Supporting Information

for

Solvent-free and room temperature microwave-assisted direct C7 allylation of indolines via sequential C–H and C–C activation

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General Information

Unless otherwise mentioned, all materials were commercially obtained and used without further purification, and all procedures were performed under the nitrogen atmosphere. Indolines 1,1 vinylcyclopropanes 2,2-3 were synthesized according to previously described methods. The microwave irradiation experiments were carried out in a dedicated CEM Discover monomode microwave apparatus, operating at a frequency of 2.45 GHz with continuous irradiation power from 0 to 300 W and performed in glass vessels (capacity 10 mL) sealed with a septum. 1H NMR, 13C NMR, and 19F NMR spectra were recorded at 400 MHz or 600MHz, 151 MHz or 101MHz, and 376 MHz respectively on a Bruker DPX instrument using Me4Si as an internal standard. New compounds for HRMS were tested on a Waters Q-Tof Micro MS/MS System ESI spectrometer. Chemical shift multiplicities are represented as follows: (s = singlet, d = doublet, m = multiplet, t = triple, dd = double doublet).

Experimental Section

1. Optimization of reaction conditions<br>

**Table S1. Optimization of additive.**<sup>a</sup>

| Entry | Additive         | Yield [%] |
|-------|------------------|-----------|
| 1     | NaOAc            | 20        |
| 2     | PivONaH2O        | 21        |
| 3     | DABCO            | trace     |
| 4     | DBU              | N.R.      |
| 5     | Phen             | trace     |
| 6     | Pyridine         | 6         |
| 7     | PivOH            | 29        |
| 8     | AcOH             | 40        |
| 9     | MesCOOH          | 47        |
| 10    | 1-AdCOOH         | 40        |

<sup>a</sup>Reaction conditions: 1a (0.2 mmol), 2a (0.4 mmol), [Ru(p-cymene)Cl]2 (5 mol%), AgSbF6 (25 mol%), additive (30 mol%), MW, 90 °C, 1 h. MW = microwave. Phen= 1,10-Phenanthroline hydrate; Isolated yield.
Table S2. Optimization of dosages\(^a\)

![Chemical structure](image1)

| Entry | 2a (mmol) | [Ru(p-cymene)Cl\(_2\)] (mol\%) | MesCOOH (mol\%) | AgSbF\(_6\) (mol\%) | Yield [%] |
|-------|-----------|--------------------------------|-----------------|---------------------|-----------|
| 1     | 0.2       | 5                              | 30              | 25                  | 23        |
| 2     | 0.4       | 5                              | 30              | 25                  | 47        |
| 4     | 0.4       | 1                              | 30              | 25                  | 21        |
| 5     | 0.4       | 2.5                            | 30              | 25                  | 37        |
| 6     | 0.4       | 5                              | 10              | 25                  | 33        |
| 7     | 0.4       | 5                              | 50              | 25                  | 57        |
| 8     | 0.4       | 5                              | 50              | 10                  | 14        |
| 9     | 0.4       | 5                              | 50              | 50                  | 20        |

\(^a\)Reaction conditions: 1a (0.2 mmol), 2a (0.2 - 0.4 mmol), Catalyst (1 - 5 mol\%), AgSbF\(_6\) (10 - 50 mol\%), MesCOOH (10 - 50 mol\%), MW, 90 °C, 1 h. MW = microwave. Isolated yield.

Table S3. Optimization of catalyst and temperature\(^a\)

![Chemical structure](image2)

| Entry | Catalyst (5 mol %) | T [°C] | Yield [%] |
|-------|---------------------|--------|-----------|
| 1     | [Cp*RuCl\(_2\)]     | 90     | N.R.      |
| 2     | RuCl\(_3\)3H\(_2\)O  | 90     | N.R.      |
| 3     | [Ru(p-cymene)Cl\(_2\)] | 90   | 57        |
| 4     | [Ru(p-cymene)Cl\(_2\)] | 110  | 10        |
| 5     | [Ru(p-cymene)Cl\(_2\)] | 70   | 68        |
| 6     | [Ru(p-cymene)Cl\(_2\)] | 50   | 83        |
| 7     | [Ru(p-cymene)Cl\(_2\)] | 25   | 65        |
| 8\(^b\) | [Ru(p-cymene)Cl\(_2\)] | 25   | 87 (>20:1)\(^d\) |
| 9\(^c\) | [Ru(p-cymene)Cl\(_2\)] | 25   | 51 (>20:1)\(^d\) |

\(^a\)Reaction conditions: 1a (0.2 mmol), 2a (0.4 mmol), Catalyst (5 mol%), AgSbF\(_6\) (25 mol%), MesCOOH (50 mol%), MW, 1 h. MW = microwave. Isolated yield. \(^b\)t = 2 h. \(^c\)Oil bath. \(^d\)The E:Z ratio was determined by \(^1\)H NMR analysis.
Table S4. Effect of the directing groups.

|     |     |     |     |
|-----|-----|-----|-----|
|     |     |     |     |
|     |     |     |     |
|     |     |     |     |

Table S5. Optimization of the Reaction Conditions under Rh catalytic system

![Reaction Scheme]

| Entry | Catalyst (mol %) | Additive (mol%) | T [°C] | Yield [%] |
|-------|------------------|-----------------|--------|-----------|
| 1     | RhCl₂·3H₂O       | AdCOOH          | 80     | N.R.      |
| 2     | [Cp*RhCl₂]₂      | AdCOOH          | 80     | 44        |
| 3     | [RhCp*(CH₃CN)₃][SbF₆]₂ | AdCOOH          | 80     | 78(10:1)⁴  |
| 4     | [RhCp*(CH₃CN)₃][SbF₆]₂ | MesCOOH         | 80     | 43        |
| 5     | [RhCp*(CH₃CN)₃][SbF₆]₂ | PivOH           | 80     | 40        |
| 6     | [RhCp*(CH₃CN)₃][SbF₆]₂ | NaOAc           | 80     | 51        |
| 7     | [RhCp*(CH₃CN)₃][SbF₆]₂ | PivONa·H₂O      | 80     | 47        |
| 8     | [RhCp*(CH₃CN)₃][SbF₆]₂ | DABCO           | 80     | trace     |
| 9     | [RhCp*(CH₃CN)₃][SbF₆]₂ | AdCOOH          | 100    | 50        |
| 10    | [RhCp*(CH₃CN)₃][SbF₆]₂ | AdCOOH          | 90     | 55        |
| 11    | [RhCp*(CH₃CN)₃][SbF₆]₂ | AdCOOH          | 70     | 68        |
| 12    | [RhCp*(CH₃CN)₃][SbF₆]₂ | AdCOOH          | 25     | trace     |
| 13ᵇ   | [RhCp*(CH₃CN)₃][SbF₆]₂ | AdCOOH          | 80     | 65        |
| 14ᶜ   | [RhCp*(CH₃CN)₃][SbF₆]₂ | AdCOOH          | 80     | 21(>20:1)⁴  |

*Reaction conditions: 1a (0.2 mmol), 2a (0.4 mmol), Catalyst (8 mol%), AgSbF₆ (20 mol%), Additive (30 mol%), MW, 80 °C, 2 h. MW = microwave. Isolated yield. ᵅAdCOOH (50 mol%). ᵇOil bath. ᵇThe E:Z ratio was determined by ¹H NMR analysis.
**Table S6. Summary of the Reaction Conditions**

![Diagram](image.png)

| entry | catalyst (mol%) | additive (mol%) | T (°C) | yield (%) |
|-------|----------------|----------------|--------|-----------|
| 1     | [Ru(p-cymene)Cl₂]₂ | AdCOOH | 90     | 40        |
| 2     | RuCl₃·3H₂O       | AdCOOH | 90     | N.R.      |
| 3     | [Cp*RuCl₂]₂      | AdCOOH | 90     | N.R.      |
| 4     | [Ru(p-cymene)Cl₂]₂ | MesCOOH | 90     | 47        |
| 5     | [Ru(p-cymene)Cl₂]₂ | AcOH   | 90     | 40        |
| 6     | [Ru(p-cymene)Cl₂]₂ | NaOAc  | 90     | 20        |
| 7     | [Ru(p-cymene)Cl₂]₂ | PivONaH₂O | 90 | 21        |
| 8     | [Ru(p-cymene)Cl₂]₂ | DABCO  | 90     | trace     |
| 9ᵇ    | [Ru(p-cymene)Cl₂]₂ | MesCOOH | 90     | 57        |
| 10ᵇ   | [Ru(p-cymene)Cl₂]₂ | MesCOOH | 70     | 68        |
| 11ᵇ   | [Ru(p-cymene)Cl₂]₂ | MesCOOH | 50     | 83        |
| 12ᵇ   | [Ru(p-cymene)Cl₂]₂ | MesCOOH | 25     | 65        |
| 13ᵇ,c | [Ru(p-cymene)Cl₂]₂ | MesCOOH | 25     | 87(>20:1)⁺ |
| 14ᶜ,d | [Cp*Rh(CH₃CN)₃](SbF₆)₂ | AdCOOH | 80     | 78(10:1)⁺ |

*Reaction conditions: 1a (0.2 mmol), 2a (0.4 mmol), [Ru(p-cymene)Cl₂]₂ (5 mol%), additive (30 mol%), MW, 1 h, 90 °C. bMesCOOH (50 mol%). c t = 2 h. d [Cp*Rh(CH₃CN)₃](SbF₆)₂ (8 mol%). e The E:Z ratio was determined by ¹H NMR analysis. MW = microwave irradiation.

