 (t, $J = 7.2$ Hz, 3H).
Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 179.3, 168.9, 168.8, 143.4, 132.0, 128.3, 123.5, 122.4, 108.1, 61.6, 61.4, 48.7, 47.1, 35.8, 26.2, 24.5, 14.0, 13.8. HRMS (ESI): Calcd for C$_{15}$H$_{24}$NO$_5$ ([M + H]$^+$) 334.1649, found 334.1637.

Diethyl 2-[(1,3-dimethyl-2-oxindolin-3-yl)methyl]-2-methylmalonate (3af)$^4$

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.26 (td, $J = 7.7$, 1.2 Hz, 1H), 7.09 (d, $J = 7.3$ Hz, 1H), 7.00 (t, $J = 7.9$ Hz, 1H), 6.84 (d, $J = 7.8$ Hz, 1H), 4.17 – 4.06 (m, 2H), 3.78 (q, $J = 7.1$ Hz, 2H), 3.21 (s, 3H), 2.75 (d, $J = 2.3$ Hz, 2H), 1.35 (s, 3H), 1.19 (t, $J = 7.1$ Hz, 3H), 1.09 (t, $J = 7.1$ Hz, 3H), 1.02 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 179.9, 172.0, 171.2, 143.2, 131.8, 128.1, 124.0, 121.9, 108.2, 61.5, 61.0, 52.9, 46.2, 41.1, 27.9, 18.8, 13.9. HRMS (ESI): Calcd for C$_{19}$H$_{26}$NO$_5$ ([M + H]$^+$) 348.1805, found 348.1795.

(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl 4-(3-(1,3-dimethyl-2-oxindolin-3-yl)propanoyl)benzoate (3ag)

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, $J = 8.4$ Hz, 2H), 7.83 (d, $J = 8.4$ Hz, 2H), 7.28 (t, $J = 7.3$ Hz, 1H), 7.21 (d, $J = 7.2$ Hz, 1H), 7.08 (t, $J = 7.5$ Hz, 1H), 6.87 (d, $J = 7.8$ Hz, 1H), 4.93 (td, $J = 10.8$, 4.3 Hz, 1H), 3.26 (s, 3H), 2.91 – 2.69 (m, 1H), 2.65 – 2.44 (m, 1H), 2.41 – 2.30 (m, 1H), 2.30 – 2.19 (m, 1H), 2.18 – 2.08 (m, 1H), 1.99 – 1.85 (m, 1H), 1.79 – 1.69 (m, 2H), 1.65 – 1.50 (m, 2H), 1.43 (s, 3H), 1.21 – 1.04 (m, 2H), 1.00 – 0.86 (m, 7H), 0.78 (d, $J = 6.9$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 198.83 (d, $J = 3.7$ Hz), 180.08, 165.19, 143.14, 139.65 (d, $J = 0.8$ Hz), 134.47, 133.25, 129.69, 128.15, 128.83, 122.71, 108.17, 75.42, 47.55, 47.20, 40.87, 34.24, 33.97, 32.30 (d, $J = 3.9$ Hz), 31.44, 26.53, 26.26, 23.81 (d, $J = 2.3$ Hz), 23.62, 22.04, 20.75, 16.53 (d, $J = 1.4$ Hz). HRMS (ESI): Calcd for C$_{30}$H$_{38}$NO$_4$ ([M + H]$^+$) 476.2795, found 476.2788.

Diethyl 2-((5-methoxy-1,3-dimethyl-2-oxindolin-3-yl)methyl)malonate (3ah)

$^1$H NMR (400 MHz, CDCl$_3$) δ 6.81 – 6.77 (m, 2H), 6.74 (d, $J = 8.0$ Hz, 1H), 4.13 (q, $J = 7.1$ Hz, 2H), 3.93 – 3.81 (m, 1H), 3.79 (s, 3H), 3.73 (m, 1H), 3.19 (s, 3H), 3.03 (dd, $J = 8.0$, 5.5 Hz, 1H), 2.57 (dd, $J = 14.3$, 5.5 Hz, 1H), 2.48 (dd, $J = 14.3$, 8.0 Hz, 1H), 1.38 (s, 3H), 1.22 (t, $J = 7.1$ Hz, 3H), 1.09 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 179.00, 168.93, 168.81, 155.98, 136.90, 133.40, 112.65, 110.80, 108.46, 61.63, 61.39, 55.83, 48.68, 47.54, 35.86, 26.30, 24.43, 13.95, 13.78. HRMS (ESI): Calcd for C$_{19}$H$_{26}$NO$_6$ ([M + H]$^+$) 364.1755, found 364.1750.
1,3-Dimethyl-3-(2,2,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (5a)\(^5,6\)

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\begin{array}{c}
\text{Me} & \text{N} & \text{O} \\
\text{Me} & \text{N} & \text{O}
\end{array}
\]

\(\text{H NMR (400 MHz, CDCl}_3\) δ 7.39 - 7.20 (m, 2H), 7.09 (td, J = 7.6, 0.8 Hz, 1H), 6.89 (d, J = 7.8 Hz, 1H), 3.25 (s, 3H), 2.88 (dd, J = 35.2, 15.3 Hz, 1H), 2.60 (ddd, J = 31.0, 15.4, 8.1 Hz, 1H), 1.43 (s, 3H). \(\text{C NMR (100 MHz, CDCl}_3\) δ 178.6, 142.8, 131.3, 128.5, 123.6, 123.5, 122.6, 108.5, 44.2 (d, J = 2.1 Hz), 36.9 (t, J = 20.4 Hz), 26.5, 25.9. \(\text{F NMR (376 MHz, CDCl}_3\) δ −81.1 (tt, J = 9.7, 2.7 Hz, 3F), −108.0 - −109.7 (m, 1F), −113.8 - −115.6 (m, 1F), −124.1 - −125.0 (m, 2F), −125.2 - −126.8 (m, 2F). HRMS (ESI): Calcd for C\(_{15}\)H\(_{13}\)F\(_9\)NO\(^+\) [M + H\(^+\)]: 394.0848; Found: 394.0843.

5-(tert-Butyl)-1,3-dimethyl-3-(2,2,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (5b)

\[
\begin{array}{c}
\text{Me} & \text{N} & \text{O} \\
\text{Me} & \text{N} & \text{O}
\end{array}
\]

\(\text{H NMR (400 MHz, CDCl}_3\) δ 7.34 - 7.32 (m, 2H), 6.81 (d, J = 8.6 Hz, 1H), 3.23 (s, 3H), 2.87 (dd, J = 35.6, 14.8 Hz, 1H), 2.61 (ddd, J = 30.7, 15.4, 8.4 Hz, 1H), 1.44 (s, 3H), 1.32 (s, 9H). \(\text{C NMR (100 MHz, CDCl}_3\) δ 178.8, 145.9, 140.4, 130.9, 124.9, 121.0, 120.9, 107.8, 44.5 (d, J = 2.3 Hz), 36.7 (t, J = 20.2 Hz), 34.6, 31.5, 26.5, 25.9. \(\text{F NMR (376 MHz, CDCl}_3\) δ −81.1 (t, J = 10.0 Hz, 3F), −107.8 - −110.7 (m, 1F), −113.7 - −115.8 (m, 1F), −124.6 - −124.7 (m, 2F), −125.7 - −126.2 (m, 2F). HRMS (ESI): Calcd for C\(_{19}\)H\(_{21}\)F\(_9\)NO\(^+\) [M + H\(^+\)]: 450.1475, found 450.1475.

1,3-Dimethyl-5-(methylthio)-3-(2,2,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (5c)

\[
\begin{array}{c}
\text{MeS} & \text{N} & \text{O} \\
\text{MeS} & \text{N} & \text{O}
\end{array}
\]

\(\text{H NMR (500 MHz, CDCl}_3\) δ 7.37 - 7.18 (m, 2H), 6.83 (d, J = 8.1 Hz, 1H), 3.24 (s, 3H), 2.89 (dd, J = 35.2, 15.3 Hz, 1H), 2.59 (ddd, J = 30.9, 15.4, 8.0 Hz, 1H), 2.48 (s, 3H), 1.43 (s, 3H). \(\text{C NMR (125 MHz, CDCl}_3\) δ 178.2, 141.2, 132.2, 131.7, 128.8, 124.4, 109.0, 44.3 (d, J = 2.1 Hz), 36.9 (t, J = 20.3 Hz), 26.6, 25.9, 18.0. \(\text{F NMR (376 MHz, CDCl}_3\) δ −79.8 - −83.9 (m, 3F), −106.2 - −110.5 (m, 1F), −111.6 - −116.8 (m, 1F), −123.8 - −125.2 (m, 2F), −125.2 - −126.7 (m, 2F). HRMS (ESI): Calcd for C\(_{16}\)H\(_{15}\)F\(_9\)NO\(^+\) [M + H\(^+\)]: 440.0725, found 440.0721.

1,3-Dimethyl-3-(2,2,3,4,4,5,5,5-nonafluoropentyl)-5-((trifluoromethyl)thio)indolin-2-one (5d)

\[
\begin{array}{c}
\text{Me} & \text{N} & \text{O} \\
\text{Me} & \text{N} & \text{O}
\end{array}
\]

\(\text{H NMR (500 MHz, CDCl}_3\) δ 7.64 (dd, J = 8.1, 1.8 Hz, 1H), 7.55 (s, 1H), 6.94 (d, J = 8.1 Hz, 1H), 3.26 (s, 3H), 2.91 (dd, J = 34.6, 15.3 Hz, 1H), 2.62 (ddd, J = 30.6, 15.5, 8.1 Hz, 1H), 1.46 (s, 3H). \(\text{C NMR (125 MHz, CDCl}_3\) δ 178.4, 145.5, 137.9, 132.5, 131.9, 129.5 (q, J = 308.4 Hz), 117.4 (d, J = 2.3 Hz), 109.4, 44.1 (d, J = 2.3 Hz), 37.0 (t, J = 20.4 Hz), 26.7, 25.8. \(\text{F NMR (376 MHz, CDCl}_3\) δ −44.0 (s, 3F),
5-Bromo-1,3-dimethyl-3-(2,2,3,4,5,5,5-nonfluoropentyl)indolin-2-one (5e)

\[
\begin{align*}
\text{1H NMR (400 MHz, CDCl}_3) & \text{ } \delta 7.44 (dd, J = 8.3, 2.0 Hz, 1H), 7.39 (s, 1H), 6.77 (d, J = 8.3 Hz, 1H), 3.22 (s, 3H), 2.88 (dd, J = 35.2, 15.4 Hz, 1H), 1.42 (s, 3H). \\
\text{13C NMR (100 MHz, CDCl}_3) & \text{ } \delta 177.9, 141.9, 133.3, 131.4, 126.8, 115.3, 110.0, 44.3 (d, J = 2.3 Hz), 36.9 (t, J = 20.4 Hz), 26.6, 25.8. \\
\text{19F NMR (376 MHz, CDCl}_3) & \text{ } \delta -81.1 (tt, J = 9.7, 2.4 Hz, 3F), -107.7 -110.49 (m, 1F), -113.5 -115.1 (m, 1F), -124.3 -125.5 (m, 2F), -125.5 -126.5 (m, 2F). \\
\text{HRMS (ESI): Calcd for C}_{13}H_{12}BrF_{9}NO^+ ([M + H]^+) & \text{ } 471.9953, \text{ found 471.9957.}
\end{align*}
\]