**2. General procedure for the synthesis of 3**

In a 10 mL glass vessel equipped with a magnetic stir bar was added indolines 1 (0.2 mmol), vinylcyclopropanes 2 (0.4 mmol), [Ru(p-cymene)Cl₂]₂ (6.1 mg, 5 mol%), MesCOOH (16.4 mg, 50 mol%) and AgSbF₆ (17.2 mg, 25 mol%). The vessel was sealed with a septum under microwave irradiated at 25°C for 2 h. The reaction mixture was then diluted with CH₂Cl₂ (25 mL) and filtered through a celite pad. After removal of organic solvent under vacuum, the desired products 3 were purified by preparative TLC on silica gel plates.
3. Control experiments and mechanistic studies

a) H/D exchange experiments

In a 10 mL glass vessel equipped with a magnetic stir bar was added indoline [D$_1$]-1a (39.6 mg, 0.2 mmol), [Ru($p$-cymene)Cl$_2$]$_2$ (6.1 mg, 5 mol%), MesCOOH (16.4 mg, 50 mol%) and AgSbF$_6$ (17.2 mg, 25 mol%). The vessel was sealed with a septum under microwave irradiated at 25°C for 2 h. The reaction mixture was then diluted with CH$_2$Cl$_2$ (25 mL) and filtered through a celite pad. After removal of organic solvent under vacuum, the residue was purified by preparative TLC on silica gel plates (PE/EA = 5/1) to recover 1a in 86% yield (D < 5%). The H/D-ratio was determined by $^1$H NMR.

b) Radical scavenger reactions

In a 10 mL glass vessel equipped with a magnetic stir bar was added indoline [D$_1$]-1a (39.6 mg, 0.2 mmol), vinylcyclopropane 2a (84.8 mg, 0.4 mmol), [Ru($p$-cymene)Cl$_2$]$_2$ (6.1 mg, 5 mol%), MesCOOH (16.4 mg, 50 mol%) and AgSbF$_6$ (17.2 mg, 25 mol%). The vessel was sealed with a septum under microwave irradiated at 25°C for 30 min. The reaction mixture was then diluted with CH$_2$Cl$_2$ (25 mL) and filtered through a celite pad. After removal of organic solvent under vacuum, the residue were purified by preparative TLC on silica gel plates (PE/EA = 3/1) to give 3aa in 32% yield (D < 5%). The H/D-ratio was determined by $^1$H NMR.
**General procedure for radical scavenger reactions**

In a 10 mL glass vessel equipped with a magnetic stir bar was added indoline 1a (39.4 mg, 0.2 mmol), vinylcyclopropane 2a (84.8 mg, 0.4 mmol), [Ru(\(p\)-cymene)Cl\(_2\)]\(_2\) (6.1 mg, 5 mol%), MesCOOH (16.4 mg, 50 mol%), AgSbF\(_6\) (17.2 mg, 25 mol%), and a radical scavenger BQ (21.6 mg, 0.2 mmol). The vessel was sealed with a septum under microwave irradiated at 25°C for 2 h. The reaction mixture was then diluted with CH\(_2\)Cl\(_2\) (25 mL) and filtered through a celite pad. After removal of organic solvent under vacuum, the residue were purified by preparative TLC on silica gel plates (PE/EA = 3/1) to give 3aa in 68% yield.

c) **Intermolecular Competition Experiment**

In a 10 mL glass vessel equipped with a magnetic stir bar was added indolines 1t (51.1 mg, 0.2 mmol), 1o (45.5 mg, 0.2 mmol), vinylcyclopropane 2a (84.8 mg, 0.4 mmol), [Ru(\(p\)-cymene)Cl\(_2\)]\(_2\) (6.1 mg, 5 mol%), MesCOOH (16.4 mg, 50 mol%) and AgSbF\(_6\) (17.2 mg, 25 mol%). The vessel was sealed with a septum under microwave irradiated at 25°C for 2 h. The reaction mixture was then diluted with CH\(_2\)Cl\(_2\) (25 mL) and filtered through a celite pad. After removal of organic solvent under vacuum, the residue were purified by preparative TLC on silica gel plates (PE/EA = 3/1) to give 3ta/3oa = 1/2, which was determined by \(^1\)H NMR analysis.
Figure S1. Intermolecular Competition Experiment

d) Kinetic isotope experiment

In a 10 mL glass vessel equipped with a magnetic stir bar was added indoline 1a (39.4 mg, 0.2 mmol) or [D1]-1a (39.6 mg, 0.2 mmol), vinylcyclopropane 2a (84.8 mg, 0.4 mmol), [Ru(ρ-cymene)Cl2]2 (6.1 mg, 5 mol%), MesCOOH (16.4 mg, 50 mol%), AgSbF6 (17.2 mg, 25 mol%). The tubes were heated at 25 °C for 11, 13, 15, 17 minutes and quenched separately with 1mL EA. Next, the reaction mixture was diluted with 25 mL EA and filtered through a celite pad. The solvent was removed in vacuum and 1H NMR was taken separately using 0.2 mmol anisole (21.6 mg) as the internal standard. The KIE was determined as kH/kD = 2.7/1.7 ≈ 1.6

Figure S2. Kinetic isotope experiment
e) Scale-up experiment

\[
\begin{align*}
1a & \quad + \quad 2a \\
\text{indoline} & \quad \text{vinylcyclopropane} \\
[\text{Ru(\text{p-cymene})Cl}_2]_2 & \quad [\text{MesCOOH}] \\
\text{AgSbF}_6 & \quad \text{EtO}_2\text{C} \quad \text{CO}_2\text{Et} \\
\text{MW, 25 }^\circ\text{C, 2 h} & \quad \text{EtO}_2\text{C} \quad \text{CO}_2\text{Et} \\
\end{align*}
\]

In a 10 mL glass vessel equipped with a magnetic stir bar was added indoline 1a (1.2 g, 6.0 mmol), vinylcyclopropane 2a (2.5 g, 12.0 mmol), [Ru(\text{p-cymene})Cl]_2 (183.6 mg, 5 mol%), MesCOOH (492.6 mg, 50 mol%) and AgSbF_6 (515.4 mg, 25 mol%). The vessel was sealed with a septum under microwave irradiated at 25°C for 2 h. The reaction mixture was then diluted with CH_2Cl_2 (100 mL) and filtered through a celite pad. After removal of organic solvent under vacuum, the residue was purified by preparative TLC on silica gel plates (PE/EA = 3/1) to give 3aa in 74% yield.

4. Derivatization of 3aa

\[
\begin{align*}
1a & \quad 2a \\
6.0 \text{ mmol} & \quad 12.0 \text{ mmol} \\
\text{gram-scale} & \quad \text{74% yield} \\
\text{gram-scale reaction and further derivatization of product 3aa} \\
\end{align*}
\]

(E)-Ethyl 6-(1-(pyrimidin-2-yl)indolin-7-yl)hex-4-enoate 4

In a 35 mL dry screw-cap tube equipped with a magnetic stir bar was added 3aa (81.8 mg, 0.2 mmol) and NaOEt (68.1 mg, 1.0 mmol) in DMSO (0.5 mL). The reaction
mixture was stirred at 150 °C for 4 h, and then cooled down to room temperature. The solution was extracted with ethyl acetate and the combined organic layer was dried over magnesium sulfate. After removal of organic solvent, the residue was purified by preparative TLC on silica gel plates (PE/EA = 5/1) to give product 4 in 86% yield.

(E)-2-(4-(1-(Pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonic acid 5
To a 50 mL schlenk flask was added 3aa (794.4 mg, 19.4 mmol) in a solution of KOH (3.26 g, 58.1 mmol) in ethanol (9.8 mL) and H₂O (9.8 mL). After refluxed for 6 h, the organic phase was evaporated under vacuum. Aqueous phase was then neutralized with 1M HCl and extracted with ether. The combined organic phase was washed with water, brine, and dried over MgSO₄. After removal of organic solvent, product 5 was obtained in 90 % yield, which is pure enough for NMR characterizations.

(E)-Diethyl-2-(4-(1-(pyrimidin-2-yl)indolin-7-yl)but-2-enoyl)malonate 6
To a 35 mL dry screw-cap tube equipped with a magnetic stir bar was added 3aa (81.8 mg, 0.2 mmol), DDQ (45.4 mg, 0.2 mmol) in toluene (1mL). The vessel was sealed and heated at 90 °C for 12 h. After cooled down to room temperature, the reaction mixture was diluted with CH₂Cl₂ (25 mL) and filtered through a celite pad. After removal of organic solvent under vacuum, the residue was purified by preparative TLC on silica gel plates (PE/EA = 6/1) to give product 6 in 38% yield.

Diethyl 2-(4-(1-(pyrimidin-2-yl)indolin-7-yl)butyl)malonate 7
To a solution of 3aa (81.8 mg, 0.2 mmol) in MeOH (1.0 mL) was added Pd/C (9.5 mg, 10 wt.%) under hydrogen atmosphere. The mixture was stirred at 25 °C for 12 h and then filtered through a short celite pad. The residue was washed with EtOAc (10 mL), filtered, and the combined filtrate was concentrated in vacuo. The crude mixture was purified by preparative TLC on silica gel plates (PE/EA: 5/1) to give product 7 in 84% yield.

Diethyl 2-(4-(1-(pyrimidin-2-yl)-1H-indol-7-yl)butyl)malonate 8
To a 35 mL dry screw-cap tube equipped with a magnetic stir bar was added 7 (82.2 mg, 0.2 mmol), DDQ (45.4 mg, 0.2 mmol) in 1,4-dioxane (1mL). The vessel was sealed and heated at 90 °C for 8 h. After cooled down to room temperature, the reaction mixture was diluted with CH₂Cl₂ (25 mL) and filtered through a celite pad. After removal of organic solvent under vacuum, the residue was purified by preparative TLC on silica gel plates (PE/EA = 5/1) to give product 8 in 90% yield.