1,3-Dimethyl-3-(2,2,3,4,5,5,5-nonfluoropentyl)-2-oxoindoline-5-carbonitrile (5f)

\[
\begin{align*}
\text{1H NMR (400 MHz, CDCl}_3) & \text{ } \delta 7.65 (dd, J = 8.2, 1.6 Hz, 1H), 7.54 (s, 1H), 6.97 (d, J = 8.2 Hz, 1H), 3.27 (s, 3H), 2.92 (dd, J = 34.5, 14.9 Hz, 1H), 2.63 (ddd, J = 30.5, 15.5, 8.0 Hz, 1H), 1.45 (s, 3H). \\
\text{13C NMR (100 MHz, CDCl}_3) & \text{ } \delta 178.2, 146.7, 133.9, 132.3, 127.0, 119.0, 109.1, 106.0, 43.9 (d, J = 2.4 Hz), 36.9 (t, J = 20.3 Hz), 26.7, 25.7. \\
\text{19F NMR (376 MHz, CDCl}_3) & \text{ } \delta -61.95 (t, J = 10.6 Hz). \\
\text{HRMS (ESI): Calcd for C}_{12}H_{13}F_{3}N_{2}O^+ ([M + H]^+) & \text{ } 244.0944, \text{ found 244.0939.}
\end{align*}
\]

1,3-Dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (5g)

\[
\begin{align*}
\text{1H NMR (500 MHz, CDCl}_3) & \text{ } \delta 7.34 (td, J = 7.7, 1.2 Hz, 1H), 7.31 -7.27 (m, 1H), 7.11 (td, J = 7.6, 0.9 Hz, 1H), 6.91 (d, J = 7.8 Hz, 1H), 3.26 (s, 3H), 2.84 (dq, J = 15.1, 10.7 Hz, 1H), 2.67 (dq, J = 15.1, 10.4 Hz, 1H), 1.43 (s, 3H). \\
\text{13C NMR (125 MHz, CDCl}_3) & \text{ } \delta 178.5, 142.8, 131.0, 128.5, 125.2 (q, J = 278.1 Hz), 123.6, 122.7, 108.5, 44.4 (d, J = 2.1 Hz), 40.6 (q, J = 28.3 Hz), 26.4, 25.0. \\
\text{19F NMR (376 MHz, CDCl}_3) & \text{ } \delta -61.95 (t, J = 10.6 Hz). \\
\text{HRMS (ESI): Calcd for C}_{13}H_{13}F_{3}NO^+ ([M + H]^+) & \text{ } 244.0944, \text{ found 244.0939.}
\end{align*}
\]

3-(2,2,3,4,4,4-Heptafluorobuty1)-1,3-dimethylindolin-2-one (5h)

\[
\begin{align*}
\text{1H NMR (400 MHz, CDCl}_3) & \text{ } \delta 7.38 -7.27 (m, 2H), 7.10 (td, J = 7.6, 0.9 Hz, 1H), 6.89 (d, J = 7.8 Hz, 1H), 3.25 (s, 3H), 2.84 (d, J = 15.4 Hz, 1H), 2.71 -2.52 (m, 1H), 1.44 (s, 3H). \\
\text{13C NMR (125 MHz, CDCl}_3) & \text{ } \delta 178.6, 142.8, 131.3, 128.5, 123.6, 123.6, 122.6, 108.5, 44.2 (d, J = 2.1 Hz), 36.7 (t, J = 20.2 Hz), 26.5, 25.8. \\
\text{19F NMR (376 MHz, CDCl}_3) & \text{ } \delta
\end{align*}
\]
−80.30 (t, J = 9.8 Hz, 3F), −107.56 − −110.28 (m, 1F), −112.72 − −117.26 (m, 1F), −126.88 − −128.90 (m, 2F). HRMS (ESI): Calcd for C₁₄H₁₃F₇NO⁺ ([M + H]⁺) 344.0880, found 344.0875.

1,3-Dimethyl-3-(2,3,3,3-tetrafluoro-2-(trifluoromethyl)propyl)indolin-2-one (5i)

¹H NMR (400 MHz, CDCl₃) δ 7.30 (td, J = 7.7, 1.2 Hz, 1H), 7.24 (d, J = 7.4 Hz, 1H), 7.07 (td, J = 7.6, 1.0 Hz, 1H), 6.86 (d, J = 7.8 Hz, 1H), 3.23 (s, 3H), 2.86 (t, J = 16.7 Hz, 1H), 2.67 (t, J = 15.3 Hz, 1H), 1.42 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 178.0, 142.8, 131.1, 128.4, 123.6, 122.4, 108.3, 45.4 (d, J = 3.8 Hz), 34.0, 33.9 (d, J = 18.6 Hz), 27.7, 26.4.

¹⁹F NMR (376 MHz, CDCl₃) δ −77.30 (d, J = 7.1 Hz, 6F), −186.34 (ddd, J = 24.2, 14.5, 7.2 Hz, 1F). HRMS (ESI): Calcd for C₁₄H₁₃F₇NO⁺ ([M + H]⁺) 344.0880, found 344.0876.

4,5,6-Trimethoxy-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5,6,6,6-undecafluorohexyl)indolin-2-one (5j)

¹H NMR (400 MHz, CDCl₃) δ 6.23 (s, 1H), 4.00 (s, 3H), 3.90 (s, 3H), 3.78 (s, 3H), 3.19 (s, 3H), 2.94 − 2.72 (m, 2H), 1.43 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 179.1, 154.8, 150.8, 138.8, 137.2, 113.5, 89.4, 61.0, 60.5, 56.3, 43.9 (d, J = 2.4 Hz), 35.9 (t, J = 19.8 Hz), 26.5, 24.5. ¹⁹F NMR (376 MHz, CDCl₃) δ −80.6 − −82.2 (m, 3F), −110.8 − −113.4 (m, 1F), −114.8 − −117.1 (m, 1F), −124.1 − −125.1 (m, 2F), −125.9 − −126.1 (m, 2F). HRMS (ESI): Calcd for C₁₈H₁₉F₉NO₄⁺ ([M + H]⁺) 484.1165, found 484.1167.

1,3-Dimethyl-3-(2,2,3,3,4,4,5,5,6,6,6-undecafluorohexyl)indolin-2-one (5k)

¹H NMR (500 MHz, CDCl₃) δ 7.32 (t, J = 8.1 Hz, 1H), 7.29 (d, J = 7.4 Hz, 1H), 7.10 (t, J = 7.5 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H), 3.25 (s, 3H), 2.89 (dd, J = 35.2, 15.3 Hz, 1H), 2.61 (ddd, J = 31.0, 15.4, 7.9 Hz, 1H), 1.44 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 178.6, 142.8, 131.3, 128.5, 123.6, 122.7, 108.5, 44.2 (d, J = 2.2 Hz), 37.0 (t, J = 20.3 Hz), 26.5, 25.9. ¹⁹F NMR (376 MHz, CDCl₃) δ −80.88 (tt, J = 9.9, 2.2 Hz, 3F), −107.88 − −109.33 (m, 1F), −113.63 − −115.62 (m, 1F), −122.13 − −122.98 (m, 2F), −123.92 (t, J = 14.9 Hz, 2F), −125.57 − −126.82 (m, 2F). HRMS (ESI): Calcd for C₁₆H₁₉F₁₁NO⁺ ([M + H]⁺) 444.0816, found 444.0810.

3-Methyl-3-(2,2,3,3,4,4,5,5,5-nonfluoropentyl)-1-phenylindolin-2-one (5l)

¹H NMR (500 MHz, CDCl₃) δ 7.62 − 7.54 (m, 2H), 7.51 − 7.42 (m, 3H), 7.37 (d, J = 7.4 Hz, 1H), 7.31 − 7.24 (m, 1H), 7.16 (td, J = 7.5, 0.8 Hz, 1H), 6.93 − 6.85 (m, 1H), 3.05 (ddd, J = 35.1, 15.2 Hz, 1H), 2.71 (ddd, J = 30.8, 15.4, 8.1 Hz, 1H), 1.59 (s, 3H). ¹³C NMR (100
MHz, CDCl$_3$) δ 178.1, 142.9, 134.3, 131.0, 129.7, 128.4, 128.3, 126.6, 123.8 (d, J = 2.1 Hz), 123.1, 109.8, 44.3 (d, J = 1.8 Hz), 37.4 (t, J = 20.3 Hz), 26.3. $^{19}$F NMR (376 MHz, CDCl$_3$) δ −81.09 (tt, J = 9.8, 3.1 Hz, 3F), −105.96 − 110.63 (m, 1F), −112.72 − 118.02 (m, 1F), −124.04 − 125.13 (m, 2F), −125.38 − 126.46 (m, 2F). HRMS (ESI): Calcd for C$_{20}$H$_{15}$F$_9$NO$^+$ ([M + H$^+$]) 456.1004, found 456.1000.

3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluorononyl)-1,3-dimethylindolin-2-one (5m)$^6$

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.39 − 7.24 (m, 2H), 7.18 − 7.04 (m, 1H), 6.91 (d, J = 7.8 Hz, 1H), 3.27 (s, 3H), 2.91 (dd, J = 35.0, 15.2 Hz, 1H), 2.63 (ddd, J = 31.0, 15.4, 8.1 Hz, 1H), 1.46 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 178.6, 142.8, 131.3, 128.5, 123.6, 122.6, 108.5, 44.2, 37.0 (t, J = 20.3 Hz), 26.4, 25.8. $^{19}$F NMR (376 MHz, CDCl$_3$) δ −80.88 (dt, J = 20.0, 9.8 Hz, 3F), −107.98 − 109.70 (m, 1F), −113.47 − 115.26 (m, 1F), −121.58 (s, 2F), −122.01 (s, 4F), −122.80 (s, 2F), −123.69 (s, 2F), −126.21 (s, 2F). HRMS (ESI): Calcd for C$_{19}$H$_{13}$F$_{17}$NO$^+$ ([M + H$^+$]) 594.0720, found 594.0715.