Ethyl 6-(1-(pyrimidin-2-yl)-1H-indol-7-yl)hexanoate 9
To a 35 mL dry screw-cap tube equipped with a magnetic stir bar was added 8 (81.8 mg, 0.2 mmol), NaOEt (68.1 mg, 1 mmol) in DMSO (0.5 mL). The vessel was sealed and heated at 150 °C for 4 h. After cooled down to room temperature, the solution was extracted with ethyl acetate and the combined organic layer was dried over magnesium sulfate. After removal of organic solvent, the residue was purified by preparative TLC on silica gel plates (PE/EA = 5/1) to give product 9 in 82% yield.

Reference

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(3) Dieskau, A. P.; Holzwarth, M. S.; Plietker, B., Fe-Catalyzed Allylic C–C-Bond Activation: Vinylcyclopropanes As Versatile a1, a3, d5-Synths in Traceless Allylic Substitutions and [3 + 2]-Cycloadditions. *J. Am. Chem. Soc.* **2012**, *134*, 5048–5051, DOI 10.1021/ja300294a.
Characterization of Products

\textit{(E)-Diethyl 2-(4-(1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate} \textbf{(3aa)}: purified using PE/EA (3:1) as an eluent, \( R_f = 0.31 \); yellow oil (71.2 mg, 87\%, E/Z > 20:1). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 8.42 (d, \( J = 3.6 \) Hz, 2H), 7.14 – 6.94 (m, 3H), 6.68 (s, 1H), 5.69 – 5.58 (m, 1H), 5.45 – 5.34 (m, 1H), 4.41 (q, \( J = 7.3 \) Hz, 2H), 4.12 – 4.22 (m, 4H), 3.40 – 3.18 (m, 3H), 3.05 (t, \( J = 7.3 \) Hz, 2H), 2.60 (m, 2H), 1.24 (m, 6H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \( \delta \) 169.0, 161.4, 157.6, 142.4, 134.8, 134.7, 131.8, 131.1, 130.5, 128.2, 128.1, 127.1, 125.8, 124.3, 124.2, 122.3, 112.2, 61.3, 53.3, 53.2, 52.2, 52.0, 36.9, 31.8, 29.9, 26.7, 14.1. HRMS (positive ESI): Calcd for C\(_{23}\)H\(_{28}\)N\(_3\)O\(_4\) (M + H\(^+\)) 410.2075, found 410.2079.

\textit{(E)-Diethyl 2-(4-(2-methyl-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate} \textbf{(3ba)}: purified using PE/EA (3:1) as an eluent, \( R_f = 0.27 \); yellow oil (81.3mg, 96\%, E/Z = 8:1). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 8.41 (t, \( J = 5.8 \) Hz, 2H), 7.13 – 6.93 (m, 3H), 6.70 – 6.58 (m, 1H), 5.65 – 5.53 (m, 1H), 5.34 (m, 1H), 5.03 – 4.90 (m, 1H), 4.21 – 4.11 (m, 4H), 3.50 – 3.18 (m, 4H), 2.64 – 2.39 (m, 3H), 1.36 (t, \( J = 9.7 \) Hz, 3H), 1.27 – 1.18 (m, 6H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \( \delta \) 169.0, 160.8, 157.6, 140.8, 140.7, 133.5, 131.8, 131.2, 131.1, 130.8, 128.4, 128.2, 126.9, 125.6, 124.2, 124.1, 122.9, 112.3, 112.2, 61.3, 60.4, 52.2, 37.1, 36.9, 32.0, 31.8, 26.7, 21.1, 14.1. HRMS (positive ESI): Calcd for C\(_{24}\)H\(_{30}\)N\(_3\)O\(_4\) (M + H\(^+\)) 424.2231, found 424.2234.

\textit{(E)-Diethyl 2-(4-(2-(tert-butyl)-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate} \textbf{(3ca)}: purified using PE/EA (3:1) as an eluent, \( R_f = 0.39 \); yellow oil (75.3mg, 81\%, E/Z = 10:1). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.42 (d, \( J = 4.8 \) Hz, 2H), 7.34 – 7.22 (m, 4H), 7.09 – 6.95 (m, 3H), 6.70 (t, \( J = 4.8 \) Hz, 1H), 5.95 (d, \( J = 8.7 \) Hz, 1H), 5.70 (dt, \( J = 15.1, 7.0 \) Hz, 1H), 5.51 – 5.32 (m, 1H), 4.21 – 4.09 (m, 4H), 3.88 – 3.74 (m, 1H), 3.51 – 3.23 (m, 3H), 2.97 (d, \( J = 15.4 \) Hz, 1H), 2.69 – 2.54 (m, 2H), 1.28 – 1.18 (m, 15H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \( \delta \) 169.1, 161.3, 157.8, 149.8, 141.9, 140.3, 133.1, 131.9, 131.2, 130.6, 128.5, 127.3, 125.4, 125.3, 124.5, 122.7, 112.8, 112.7, 66.7, 61.3, 52.2, 52.1, 38.5, 37.2, 34.4, 31.9, 31.4, 26.8, 14.1. HRMS (positive ESI): Calcd for C\(_{33}\)H\(_{39}\)N\(_3\)O\(_4\) (M + H\(^+\)) 542.3014, found 542.3015.

\textit{(E)-Diethyl 2-(4-(2-phenyl-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate} \textbf{(3da)}: purified using PE/EA (3:1) as an eluent, \( R_f = 0.38 \); yellow oil (87.3mg, 90\%, E/Z = 7:1). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.45-8.39 (m, 2H\(\text{E}[\text{E}] + 2\text{H}\text{[Z]}\)), 7.38-7.32 (m,
2H[E] + 2H[Z], 7.30-7.26 (m, 2H[E] + 2H[Z]), 7.22-7.19 (m, 1H[E] + 1H[Z]), 7.10 – 6.98 (m, 3H[E] + 3H[Z]), 6.74-6.70 (m, 1H[E] + 1H[Z]), 6.01-5.96 (m, 1H[E] + 1H[Z]), 5.72-5.65 (m, 1H[E] + 1H[Z]), 5.48 – 5.44 (m, 1H[Z]), 5.41-5.34 (m, 1H[E]), 4.21 – 4.10 (m, 4H[E] + 4H[Z]), 3.84 (dd, $J = 15.5, 9.1$ Hz, 1H[E] + 1H[Z]), 3.59 (dd, $J = 16.5, 7.5$ Hz, 1H[Z]), 3.44 (dd, $J = 15.9, 6.9$ Hz, 1H[E]), 3.37-3.31 (m, 2H[E] + 2H[Z]), 2.97 (d, $J = 15.5$ Hz, 1H[E] + 1H[Z]), 2.70 – 2.54 (m, 2H[E] + 2H[Z]), 1.25 – 1.21 (m, 6H[E] + 6H[Z]).

$^{13}$C NMR (151 MHz, CDCl₃) $\delta$ 169.0, 161.3, 158.1, 157.8, 143.5, 142.0, 141.9, 132.9, 131.9, 131.2, 130.8, 130.5, 128.6, 128.5, 128.4, 127.3, 127.1, 125.9, 125.7, 124.7, 122.7, 112.8, 67.0, 66.9, 61.4, 61.3, 52.2, 52.0, 38.5, 37.3, 32.0, 31.9, 26.8, 14.1.

HRMS (positive ESI): Caled for C$_{29}$H$_{32}$N$_{3}$O$_{4}$ (M + H$^+$) 546.2388, found 546.2390.

**(E)-Diethyl2-(4-(2-chloro-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate**(3ea): purified using PE/EA (3:1) as an eluent, $R_f = 0.33$; yellow oil (57.6mg, 65%, E/Z = 5:1). $^1$H NMR (400 MHz, CDCl₃) $\delta$ 8.45 – 8.39 (m, 2H[E] + 2H[Z]), 7.32 – 7.23 (m, 4H[E] + 4H[Z]), 7.22 – 7.19 (m, 1H[E] + 1H[Z]), 7.10 – 6.98 (m, 3H[E] + 3H[Z]), 6.76 – 6.72 (m, 1H[E] + 1H[Z]), 6.00 – 5.90 (m, 1H[E] + 1H[Z]), 5.70 – 5.61 (m, 1H[E] + 1H[Z]), 5.48 – 5.44 (m, 1H[Z]), 5.41 – 5.34 (m, 1H[E]), 4.21 – 4.10 (m, 4H[E] + 4H[Z]), 3.84 (dd, $J = 15.5, 9.1$ Hz, 1H[E] + 1H[Z]), 3.59 (dd, $J = 16.5, 7.5$ Hz, 1H[Z]), 3.44 (dd, $J = 15.9, 6.9$ Hz, 1H[E]), 3.37-3.31 (m, 2H[E] + 2H[Z]), 2.97 (d, $J = 15.5$ Hz, 1H[E] + 1H[Z]), 2.70 – 2.54 (m, 2H[E] + 2H[Z]), 1.25 – 1.21 (m, 6H[E] + 6H[Z]).

$^{13}$C NMR (151 MHz, CDCl₃) $\delta$ 169.0, 161.2, 157.8, 142.1, 141.6, 132.8, 132.6, 131.7, 131.0, 130.5, 128.8, 128.6, 127.4, 127.2, 126.0, 124.8, 124.7, 122.7, 113.0, 66.5, 66.4, 61.4, 61.3, 52.1, 52.0, 38.3, 37.3, 32.0, 31.8, 26.7, 14.1. HRMS (positive ESI): Caled for C$_{29}$H$_{30}$ClN$_{3}$O$_{4}$ (M + H$^+$) 520.1998, found 520.2000.