Ethyl 3-(1,3-dimethyl-2-oxoindolin-3-yl)-2,2-difluoropropanoate (5n)$^8$

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.28 (td, J = 7.7, 1.2 Hz, 1H), 7.18 (d, J = 7.2 Hz, 1H), 7.08 − 7.00 (m, 1H), 6.85 (d, J = 7.8 Hz, 1H), 4.02 (dq, J = 10.7, 7.2 Hz, 1H), 3.92 (dq, J = 10.7, 7.2 Hz, 1H), 3.22 (s, 3H), 2.93 − 2.65 (m, 2H), 1.39 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 178.8, 163.5 (t, J = 32.2 Hz), 143.4, 130.8, 128.5, 123.8, 122.2, 114.6 (dd, J = 255.4, 248.8 Hz), 108.4, 62.9, 44.4 (d, J = 6.2 Hz), 41.2 (dd, J = 24.5, 22.3 Hz), 26.4, 25.5, 13.7. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -98.7 (dt, J = 267.4, 12.7 Hz, 1F), -106.2 (ddd, J = 267.3, 21.5, 15.3 Hz, 1F). HRMS (ESI): Calcd for C$_{15}$H$_{18}$F$_2$NO$_3$$^+$ ([M + H$^+$]) 298.1249, found 298.1244.

1-Methyl-1-(2,2,3,3,4,4,5,5,5-nonfluoropentyl)-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one (5o)$^9$

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.12 (d, J = 7.4 Hz, 1H), 7.06 (d, J = 7.5 Hz, 1H), 6.97 (t, J = 7.5 Hz, 1H), 4.03 − 3.62 (m, 2H), 3.00 − 2.71 (m, 3H), 2.59 (ddd, J = 31.2, 15.4, 8.2 Hz, 1H), 2.05 − 2.02 (m, 2H), 1.44 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 177.4, 138.6, 129.9, 127.3, 122.1, 121.5 (t, J = 2.4 Hz), 120.6, 45.5 (d, J = 2.1 Hz), 39.1, 36.8 (t, J = 20.7 Hz), 25.4, 24.6, 21.1. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -81.08 (tt, J = 10.2, 3.1 Hz, 3F), -108.19 − 109.42 (m, 1F), -113.72 − 115.53 (m, 1F), -124.24 − 124.89 (m, 2F), -125.38 − 126.13 (m, 2F). HRMS (ESI): Calcd for C$_{17}$H$_{15}$F$_9$NO$^+$ ([M + H$^+$]) 420.1004; Found: 420.0997.
1,3,5-Trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (5p)\(^9\)

\[
\begin{align*}
\text{H NMR} & \quad (500 \text{ MHz}, \text{CDCl}_3) \delta 7.15 – 7.05 (m, 2H), 6.78 (d, J = 7.9 \text{ Hz}, 1H), 3.23 (s, 3H), 2.86 (dd, J = 35.3, 15.3 \text{ Hz}, 1H), 2.57 (ddd, J = 31.1, 15.4, 7.9 \text{ Hz}, 1H), 2.36 (s, 3H), 1.42 (s, 3H). \\
\text{13C NMR} & \quad (125 \text{ MHz}, \text{CDCl}_3) \delta 178.5, 140.4, 132.2, 131.3, 128.8, 124.4, 108.2, 44.3 (d, J = 2.1 \text{ Hz}), 36.9 (t, J = 19.9 \text{ Hz}), 26.5, 26.0, 21.1. \\
\text{19F NMR} & \quad (376 \text{ MHz}, \text{CDCl}_3) \delta – 81.1 (tt, J = 9.5, 2.7 \text{ Hz}, 3F), –108.3 – –109.4 (m, 1F), –112.7 – –119.0 (m, 1F), –124.8 – –124.8 (m, 2F), –125.5 – –126.3 (m, 2F). \\
\text{HRMS} & \quad (\text{ESI}): \text{Calcd for C}_{16}H_{15}F_9NO}^+ ([\text{M} + \text{H}]^+) 408.1004, \text{found 408.1006.}
\end{align*}
\]

5-Methoxy-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (5q)\(^9\)

\[
\begin{align*}
\text{H NMR} & \quad (500 \text{ MHz}, \text{CDCl}_3) \delta 6.89 (d, J = 2.4 \text{ Hz}, 1H), 6.84 (dd, J = 8.5, 2.5 \text{ Hz}, 1H), 6.79 (d, J = 8.4 \text{ Hz}, 1H), 3.80 (s, 3H), 3.22 (s, 3H), 2.87 (dd, J = 35.3, 15.3 \text{ Hz}, 1H), 2.57 (ddd, J = 31.1, 15.4, 7.8 \text{ Hz}, 1H), 1.42 (s, 3H). \\
\text{13C NMR} & \quad (125 \text{ MHz}, \text{CDCl}_3) \delta 178.2, 156.0, 136.3, 132.7, 112.5, 111.3, 108.8, 55.8, 44.6, 36.9 (t, J = 20.4 \text{ Hz}), 26.6, 25.9. \\
\text{19F NMR} & \quad (376 \text{ MHz}, \text{CDCl}_3) \delta – 81.1 (tt, J = 10.2, 2.8 \text{ Hz}, 3F), –108.3 – –108.5 (m, 1F), –114.0 – –115.4 (m, 1F), –124.5 – –124.7 (m, 2F), –125.7 – –126.1 (m, 2F). \\
\text{HRMS} & \quad (\text{ESI}): \text{Calcd for C}_{16}H_{15}F_9NO}^+ ([\text{M} + \text{H}]^+) 424.0954, \text{found 424.0956.}
\end{align*}
\]

5-Fluoro-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (5r)\(^9\)

\[
\begin{align*}
\text{H NMR} & \quad (400 \text{ MHz}, \text{CDCl}_3) \delta 7.14 – 6.95 (m, 2H), 6.83 (dd, J = 8.3, 4.1 \text{ Hz}, 1H), 3.25 (s, 3H), 2.90 (dd, J = 34.6, 16.0 \text{ Hz}, 1H), 2.60 (ddd, J = 30.9, 15.5, 8.0 \text{ Hz}, 1H), 1.44 (s, 3H). \\
\text{13C NMR} & \quad (100 \text{ MHz}, \text{CDCl}_3) \delta 178.2, 159.3 (d, J = 240.7 \text{ Hz}), 138.7 (d, J = 2.1 \text{ Hz}), 132.9 (d, J = 8.0 \text{ Hz}), 114.8 (d, J = 23.5 \text{ Hz}), 111.8 (d, J = 25.2 \text{ Hz}), 109.0 (d, J = 8.2 \text{ Hz}), 44.6, 36.9 (t, J = 20.4 \text{ Hz}), 26.6, 25.7. \\
\text{19F NMR} & \quad (376 \text{ MHz}, \text{CDCl}_3) \delta – 79.90 – –82.22 (m, 3F), –105.96 – –109.97 (m, 1F), –114.65 (ddt, J = 271.3, 28.4, 12.8 \text{ Hz}, 1F), –120.49 (tt, J = 8.2, 3.4 \text{ Hz}, 1F), –123.74 – –125.48 (m, 2F), –125.16 – –127.17 (m, 2F). \\
\text{HRMS} & \quad (\text{ESI}): \text{Calcd for C}_{16}H_{12}F_{10}N_2O}^+ ([\text{M} + \text{H}]^+) 412.0754, \text{found 412.0750.}
\end{align*}
\]

5-Chloro-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (5s)\(^9\)

\[
\begin{align*}
\text{H NMR} & \quad (400 \text{ MHz}, \text{CDCl}_3) \delta 7.30 (dd, J = 8.3, 2.1 \text{ Hz}, 1H), 7.26 (s, 1H), 6.82 (d, J = 8.3 \text{ Hz}, 1H), 3.24 (s, 3H), 2.89 (dd, J = 36.1, 15.4 \text{ Hz}, 1H), 2.58 (ddd, J = 30.8, 15.5, 8.0 \text{ Hz}, 1H), 1.43 (s, 3H). \\
\text{13C NMR} & \quad (100 \text{ MHz}, \text{CDCl}_3) \delta 178.1, 141.4, 132.9, 128.6, 128.1, 124.1, 109.5, 44.4 (d, J = 2.2 \text{ Hz}), 36.9 (t, J = 20.3 \text{ Hz}), 26.6, 25.8. \\
\text{19F NMR} & \quad (376 \text{ MHz}, \text{CDCl}_3) \delta – 81.1 (tt, J = 9.7, 2.6 \text{ Hz}, 3F), –105.11 – –111.18 (m, 1F), –112.71 – –118.99 (m, 1F), –122.82 – –125.27 (m, 2F), –125.27 – –128.19 (m, 2F). \\
\text{HRMS} & \quad (\text{ESI}): \text{Calcd for C}_{15}H_{12}ClF_9N_2O}^+ ([\text{M} + \text{H}]^+) 428.0458, \text{found 428.0461.}
\end{align*}
\]
1,3-Dimethyl-3-(2,2,3,4,4,5,5,5-nonafluoropentyl)-5-(trifluoromethyl)indolin-2-one (5t) \(^9\)

\[ ^1H \text{NMR (500 MHz, CDCl}_3 \] \( \delta 7.61 (d, J = 9.0 \text{ Hz, 1H}), 7.51 \text{ (s, 1H), 6.97 (d, } J = 8.2 \text{ Hz, 1H}, 3.28 \text{ (s, 3H), 2.93 (dd, } J = 35.0, 15.4 \text{ Hz, 1H), 2.63 (ddd, } J = 30.5, 15.5, 8.0 \text{ Hz, 1H), 1.46 (s, 3H).} \]

\[ ^13C \text{NMR (125 MHz, CDCl}_3 \] \( \delta 178.5, 145.8, 131.8, 126.4 \text{ (q, } J = 4.0 \text{ Hz), 125.0 (q, } J = 32.7 \text{ Hz), 124.3 (q, } J = 271.4 \text{ Hz), 120.8 – 120.6 (m, 108.4, 44.1 (d, } J = 2.3 \text{ Hz), 37.0 (t, } J = 20.3 \text{ Hz), 26.7, 25.8.} \]

\[ ^19F \text{NMR (376 MHz, CDCl}_3 \] \( \delta -61.5 \text{ (s, 3F), -81.1 (tt, } J = 9.7, 2.6 \text{ Hz, 3F), -107.9 – -109.6 (m, 1F), -113.8 – -116.0 (m, 1F), -124.2 – -124.7 (m, 2F), -125.6 – -126.3 (m, 2F).} \]

HRMS (ESI): Calcd for C\(_{16}\)H\(_{12}\)F\(_{12}\)NO\(_3\) \( ([M + H]^+) \) 462.0722, found 462.07118.

Methyl 1,3-dimethyl-3-(2,2,3,4,4,5,5,5-nonafluoropentyl)-2-oxoindoline-5-carboxylate (5u) \(^{10}\)

\[ ^1H \text{NMR (400 MHz, CDCl}_3 \] \( \delta 8.09 (dd, J = 8.3, 1.7 \text{ Hz, 1H), 7.98 \text{ (s, 1H), 6.95 (d, } J = 8.2 \text{ Hz, 1H), 3.94 \text{ (s, 3H), 3.30 (s, 3H), 2.93 (d, } J = 35.0 \text{ Hz, 1H), 2.67 (ddd, } J = 30.6, 15.4, 8.0 \text{ Hz, 1H), 1.47 (s, 3H).} \]

\[ ^13C \text{NMR (100 MHz, CDCl}_3 \] \( \delta 178.8, 166.7, 146.9, 131.2, 124.8, 124.8, 124.7, 108.1, 52.1, 43.9, 37.00 \text{ (t, } J = 20.0 \text{ Hz), 26.7, 25.9.} \]

\[ ^19F \text{NMR (376 MHz, CDCl}_3 \] \( \delta -81.1 \text{ (tt, } J = 9.7, 2.5 \text{ Hz, 3F), -107.4 – -109.8 (m, 1F), -112.5 – -116.8 (m, 1F), -123.0 – -125.5 (m, 2F), -124.7 – -128.4 (m, 2F).} \]

HRMS (ESI): Calcd for C\(_{17}\)H\(_{15}\)F\(_9\)NO\(_3\) \( ([M + H]^+) \) 452.0903, found 452.0900.