**(E)-Diethyl2-(4-(2-bromo-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate**(3fa): purified using PE/EA (3:1) as an eluent, $R_f = 0.36$; yellow oil (73.3mg, 75%, E/Z = 3:1). $^1$H NMR (400 MHz, CDCl₃) $\delta$ 8.45-8.39 (m, 2H[E] + 2H[Z]), 7.43-7.38 (m, 2H[E] + 2H[Z]), 7.27 – 7.21 (m, 2H[E] + 2H[Z]), 7.10 – 6.98 (m, 3H[E] + 3H[Z]), 6.76 – 6.72 (m, 1H[E] + 1H[Z]), 6.00 – 5.90 (m, 1H[E] + 1H[Z]), 5.70 – 5.61 (m, 1H[E] + 1H[Z]), 5.48 – 5.44 (m, 1H[Z]), 5.41 – 5.34 (m, 1H[E]), 4.21 – 4.10 (m, 4H[E] + 4H[Z]), 3.84 (dd, $J = 15.5, 9.1$ Hz, 1H[E] + 1H[Z]), 3.59 (dd, $J = 16.5, 7.5$ Hz, 1H[Z]), 3.44 (dd, $J = 15.9, 6.9$ Hz, 1H[E]), 3.37-3.31 (m, 2H[E] + 2H[Z]), 2.97 (d, $J = 15.5$ Hz, 1H[E] + 1H[Z]), 2.70 – 2.54 (m, 2H[E] + 2H[Z]), 1.25 – 1.21 (m, 6H[E] + 6H[Z]). $^{13}$C NMR (151 MHz, CDCl₃) $\delta$ 169.0, 161.2, 157.8, 142.6, 141.7, 141.6, 132.5, 131.7, 131.6, 131.4, 131.0, 130.9, 157.8, 142.6, 141.7, 141.6, 132.5, 131.7, 131.6, 131.4, 131.0, 130.9.
130.5, 128.8, 128.6, 127.5, 127.4, 126.1, 124.9, 124.7, 122.7, 120.9, 113.0, 66.5, 61.4, 61.3, 52.1, 52.0, 38.3, 37.3, 32.0, 31.8, 26.7, 14.1. HRMS (positive ESI): Calcd for C_{29}H_{50}BrN_{3}O_{4} (M + H^+) 564.1493, found 564.1495.

(E)-Diethyl 2-(4-(2-methyl-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate (3ga): purified using PE/EA (3:1) as an eluent, R_{f} = 0.27; yellow oil (77.0 mg, 91%, E/Z > 20:1). ^1H NMR (600 MHz, CDCl_3) δ 8.41 (t, J = 5.8 Hz, 2H), 7.13 – 6.93 (m, 3H), 6.70 – 6.58 (m, 1H), 5.65 – 5.53 (m, 1H), 5.34 (m, 1H), 5.03 – 4.90 (m, 1H), 4.21 – 4.11 (m, 4H), 3.50 – 3.18 (m, 4H), 2.64 – 2.39 (m, 3H), 1.36 (t, J = 9.7 Hz, 3H), 1.27 – 1.18 (m, 6H). ^13C NMR (151 MHz, CDCl_3) δ 169.0, 160.8, 157.6, 140.8, 140.7, 133.5, 131.8, 131.2, 130.8, 128.4, 128.2, 126.9, 125.6, 124.2, 124.1, 122.9, 112.3, 112.2, 61.3, 60.4, 52.2, 37.1, 36.9, 32.0, 31.8, 26.7, 21.1, 14.1. HRMS (positive ESI): Calcd for C_{29}H_{50}N_{3}O_{4} (M + H^+) 424.2231, found 424.2234.

(E)-Diethyl 2-(4-(4-methyl-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate (3ha): purified using PE/EA (3:1) as an eluent, R_{f} = 0.25; yellow oil (76.2 mg, 90%, E/Z > 20:1). ^1H NMR (600 MHz, CDCl_3) δ 8.44 – 8.34 (m, 2H), 6.96 (d, J = 7.6 Hz, 1H), 6.89 – 6.78 (m, 1H), 6.68-6.64 (m, 1H), 5.69 – 5.57 (m, 1H), 5.43 – 5.29 (m, 1H), 4.41 (q, J = 7.6 Hz, 2H), 4.20 – 4.10 (m, 4H), 3.40 – 3.13 (m, 3H), 2.95 (t, J = 7.5 Hz, 2H), 2.65 – 2.55 (m, 2H), 2.24 (s, 3H), 1.24 (t, J = 7.1 Hz, 6H). ^13C NMR (151 MHz, CDCl_3) δ 169.0, 161.5, 157.6, 142.0, 141.9, 133.4, 132.0, 131.6, 128.2, 127.7, 125.5, 112.7, 61.33, 61.30, 53.0, 52.2, 52.0, 36.7, 31.9, 31.5, 28.6, 26.7, 18.5, 14.1. HRMS (positive ESI): Calcd for C_{29}H_{50}N_{3}O_{4} (M + H^+) 424.2231, found 424.2235.

(E)-Diethyl 2-(4-(4-methoxy-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate (3ia): purified using PE/EA (3:1) as an eluent, R_{f} = 0.33; yellow oil (80.8 mg, 92%, E/Z > 20:1). ^1H NMR (600 MHz, CDCl_3) δ 8.46 – 8.39 (m, 2H), 7.01 (t, J = 6.9 Hz, 1H), 6.68 (dd, J = 15.3, 10.9 Hz, 1H), 6.60 (d, J = 8.4 Hz, 1H), 5.66 – 5.57 (m, 1H), 5.41 – 5.32 (m, 1H), 4.44- 4.38 (m, 2H), 4.23 – 4.07 (m, 4H), 3.82 (s, 3H), 3.42 – 3.11 (m, 3H), 2.98 (t, J = 7.4 Hz, 2H), 2.63 – 2.55 (m, 2H), 1.27 – 1.21 (m, 6H). ^13C NMR (151 MHz, CDCl_3) δ 169.0, 161.5, 157.6, 154.3, 143.7, 132.2, 131.5, 129.2, 126.7, 125.4, 123.3, 121.8, 121.7, 112.3, 106.9, 61.3, 55.5, 53.7, 52.3, 36.4, 31.8, 31.2, 26.7, 14.1. HRMS (positive ESI): Calcd for C_{29}H_{50}N_{3}O_{5} (M + H^+) 440.2180, found 440.2184.

(E)-Diethyl 2-(4-(5-(benzylxoy)-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate (3ja): purified using PE/EA (3:1) as an eluent, R_{f} = 0.27; yellow oil (95.5 mg, 93%,
(E)-Diethyl

-2-(4-(4-fluoro-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate (3ka): purified using PE/EA (3:1) as an eluent, Rf = 0.32; yellow oil (80.3mg, 94%, E/Z > 20:1).^1^H NMR (400 MHz, CDCl3) δ 8.44 (d, J = 4.8 Hz, 2H), 7.03 – 6.95 (m, 1H), 6.77 – 6.65 (m, 2H), 5.66 – 5.52 (m, 1H), 5.44 – 5.29 (m, 1H), 4.48 – 4.40 (m, 2H), 4.24 – 4.07 (m, 4H), 3.39 – 3.14 (m, 2H), 3.07 (t, J = 7.7 Hz, 2H), 2.58 (t, J = 7.3 Hz, 2H), 1.27 – 1.19 (q, J = 7.6 Hz, 6H).^1^C NMR (151 MHz, CDCl3) δ 169.0, 161.2, 157.7, 157.6 (JCF = 245.3 Hz), 157.6, 144.4 (JCF = 7.5 Hz), 131.6, 130.9, 129.8 (JCF = 8.0 Hz), 127.3, 126.0 (JCF = 3.2 Hz), 125.9, 120.4 (JCF = 21.2 Hz), 112.7, 111.0, 110.8, 61.4, 61.3, 53.6, 52.2, 36.5, 31.8, 25.9, 14.1. ^19^F NMR (565 MHz, CDCl3) δ -122.6. HRMS (positive ESI): Calcd for C23H26F3N4O4(M + H^+^) 428.1980, found 428.1981.

(E)-Diethyl 2-(4-(4-chloro-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate (3la): purified using PE/EA (3:1) as an eluent, Rf = 0.29; yellow oil (85.1mg, 96%, E/Z > 20:1).^1^H NMR (400 MHz, CDCl3) δ 8.43 (d, J = 4.8 Hz, 2H), 6.99 (s, 2H), 6.76 – 6.71 (m, 1H), 5.67 – 5.53 (m, H), 5.45 – 5.31 (m, H), 4.47 – 4.39 (m, 2H), 4.23 – 4.10 (m, 4H), 3.41 – 3.16 (m, 3H), 3.09 (t, J = 7.8 Hz, 2H), 2.59 (t, J = 7.0 Hz, 2H), 1.28 – 1.19 (m, 6H).^1^C NMR (151 MHz, CDCl3) δ 169.0, 161.2, 157.6, 143.6, 132.9, 131.3, 130.6, 128.8, 128.0, 127.5, 123.9, 112.8, 61.4, 6.32, 52.1, 36.6, 31.8, 29.2, 26.7, 14.2, 14.1. HRMS (positive ESI): Calcd for C23H26ClN3O4 (M + H^+^) 444.1685, found 444.1684.