3-(4-Methoxyphenyl)-5a,10-dimethyl-1,4,5,5a,10,10a-hexahydro-[1,2]diazepino[3,4-b]indole (6)

\[ ^1H \text{NMR (400 MHz, CDCl}_3 \] \( \delta 7.64 – 7.47 (m, 2H), 7.18 \text{ (td, } J = 7.7, 1.2 \text{ Hz, 1H), 7.04 (d, } J = 7.9 \text{ Hz, 1H), 6.89 – 6.83 (m, 2H), 6.77 (t, } J = 7.4 \text{ Hz, 1H), 6.50 (d, } J = 7.8 \text{ Hz, 1H), 6.13 (d, } J = 4.5 \text{ Hz, 1H), 4.28 (d, } J = 4.5 \text{ Hz, 1H), 3.83 (s, 3H), 2.71 (s, 3H), 2.68 – 2.40 (m, 3H), 1.77 – 1.58 (m, 1H), 1.42 (s, 3H).} \]

\[ ^13C \text{NMR (100 MHz, CDCl}_3 \] \( \delta 159.53, 151.28, 150.04, 134.80, 133.10, 128.29, 127.08, 121.79, 117.87, 113.38, 106.79, 92.74, 55.83, 45.97, 35.96, 31.65, 29.02, 26.07.} \]

HRMS (ESI): Calcd for C\(_{20}\)H\(_{24}\)N\(_3\)O\(_6\) \( ([M + H]^+) \) 322.1914, found 322.1907.

2-((5-Methoxy-1,3-dimethyl-2-oxoindolin-3-yl)methyl)malonic acid (7)

\[ ^1H \text{NMR (400 MHz, MeOH-}d_4 \] \( \delta 6.96 – 6.90 \text{ (m, 2H), 6.90 – 6.85 (m, 1H), 3.79 (s, 3H), 3.37 (s, 1H), 3.19 (s, 3H), 2.49 (s, 2H), 1.37 (s, 3H).} \]

\[ ^13C \text{NMR (101 MHz, MeOH-}d_4 \] \( \delta 180.04, 170.95, 156.53, 136.45, 133.26, 112.86, 110.30, 108.90, 54.84, 48.50, 47.70, 35.87, 25.21, 23.14.} \]

HRMS (ESI): Calcd for C\(_{15}\)H\(_{18}\)NO\(_6\) \( ([M + H]^+) \) 322.1194, found 322.1193.
(\([\text{M + H}]^+)\) 308.1129, found 308.1126.

3-(5-Methoxy-1,3-dimethyl-2-oxoindolin-3-yl)propanoic acid (8)³

\(^1\text{H}\) NMR (500 MHz, DCM-\(d_2\)) \(\delta\) 6.84 (m, 2H), 6.81 (d, \(J = 9.1\) Hz, 1H), 3.81 (s, 3H), 3.19 (s, 3H), 2.27 – 2.14 (m, 1H), 2.14 – 2.03 (m, 2H), 2.01 – 1.88 (m, 1H), 1.38 (s, 3H). \(^{13}\text{C}\) NMR (126 MHz, DCM-\(d_2\)) \(\delta\) 179.30, 176.78, 156.21, 136.82, 134.21, 112.19, 110.10, 108.44, 55.69, 47.82, 32.72, 29.04, 26.05, 23.38. HRMS (ESI): Calcd for C\(_{14}\)H\(_{18}\)NO\(_4\)+ ([M + H]\(^+\)) 264.1230, found 264.1232.

1,3-Dioxoisindolin-2-yl 3-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)propanoate (9)

\(^1\text{H}\) NMR (400 MHz, DCM-\(d_2\)) \(\delta\) 7.92 – 7.87 (m, 2H), 7.83 (dd, \(J = 5.5, 3.1\) Hz, 2H), 6.88 (dd, \(J = 7.0, 2.4\) Hz, 2H), 6.85 (d, \(J = 9.3\) Hz, 1H), 3.84 (s, 3H), 3.23 (s, 3H), 2.53 – 2.41 (m, 1H), 2.40 – 2.27 (m, 2H), 2.25 – 2.12 (m, 1H), 1.43 (s, 3H). \(^{13}\text{C}\) NMR (126 MHz, CDCl\(_3\)) \(\delta\) 179.07, 168.88, 161.78, 156.41, 136.60, 134.76, 133.85, 128.88, 123.99, 112.50, 110.28, 108.65, 55.83, 47.80, 32.53, 26.48, 26.37, 23.43. HRMS (ESI): Calcd for C\(_{22}\)H\(_{21}\)N\(_2\)O\(_6\)+ ([M + H]\(^+\)) 409.1394, found 409.1400.