(E)-Diethyl 2-(4-(4-bromo-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate (3ma): purified using PE/EA (3:1) as an eluent, Rf = 0.33; yellow oil (53.1mg, 54%, E/Z > 20:1).^1^H NMR (600 MHz, CDCl3) δ 8.52 – 8.32 (m, 2H), 7.18 – 7.08 (m, 1H), 6.91 (t, J = 18.4 Hz, 1H), 6.73 (d, J = 4.3 Hz, 1H), 5.63 – 5.51 (m, 1H), 5.45 – 5.32 (m, 1H), 4.42 (q, J = 7.8 Hz, 2H), 4.22 – 4.09 (m, 4H), 3.41 – 2.98 (m, 5H), 2.62 – 2.52 (m, 2H), 1.29 – 1.18 (m, 6H).^1^C NMR (151 MHz, CDCl3) δ 169.0, 161.2, 157.7,
143.4, 135.2, 131.2, 130.5, 129.9, 127.6, 126.9, 116.6, 112.8, 61.4, 52.5, 52.1, 51.9, 36.6, 31.8, 31.5, 26.7, 14.1. HRMS (positive ESI): Calcd for C_{23}H_{27}BrN_{3}O_{4} (M + H') 488.1180, found 488.1182.

(E)-Diethyl 2-(4-(5-methyl-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate (3na): purified using PE/EA (3:1) as an eluent, Rf = 0.37; yellow oil (73.6mg, 86%, E/Z = 11:1). 1H NMR (600 MHz, CDCl3) δ 8.47 – 8.31 (m, 2H), 6.92 (s, 1H), 6.85 (s, 1H), 6.66 (d, J = 4.3 Hz, 1H), 5.71 – 5.59 (m, 1H), 5.45 – 5.31 (m, 1H), 4.40 (q, J = 7.2 Hz, 2H), 4.22 – 4.09 (m, 4H), 3.40 – 3.16 (m, 3H), 3.00 (t, J = 7.3 Hz, 2H), 2.63 – 2.58 (m, 2H), 2.31 (s, 3H), 1.30 – 1.16 (m, 6H). 13C NMR (151 MHz, CDCl3) δ 169.0, 161.5, 157.7, 140.0, 134.9, 133.9, 131.9, 130.2, 128.7, 127.0, 123.2, 112.0, 61.3, 53.3, 52.3, 36.8, 31.9, 31.6, 29.9, 26.7, 21.0, 14.1. HRMS (positive ESI): Calcd for C_{24}H_{30}N_{3}O_{4} (M + H') 424.2231, found 424.2233.

(E)-Diethyl 2-(4-(5-methoxy-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate (3oa): purified using PE/EA (3:1) as an eluent, Rf = 0.26; yellow oil (79.1mg, 90%, E/Z > 20:1). 1H NMR (600 MHz, CDCl3) δ 8.40 (t, J = 6.7 Hz, 2H), 6.73 – 6.56 (m, 3H), 5.72 – 5.61 (m, 1H), 5.49 – 5.36 (m, 1H), 4.41 (t, J = 7.4 Hz, 2H), 4.23 – 4.10 (m, 4H), 3.78 (s, 3H), 3.40 – 2.93 (m, 5H), 2.63 – 2.55 (m, 2H), 1.24 (t, J = 7.1 Hz, 6H). 13C NMR (151 MHz, CDCl3) δ 169.0, 161.6, 157.7, 157.1, 136.2, 134.0, 131.7, 127.3, 126.0, 113.1, 111.9, 108.6, 61.3, 55.6, 53.4, 52.22, 52.0, 36.9, 31.8, 30.4, 26.7, 14.1. HRMS (positive ESI): Calcd for C_{24}H_{30}N_{3}O_{3} (M + H') 440.2180, found 440.2181.

(E)-Diethyl 2-(4-(5-(benzyloxy)-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate (3pa): purified using PE/EA (3:1) as an eluent, Rf = 0.27; yellow oil (82.4mg, 80%, E/Z > 20:1). 1H NMR (600 MHz, CDCl3) δ 8.40 (t, J = 7.1 Hz, 2H), 7.43 – 7.37 (m, 5H), 6.78 – 6.61 (m, 3H), 5.66 – 5.58 (m, 1H), 5.48 – 5.34 (m, 1H), 5.03 (s, 2H), 4.45 – 4.38 (m, 2H), 4.22 – 4.06 (m, 4H), 3.41 – 3.18 (m, 3H), 3.07 – 3.01 (m, 2H), 2.64 – 2.55 (m, 2H), 1.26 – 1.16 (m, 6H). 13C NMR (151 MHz, CDCl3) δ 169.0, 161.4, 157.7, 153.5, 143.8, 137.5, 132.2, 129.2, 128.5, 126.8, 125.8, 123.6, 122.4, 112.4, 108.5, 70.1, 61.4, 53.7, 52.3, 36.4, 31.9, 31.2, 26.8, 26.8, 14.1. HRMS (positive ESI): Calcd for C_{30}H_{34}N_{3}O_{3} (M + H') 516.2493, found 516.2495.

(E)-Diethyl 2-(4-(5-fluoro-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate (3qa): purified using PE/EA (3:1) as an eluent, Rf = 0.28; yellow oil (77.1mg, 91%, E/Z = 10:1). 1H NMR (600 MHz, CDCl3) δ 8.43 (d, J = 4.3 Hz, 2H), 7.05 – 7.00 (m, 1H), 6.79 – 6.62 (m, 2H), 5.65 – 5.47 (m, 1H), 5.27 – 5.09 (m, 1H), 4.42 (t, J = 7.5 Hz,
2H), 4.22 – 4.06 (m, 4H), 3.45 – 3.13 (m, 3H), 2.99 (t, J = 7.3 Hz, 2H), 2.49 (t, J = 7.0 Hz, 2H), 1.27 – 1.20 (m, 6H). 13C NMR (151 MHz, CDCl3) δ 169.0, 162.1, 161.1, 160.5, 157.7, 144.0, 143.9, 130.4, 130.2, 126.3, 125.1, 122.6, 122.5, 118.7, 118.6, 112.7, 110.6, 110.4, 61.3, 54.0, 52.1, 51.9, 31.8, 30.6, 30.5, 29.2, 26.6, 14.1, 14.0. 13C NMR (376 MHz, CDCl3) δ -119.2. HRMS (positive ESI): Calcd for C23H27FN3O4 (M + H+) 428.1980, found 428.1982.

(E)-Diethyl 2-(4-(5-chloro-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate (3ra): purified using PE/EA (3:1) as an eluent, Rf = 0.23; yellow oil (79.8mg, 90%, E/Z > 20:1). 1H NMR (400 MHz, CDCl3) δ 8.43 (d, J = 4.3, 2H), 7.07 (d, J = 1.9 Hz, 1H), 7.00 (d, J = 2.0 Hz, 1H), 6.75 – 6.66 (m, 1H), 5.67 – 5.57 (m, 1H), 5.48 – 5.38 (m, 1H), 4.46 – 4.37 (m, 2H), 4.25 – 4.11 (m, 4H), 3.42 – 3.15 (m, 3H), 3.03 (t, J = 7.7 Hz, 2H), 2.61 (t, J = 6.8 Hz, 2H), 1.27-1.22 (m, 6H). 13C NMR (151 MHz, CDCl3) δ 170.0, 161.3, 157.7, 141.2, 136.6, 132.0, 130.9, 129.2, 128.0, 122.5, 112.6, 61.4, 53.3, 52.1, 36.7, 31.8, 29.8, 14.1. HRMS (positive ESI): Calcd for C23H27ClN3O4 (M + H+) 444.1685, found 444.1689.

(E)-Diethyl 2-(4-(5-bromo-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate (3sa): purified using PE/EA (3:1) as an eluent, Rf = 0.21; yellow oil (71.2mg, 73%, E/Z > 20:1). 1H NMR (600 MHz, CDCl3) δ 8.43 (t, J = 7.4 Hz, 2H), 7.21 (s, 1H), 7.15 (s, 1H), 6.72 (t, J = 4.5 Hz, 1H), 5.66 – 5.55 (m, 1H), 5.47 – 5.33 (m, 1H), 4.41 (q, J = 7.8 Hz, 2H), 4.24 – 4.12 (m, 4H), 3.41 – 3.15 (m, 3H), 3.03 (t, J = 7.5 Hz, 2H), 2.60 (t, J = 7.0 Hz, 2H), 1.25 (t, J = 7.1 Hz, 6H). 13C NMR (151 MHz, CDCl3) δ 170.0, 161.2, 157.7, 141.7, 137.0, 132.4, 130.8, 128.0, 126.5, 116.9, 112.6, 61.4, 53.3, 52.1, 51.9, 36.7, 31.8, 31.5, 3.67, 26.7, 14.1 HRMS (positive ESI): Calcd for C23H27BrN3O4 (M + H+) 488.1880, found 488.1184.

(E)-Diethyl-2-(4-(5-(methoxycarbonyl)-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate (3ta): purified using PE/EA (3:1) as an eluent, Rf = 0.23; yellow oil (56.1mg, 72%, E/Z = 4:1). 1H NMR (600 MHz, CDCl3) δ 8.49 – 8.41 (m, 2H[E] + 2H[Z]), 7.77 (s, 2H[E] + 2H[Z]), 6.81 – 6.70 (m, H[E] + H[Z]), 5.64 – 5.56 (m, 1H[E] + 1H[Z]), 5.45 – 5.40 (m, 1H[Z]), 5.39 – 5.32 (m, 1H[E]), δ 4.47 – 4.40 (m, 2H[E] + 2H[Z]) 4.21 – 4.12 (m, 4H[E] + 4H[Z]), 3.91 – 3.87 (m, 3H[E] + 3H[Z]), 3.40 – 3.27 (m, 3H[E] + 3H[Z]), 3.13 – 3.08 (m, 2H[E] + 2H[Z]), 2.61 – 2.54 (m, 2H[E] + 2H[Z]), 1.25 – 1.21 (m, 6H[E] + 6H[Z]).
$^{13}$C NMR (151 MHz, CDCl$_3$) δ 169.0, 167.1, 160.8, 157.7, 146.6, 134.9, 130.9, 130.7, 130.4, 129.5, 127.6, 126.4, 125.6, 123.8, 113.0, 61.4, 61.3, 53.5, 53.4, 52.1, 51.9, 37.1, 31.9, 31.8, 29.2, 26.7, 14.1. HRMS (positive ESI): Calcd for C$_{25}$H$_{30}$N$_3$O$_6$ (M + H$^+$) 468.2129, found 468.2133.

(E)-Diethyl
2-(4-(5-methyl-2-phenyl-1-(pyrimidin-2-yl)indolin-7-yl)but-2-ene-1-yl)malonate (3ua): purified using PE/EA (3:1) as an eluent, R$_f$ = 0.35; yellow oil (81.9mg, 82%, E/Z = 5:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.45 – 8.39 (m, 2H$_{[E]}$ + 2H$_{[Z]}$), 7.38 – 7.32 (m, 2H$_{[E]}$ + 2H$_{[Z]}$), 7.30 – 7.26 (m, 2H$_{[E]}$ + 2H$_{[Z]}$), 7.22 – 7.19 (m, 1H$_{[E]}$ + 1H$_{[Z]}$), δ 6.86 (d, J = 6.8 Hz, 2H$_{[E]}$ + 2H$_{[Z]}$), 6.72 – 6.68 (m, 1H$_{[E]}$ + 1H$_{[Z]}$), 6.01 – 5.96 (m, 1H$_{[E]}$ + 1H$_{[Z]}$), 5.72 – 5.65 (m, 1H$_{[E]}$ + 1H$_{[Z]}$), 5.48 – 5.43 (m, 1H$_{[Z]}$), 5.42 – 5.34 (m, 1H$_{[E]}$), 4.21 – 4.10 (m, 4H$_{[E]}$ + 4H$_{[Z]}$), 3.80 (dd, J = 15.5, 9.1 Hz, 1H$_{[E]}$ + 1H$_{[Z]}$), 3.55 (dd, J = 16.5, 7.5 Hz, 1H$_{[Z]}$), 3.42 (dd, J = 15.9, 6.9 Hz, 1H$_{[E]}$), 3.40 – 3.33 (m, 2H$_{[E]}$ + 2H$_{[Z]}$), 2.92 (d, J = 15.5 Hz, 1H$_{[E]}$ + 1H$_{[Z]}$), 2.70 – 2.54 (m, 2H$_{[E]}$ + 2H$_{[Z]}$), 2.27 (s, 3H$_{[E]}$ + 3H$_{[Z]}$), 1.25 – 1.21 (m, 6H$_{[E]}$ + 6H$_{[Z]}$).$^{13}$C NMR (151 MHz, CDCl$_3$) δ 169.0, 161.5, 157.8, 143.5, 139.5, 134.3, 133.0, 131.9, 131.3, 130.2, 129.1, 128.9, 128.5, 127.1, 127.0, 125.7, 123.5, 112.6, 112.5, 67.0, 61.3, 52.2, 52.0, 38.4, 37.1, 31.9, 31.8, 26.7, 21.0, 14.1. HRMS (positive ESI): Calcd for C$_{30}$H$_{30}$N$_3$O$_4$ (M + H$^+$) 500.2544, found 500.2547.

(E)-Diethyl-2-(4-(5-chloro-2-phenyl-1-(pyrimidin-2-yl)indolin-7-yl)but-2-ene-1-yl)malonate (3va): purified using PE/EA (3:1) as an eluent, R$_f$ = 0.32; yellow oil (92.6mg, 89%, E/Z > 20:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.44 (d, J = 4.8 Hz, 2H), 7.36 – 7.18 (m, 5H), 7.03 (d, J = 9.2 Hz, 2H), 5.98 (d, J = 8.7 Hz, 1H), 5.70 – 5.59 (m, 1H), 5.47 – 5.37 (m, 1H), 4.26 – 4.11 (m, 4H), 3.85 – 3.76 (m, 1H), 3.46 – 3.20 (m, 3H), 2.94 (t, J = 12.7 Hz, 1H), 2.65 – 2.53 (m, 2H), 1.27 – 1.16 (m, 6H).$^{13}$C NMR (151 MHz, CDCl$_3$) δ 169.0, 161.2, 157.8, 143.0, 140.7, 134.9, 132.1, 130.9, 129.6, 128.6, 128.3, 128.1, 127.3, 125.5, 122.9, 113.1, 67.1, 61.4, 52.0, 38.3, 37.0, 31.8, 28.7, 14.1. HRMS (positive ESI): Calcd for C$_{29}$H$_{30}$ClN$_3$O$_4$ (M + H$^+$) 520.1998, found 520.1997.

(E)-Diethyl 2-(4-(6-fluoro-1-(pyrimidin-2-yl)indolin-7-yl)but-2-ene-1-yl)malonate (3wa): purified using PE/EA (3:1) as an eluent, R$_f$ = 0.29; yellow oil (81.2mg, 95%, E/Z = 5:1).$^1$H NMR (600 MHz, CDCl$_3$) δ 8.43 (d, J = 4.0 Hz, 2H$_{[E]}$ + 2H$_{[Z]}$), 7.05 – 6.97 (m, 1H$_{[E]}$ + 1H$_{[Z]}$), 6.77 – 6.66 (m, 2H$_{[E]}$ + 2H$_{[Z]}$), 5.63 – 5.49 (m, 1H$_{[E]}$ + 1H$_{[Z]}$), 5.30 – 5.25 (m, 1H$_{[Z]}$), 5.25-5.17 (m, 1H$_{[E]}$), 4.46 – 4.38 (m, 2H$_{[E]}$ + 2H$_{[Z]}$), 4.20 –
4.09 (m, 4H[E] + 4H[Z]), 3.45 – 3.19 (m, 3H[E] + 3H[Z]), 2.99 (t, J = 7.2 Hz, 2H[E] + 2H[Z]), 2.49 (t, J = 7.0 Hz, 2H[E] + 2H[Z]), 1.25 – 1.21 (m, 6H[E] + 6H[Z]). 13C NMR (101 MHz, CDCl3) δ 169.0, 161.3 (J_C,F = 241.3) 161.1, 157.7, 143.9 (J_C,F = 8.1), 130.4, 130.2 (J_C,F = 2.2), 126.3, 122.5 (J_C,F = 10.3), 118.6 (J_C,F = 19.1), 112.7, 110.5 (J_C,F = 24.2), 61.3, 54.0, 52.1, 31.8, 30.5, 29.2, 14.0. 19F NMR (376 MHz, CDCl3) δ -119.2. HRMS (positive ESI): Calcd for C_{23}H_{27}FN_{3}O_{4} (M + H') 428.1980, found 428.1984.

(E)-Diethyl 2-(4-(6-chloro-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate (3xa): purified using PE/EA (3:1) as an eluent, R_f = 0.23; yellow oil (80.7mg, 91%, E/Z = 14:1). 1H NMR (600 MHz, CDCl3) δ 8.42 (d, J = 4.7 Hz, 2H), 7.11 – 7.06 (m, 1H), 7.03 (t, J = 6.7 Hz, 1H), 6.73 (t, J = 4.8 Hz, 1H), 5.60 – 5.47 (m, 1H), 5.21 – 5.14 (m, 1H), 4.43 (t, J = 7.6 Hz, 2H), 4.20 – 4.07 (m, 4H), 3.45 (d, J = 6.3 Hz, 2H), 3.28 (t, J = 7.6 Hz, 1H), 2.99 (q, J = 7.4 Hz, 2H), 2.49 (t, J = 7.1 Hz, 2H), 1.24 – 1.16 (m, 6H). 13C NMR (151 MHz, CDCl3) δ 169.0, 161.3, 157.7, 144.4, 134.0, 133.7, 130.3, 130.1, 128.9, 126.6, 125.5, 125.0, 123.0, 112.8, 61.3, 54.0, 53.8, 52.2, 51.8, 34.4, 31.8, 30.0, 29.6, 14.1. HRMS (positive ESI): Calcd for C_{24}H_{30}N_{3}O_{4} (M + H') 424.2231, found 424.2233.

(E)-Diethyl 2-(4-(6-bromo-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate (3ya): purified using PE/EA (3:1) as an eluent, R_f = 0.26; yellow oil (76.0mg, 78%, E/Z > 20:1). 1H NMR (600 MHz, CDCl3) δ 8.44 – 8.39 (m, 2H), 7.27 (d, J = 7.7 Hz, 1H), 6.96 (d, J = 7.7 Hz, 1H), 6.73 (s, 1H), 5.58 – 5.45 (m, 1H), 5.21 – 5.05 (m, 1H), 4.42 (t, J = 7.3 Hz, 2H), 4.19 – 4.05 (m, 4H), 3.49 (d, J = 5.9 Hz, 2H), 3.28 (t, J = 7.5 Hz, 1H), 2.96 (t, J = 7.4 Hz, 2H), 2.48 (t, J = 7.1 Hz, 2H), 1.21 (t, J = 7.1 Hz, 6H). 13C NMR (151 MHz, CDCl3) δ 169.0, 161.3, 157.6, 144.4, 134.9, 130.5, 130.3, 128.9, 126.7, 125.0, 123.4, 112.8, 61.3, 61.2, 53.9, 52.1, 36.9, 31.80, 29.7, 26.8, 14.1, 14.0. HRMS (positive ESI): Calcd for C_{23}H_{26}BrN_{3}O_{4} (M + H') 488.1180, found 488.1181.