3-(2-Iodoethyl)-5-methoxy-1,3-dimethylindolin-2-one (10)

\(^1\text{H}\) NMR (500 MHz, DCM-\(d_2\)) \(\delta\) 6.83 (d, \(J = 7.6\) Hz, 2H), 6.80 – 6.76 (m, 1H), 3.80 (s, 3H), 3.16 (s, 3H), 2.84 (ddd, \(J = 12.6, 9.3, 5.2\) Hz, 1H), 2.74 (ddd, \(J = 12.3, 9.3, 4.5\) Hz, 1H), 2.50 (td, \(J = 12.9, 5.2\) Hz, 1H), 2.33 (td, \(J = 13.0, 4.5\) Hz, 1H), 1.34 (s, 3H). \(^{13}\text{C}\) NMR (126 MHz, DCM-\(d_2\)) \(\delta\) 178.49, 156.21, 136.92, 133.61, 112.13, 110.13, 108.46, 55.72, 50.44, 42.76, 26.08, 23.20, -1.69. HRMS (ESI): Calcd for C\(_{13}\)H\(_{15}\)INO\(_2\)+ ([M + H]\(^+\)) 346.0298, found 346.0301.

2-(5-Methoxy-1,3-dimethyl-2-oxoindolin-3-yl)ethyl acetate (11)

\(^1\text{H}\) NMR (500 MHz, DCM-\(d_2\)) \(\delta\) 6.84 (dd, \(J = 6.4, 2.5\) Hz, 2H), 6.80 (d, \(J = 9.1\) Hz, 1H), 3.89 (ddd, \(J = 12.3, 9.3, 4.5\) Hz, 1H), 3.82 (s, 3H), 3.68 (dt, \(J = 11.2, 7.2\) Hz, 1H), 3.19 (s, 3H), 2.31 (dt, \(J = 14.4, 7.4\) Hz, 1H), 2.08 (dt, \(J = 12.2, 6.8\) Hz, 1H), 1.85 (s, 3H), 1.37 (s, 3H). \(^{13}\text{C}\) NMR (126 MHz, DCM-\(d_2\)) \(\delta\) 179.32, 170.34, 156.06, 136.87, 134.29, 111.90, 110.29, 108.31, 60.73, 55.71, 46.73, 36.27, 26.05, 24.41, 20.40. HRMS (ESI): Calcd for C\(_{15}\)H\(_{19}\)NO\(_4\)Na\(^+\) ([M + Na]\(^+\)) 300.1206, found 300.1206.
3-(2-Hydroxyethyl)-5-methoxy-1,3-dimethylindolin-2-one (12)

\[
\text{H NMR (500 MHz, DCM-}d_2\text{) }\delta 6.83 \text{ (m, 2H), 6.81 (d, } J = 9.4 \text{ Hz, 1H), 3.82 (s, 3H), 3.65 (s, 1H), 3.45 (dq, } J = 12.5, 6.4 \text{ Hz, 1H), 3.20 (s, 3H), 2.41 (s, 1H), 2.11 (m, 1H), 1.96 (m, 1H), 1.40 (s, 3H).}
\]

\[
\text{C NMR (101 MHz, DCM-}d_2\text{) }\delta 180.94, 156.22, 136.49, 135.65, 111.83, 110.07, 108.46, 59.14, 55.70, 47.28, 40.04, 26.18, 23.27. \]

HRMS (ESI): Calcd for C_{13}H_{18}NO_3^+ ([M + H]^+) 236.1281, found 236.1282.

3-(2-Isocyanatoethyl)-5-methoxy-1,3-dimethylindolin-2-one (13)

\[
\text{H NMR (500 MHz, CDCl}_3\text{) }\delta 6.81 \text{ (dd, } J = 10.4, 2.2 \text{ Hz, 2H), 6.77 (d, } J = 8.2 \text{ Hz, 1H), 3.81 (s, 3H), 3.20 (s, 3H), 3.05 (q, } J = 6.6, 5.7 \text{ Hz, 2H), 2.13 (dt, } J = 13.7, 6.8 \text{ Hz, 1H), 1.97 (dt, } J = 14.0, 7.0 \text{ Hz, 1H), 1.37 (s, 3H).}
\]

\[
\text{C NMR (126 MHz, CDCl}_3\text{) }\delta 180.05, 156.43, 156.08, 136.32, 134.57, 112.25, 110.21, 108.74, 55.84, 47.45, 37.45, 36.93, 26.39, 23.95. \]

HRMS (ESI): Calcd for C_{14}H_{17}N_2O_3^+ ([M + H]^+) 261.1234, found 261.1232.

3-(2-Aminoethyl)-5-methoxy-1,3-dimethylindolin-2-one (14)

\[
\text{H NMR (400 MHz, CDCl}_3\text{) }\delta 6.83 – 6.76 \text{ (m, 2H), 6.74 (d, } J = 8.2 \text{ Hz, 1H), 3.80 (s, 3H), 3.18 (s, 3H), 2.39 (m, 1H), 2.30 (m, 1H), 2.07 (ddd, } J = 13.2, 10.0, 5.8 \text{ Hz, 1H), 1.90 (ddd, } J = 13.2, 10.1, 5.1 \text{ Hz, 1H), 1.36 (s, 2H), 1.35 (s, 3H).}
\]

\[
\text{C NMR (126 MHz, CDCl}_3\text{) }\delta 180.19, 156.08, 136.64, 135.11, 111.75, 110.21, 108.28, 55.78, 47.68, 42.14, 38.10, 26.25, 24.27. \]

MS on Bruker Q-Tof (ESI): Calcd for C_{13}H_{19}N_2O_3^+ ([M + H]^+) 235.1441, found 235.1441.
10. Copies of NMR Spectra
11. References