(E)-Diethyl 2-(4-(1-(pyrimidin-2-yl)-1,2,3,4-tetrahydroquinolin-8-yl)but-2-en-1-yl)malonate (3za): purified using PE/EA (3:1) as an eluent, R_f = 0.36; yellow oil (60.1mg, 71%, E/Z = 3:1). 1H NMR (400 MHz, CDCl3) δ 8.36 (s, 2H[E] + 2H[Z]), 7.10 – 7.04 (m, 3H[E] + 3H[Z]), 6.62 – 6.58 (m, 1H[E] + 1H[Z]), 5.65 – 5.58 (m, 1H[E] + 1H[Z]), 5.41 – 5.31 (m, 1H[E] + 1H[Z]), 4.82 (s, 1H[E] + 1H[Z]), 4.20 – 4.12 (m, 4H[E] + 4H[Z]), 3.37 (t, J = 7.6 Hz, 1H[E]), 3.28 (t, J = 7.6 Hz, 4H[Z]), 3.20 (d, J = 7.3 Hz, 1H[E]), 3.09 (d, J = 6.7 Hz, 2H[E]), 2.69 (s, 2H[E] + 2H[Z]), 2.60-2.53 (m, 2H[E] + 2H[Z]), 2.19-1.90 (m, 2H[E] + 2H[Z]).
(E)-Diethyl 2-(4-(9-(pyrimidin-2-yl)-9H-carbazol-1-yl)but-2-en-1-yl)malonate (3a’): purified using PE/EA (3:1) as an eluent, Rf = 0.30; yellow oil (71.3mg, 78%, E/Z = 10:1). \( ^1 \text{H} \) NMR (600 MHz, CDCl\(_3\)) \( \delta \) 8.86 (d, \( J = 4.4 \) Hz, 2H), 8.15 – 7.90 (m, 3H), 7.46 – 7.13 (m, 5H), 5.53 – 5.39 (m, 1H), 5.21 – 5.05 (m, 1H), 4.20 – 4.04 (m, 4H), 3.43 – 3.24 (m, 3H), 2.53 – 2.40 (m, 2H), 1.26 – 1.17 (m, 6H). \( ^{13} \text{C} \) NMR (151 MHz, CDCl\(_3\)) \( \delta \) 169.0, 158.9, 158.3, 141.3, 138.3, 130.9, 128.5, 127.3, 126.7, 126.6, 126.3, 125.6, 122.4, 122.0, 119.8, 118.2, 117.9, 112.6, 61.4, 61.3, 51.9, 51.8, 37.4, 32.2, 31.7, 26.8, 14.1. HRMS (positive ESI): Calcd for C\(_{27}\)H\(_{37}\)N\(_3\)O\(_4\) (M + H\(^+\)) 458.2075, found 458.2076.

(3b’a): purified using PE/EA (3:1) as an eluent, Rf = 0.25; yellow oil (76.2mg, 90%, E/Z > 20:1).

(3ab): purified using PE/EA (3:1) as an eluent, Rf = 0.26; yellow oil (65.6mg, 86%, E/Z > 20:1). \( ^1 \text{H} \) NMR (600 MHz, CDCl\(_3\)) \( \delta \) 8.47 – 8.35 (m, 2H), 7.10 (d, \( J = 6.3 \) Hz, 1H), 7.02 (q, \( J = 7.0 \) Hz, 2H), 6.69 (d, \( J = 4.6 \) Hz, 1H), 5.70 – 5.60 (m, 1H), 5.44 – 5.33 (m, 1H), 4.41 (q, \( J = 7.8 \) Hz, 2H), 3.70 (d, \( J = 7.9 \) Hz, 6H), 3.44 – 3.22 (m, 3H), 3.05 (t, \( J = 8.0 \) Hz, 1H).
= 7.4 Hz, 2H), 2.67 – 2.55 (m, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 169.4, 161.4, 157.7, 142.4, 134.8, 132.0, 131.3, 128.2, 125.5, 122.4, 112.2, 53.2, 52.5, 51.9, 36.9, 31.9, 29.9, 26.8. HRMS (positive ESI): Calcd for C$_2$H$_4$N$_3$O$_4$ (M + H$^+$) 382.1762, found 382.1766.

**(E)-Dibutyl 2-(4-(1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate (3ac):**
purified using PE/EA (3:1) as an eluent, R$_f$ = 0.26; yellow oil (81.0mg, 87%, E/Z > 20:1). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.44 – 8.40 (m, 2H), 7.13 – 6.99 (m, 3H), 6.69 – 6.66 (m, 1H), 5.70 – 5.56 (m, 1H), 5.45 – 5.32 (m, 1H), 4.44 – 4.38 (m, 2H), 4.15 – 4.11 (m, 4H), 3.40 – 3.20 (m, 3H), 3.05 (t, J = 7.4 Hz, 2H), 2.64 – 2.56 (m, 2H), 1.63 – 1.55 (m, 4H), 1.40 – 1.29 (m, 3H), 0.90 (t, J = 7.0 Hz, 6H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 169.1, 161.4, 157.6, 142.4, 134.7, 131.8, 128.2, 127.2, 125.8, 124.3, 122.3, 112.2, 65.2, 53.3, 53.2, 52.3, 36.9, 31.9, 31.8, 30.5, 29.9, 19.0, 13.6. HRMS (positive ESI): Calcd for C$_{27}$H$_{36}$N$_3$O$_4$ (M + H$^+$) 466.2701, found 466.2705.

**(E)-Dipropyl 2-(4-(1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate (3ad):**
purified using PE/EA (3:1) as an eluent, R$_f$ = 0.28; yellow oil (64.7mg, 74%, E/Z > 20:1). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.47 – 8.34 (m, 2H), 7.13 – 6.95 (m, 3H), 6.68 (s, 1H), 5.71 – 5.58 (m, 1H), 5.46 – 5.34 (m, 1H), 4.41 (t, J = 7.4 Hz, 2H), 4.12 – 4.01 (m, 4H), 3.42 – 3.20 (m, 3H), 3.05 (t, J = 7.3 Hz, 2H), 2.65-2.57 (m, 2H), 1.67 – 1.59 (m, 4H), 0.91 (t, J = 7.3 Hz, 6H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 169.1, 161.4, 157.6, 142.4, 134.7, 131.1, 130.5, 128.2, 127.2, 124.2, 122.3, 112.2, 66.9, 53.3, 53.2, 52.3, 36.9, 31.9, 29.9, 26.7, 21.9, 10.3. HRMS (positive ESI): Calcd for C$_{25}$H$_{31}$N$_3$O$_4$ (M + H$^+$) 438.2388, found 438.2391.

**(E)-Dibenzyl 2-(4-(1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate (3ae):**
purified using PE/EA (3:1) as an eluent, R$_f$ = 0.28; yellow oil (96.0mg, 90%, E/Z = 7:1). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.39 (t, J = 4.7 Hz, 2H), 7.34 – 7.21 (m, 10H), 7.13 – 6.94 (m, 3H), 6.66 – 6.60 (m, 1H), 5.65 – 5.56 (m, 1H), 5.43 – 5.26 (m, 1H), 5.17 – 5.01 (m, 4H), 4.40 (t, J = 7.7 Hz, 2H), 3.49 (t, J = 7.6 Hz, 1H), 3.20 (d, J = 6.8 Hz, 2H), 3.04 (t, J = 7.6 Hz, 2H), 2.63 (t, J = 7.1 Hz, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 168.7, 161.4, 161.3, 157.6, 142.4, 135.4, 134.8, 132.1, 131.4, 130.7, 130.4, 128.5, 128.3, 128.2, 126.8, 125.5, 124.3, 124.2, 122.4, 112.3, 67.1, 53.2, 52.2, 52.0, 36.9, 31.9, 31.8, 29.9, 26.8. HRMS (positive ESI): Calcd for C$_{33}$H$_{32}$N$_3$O$_4$ (M + H$^+$) 534.2388, found 534.2393.

**(E)-Bis(2,2,2-trifluoroethyl)**
2-(4-(1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate (3af): purified using PE/EtOAc (3:1) as an eluent, Rf = 0.32; yellow oil (78.6mg, 76%, E/Z = 8:1). 

1H NMR (600 MHz, CDCl3) δ 8.42 (t, J = 5.9 Hz, 2H[Et] + 2H[Z]), 7.11 (t, J = 4.3 Hz, H[Et] + H[Z]), 7.05 - 6.94 (m, 2H[Et] + 2H[Z]), 6.70 - 6.67 (m, H[Et] + H[Z]), 5.73 - 5.65 (m, H[Et] + H[Z]), 5.41 - 5.37 (m, H[Z]), 5.36 - 5.28 (m, H[Et]), 4.54 - 4.35 (m, 6H[Et] + 6H[Z]), 3.58 (t, J = 7.5 Hz, H[Et] + H[Z]), 3.39 (d, J = 7.2 Hz, H[Z]), 3.29 (d, J = 6.9 Hz, 2H[Et]), 3.04 (t, J = 7.6 Hz, 2H[Et] + 2H[Z]), 2.70 - 2.61 (m, 2H[Et] + 2H[Z]). 

13C NMR (151 MHz, ) δ 166.6, 161.3, 157.6, 142.5, 142.4, 135.0, 134.9, 133.2, 132.3, 130.4, 130.1, 128.3, 127.9, 125.3, 124.4, 124.3, 124.2, 122.5 (JC-F = 277.5 Hz), 112.3, 61.0 (JC-F = 36.7 Hz), 53.3, 53.3, 51.2, 50.9, 37.0, 31.7, 31.6, 29.9, 26.5. 

HRMS (positive ESI): Calcd for C23H21FN3O4 (M + H+): 518.1509, found 518.1512.

(E)-2,2-dimethyl-5-(4-(1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)-1,3-dioxane-4,6-dione (3ag): purified using PE/EtOAc (3:1) as an eluent, Rf = 0.36; yellow oil (51.3mg, 65%, E/Z > 20:1). 

1H NMR (400 MHz, CDCl3) δ 8.42 (d, J = 4.8 Hz, 2H), 7.14 - 6.99 (m, 3H), 6.71 (t, J = 4.8 Hz, 1H), 5.69 (dt, J = 15.1, 6.9 Hz, 1H), 5.40 - 5.26 (m, 1H), 4.39 - 4.33 (m, 2H), 3.53 (t, J = 5.1 Hz, 1H), 3.30 (d, J = 6.9 Hz, 2H), 3.05 (t, J = 7.7 Hz, 2H), 2.80 - 2.73 (m, 2H), 1.81 (s, 3H), 1.76 (s, 3H). 

13C NMR (101 MHz, CDCl3) δ 165.2, 161.3, 157.7, 142.5, 134.9, 132.1, 130.7, 128.6, 125.0, 124.4, 112.3, 104.9, 53.3, 46.5, 31.9, 29.9, 28.5, 26.8, 24.3. 

HRMS (positive ESI): Calcd for C22H23N3O4 (M + H+) 394.1762, found 394.1761.

(E)-2-(4-(1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malononitrile (3ah): purified using PE/EtOAc (3:1) as an eluent, Rf = 0.24; yellow oil (44.7mg, 71%, E/Z = 4:1). 

1H NMR (600 MHz, CDCl3) δ 8.46-8.44 (m, 2H[Et] + 2H[Z]), 7.18 - 7.12 (m, 1H[Et] + 1H[Z]), 7.08 -7.03 (m, 2H[Et] + 2H[Z]), 6.75-6.70 (m, 1H[Et] + 1H[Z]), 5.93 - 5.85 (m, 1H[Et] + 1H[Z]), 5.54 - 5.48 (m, 1H[Z]), 5.40 - 5.34 (m, 1H[Et]), 4.42 (q, J = 7.8 Hz, 2H[Et] + 2H[Z]), 3.66 (t, J = 6.7 Hz, 1H[Et]), 3.53 (t, J = 7.1 Hz, 1H[Z]), 3.43 (t, J = 6.8 Hz, 2H[Et] + 2H[Z]), 3.06 (t, J = 7.7 Hz, 2H[Et] + 2H[Z]), 2.68 - 2.65 (m, 2H[Et] + 2H[Z]). 

13C NMR (151 MHz, CDCl3) δ 161.3, 161.2, 157.8, 157.7, 142.5, 142.4, 136.9, 135.7, 135.3, 135.1, 129.6, 129.1, 128.5, 128.1, 124.6, 124.3, 122.9, 122.0, 121.2, 112.6, 112.5, 112.4, 60.4, 53.4, 53.3, 37.2, 33.9, 32.1, 29.9, 29.8, 28.8, 23.3, 22.7, 21.0, 14.2. 

HRMS (positive ESI): Calcd for C19H18N5 (M + H+) 316.1557, found 316.1561.

(E)-7-(5,5-bis(phenylsulfonyl)pent-2-en-1-yl)-1-(pyrimidin-2-yl)indoline (3ai): purified using PE/EtOAc (3:1) as an eluent, Rf = 0.28; yellow oil (63.2mg, 58%, E/Z
(E)-Methyl 2-cyano-6-(1-(pyrimidin-2-yl)indolin-7-yl)hex-4-enoate (3aj): purified using PE/EA (3:1) as an eluent, Rf = 0.26; yellow oil (54.3mg, 78%, E/Z = 3:1).

1H NMR (600 MHz, CDCl3) δ 8.45-8.41 (m, 2H[E] + 2H[Z]), 7.12 (d, J = 5.5 Hz, 1H[E] + 1H[Z]), 7.08 – 7.01 (m, 2H[E] + 2H[Z]), 6.73-6.69 (m, 1H[E] + 1H[Z]), 5.85-5.73 (m, 1H[E] + 1H[Z]), 5.53 – 5.47 (m, 1H[Z]), 5.44 – 5.35 (m, 1H[E]), 4.46 – 4.37 (m, 2H[E] + 2H[Z]), 3.77 (d, J = 6.8 Hz, 3H[E] + 3H[Z]), 3.50 (dd, J = 7.3, 6.2 Hz, 1H[E]), 3.47 – 3.42 (m, 1H[Z]), 3.40 (d, J = 7.3 Hz, 2H[E]), 3.34 (d, J = 6.8 Hz, 2H[E]), 3.06 (t, J = 7.6 Hz, 2H[E] + 2H[Z]), 2.67-2.60 (m, 2H[E] + 2H[Z]).

13C NMR (151 MHz, CDCl3) δ 166.2, 166.1, 161.3, 157.7, 142.5, 142.4, 135.0, 134.9, 134.5, 130.1, 129.8, 128.4, 128.0, 124.4, 124.2, 123.2, 122.6, 116.2, 112.4, 112.3, 53.4, 53.3, 53.2, 37.8, 37.3, 37.1, 33.0, 31.9, 29.9, 27.8. HRMS (positive ESI): Calcd for C20H27N3O5S2 (M + H+®) 546.1516, found 546.1517.

(E)-2-(phenylsulfonyl)-6-(1-(pyrimidin-2-yl)indolin-7-yl)hex-4-enenitrile (3ak): purified using PE/EA (3:1) as an eluent, Rf = 0.26; yellow oil (48.3mg, 56%, E/Z = 4:1).

1H NMR (600 MHz, CDCl3) δ 8.44 (d, J = 4.8 Hz, 2H[Z]), 8.42 (d, J = 4.7 Hz, 2H[E]), 8.00 (t, J = 7.3 Hz, 2H[E] + 2H[Z]), 7.76 (t, J = 7.5 Hz, H[E] + H[Z]), 7.64 (t, J = 7.8 Hz, 2H[E] + 2H[Z]), 7.16 – 7.08 (m, H[E] + H[Z]), 7.05 – 6.96 (m, 2H[E] + 2H[Z]), 6.73 – 6.68 (m, H[E] + H[Z]), 5.89 – 5.71 (m, H[E] + H[Z]), 5.48 – 5.42 (m, H[Z]), 5.34 – 5.21 (m, H[E]), 4.45 – 4.33 (m, 2H[E] + 2H[Z]), 3.88 (dd, J = 10.9, 4.2 Hz, H[E]), 3.75 (dd, J = 10.7, 4.7 Hz, H[Z]), 3.46 – 3.29 (m, 2H[E] + 2H[Z]), 3.09 – 2.99 (m, 2H[E] + 2H[Z]), 2.93 – 2.81 (m, H[E] + H[Z]), 2.64 – 2.47 (m, H[E] + H[Z]).

13C NMR (151 MHz, CDCl3) δ 161.2, 157.7, 157.5, 142.5, 142.4, 135.6, 135.3, 135.1, 135.0, 134.6, 129.8, 129.7, 129.6, 129.3, 128.5, 128.0, 127.5, 124.4, 124.3, 122.7, 122.4, 121.6, 113.8,
112.4, 57.6, 57.1, 53.2, 37.2, 32.0, 30.1, 29.9, 29.8, 24.8. HRMS (positive ESI): Caled for C_{24}H_{32}NaO_2S (M + H^+) 431.1536, found 431.1537.

*(E)-2,2-dimethyl-5-(4-(1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)-1,3-dioxane-4,6-dione*(3fe): purified using PE/EA (3:1) as an eluent, R_f = 0.29; yellow oil (101.4mg, 90%, E/Z = 4:1). \( ^1\)H NMR (600 MHz, CDCl_3) \( \delta \) 8.39 (d, \( J = 3.8 \) Hz, 2H\(_{[E]}\)), 8.36 (d, \( J = 3.9 \) Hz, 2H\(_{[Z]}\)), 7.32 – 7.23 (m, 10H\(_{[E]} + 10H_{[Z]}\)), 6.97 (d, \( J = 8.3 \) Hz, H\(_{[E]} + H_{[Z]}\)), 6.67 – 6.53 (m, 2H\(_{[E]} + 2H_{[Z]}\)), 5.67 – 5.53 (m, H\(_{[E]} + H_{[Z]}\)), 5.38 – 5.25 (m, H\(_{[E]} + H_{[Z]}\)), 5.14 – 5.04 (m, 5H\(_{[E]} + 5H_{[Z]}\)), 4.39 (t, \( J = 7.5 \) Hz, 2H\(_{[E]} + 2H_{[Z]}\)), 3.79 (s, 3H\(_{[E]} + 3H_{[Z]}\)), 3.51 – 3.40 (m, H\(_{[E]} + H_{[Z]}\)), 3.29 (d, \( J = 7.0 \) Hz, H\(_{[Z]}\)), 3.16 (d, \( J = 6.6 \) Hz, H\(_{[E]}\)), 2.97 (t, \( J = 7.5 \) Hz, 2H\(_{[E]} + 2H_{[Z]}\)), 2.67 – 2.59 (m, 2H\(_{[E]} + 2H_{[Z]}\)). \( ^{13}\)C NMR (151 MHz, CDCl_3) \( \delta \) 168.7, 161.5, 161.4, 157.6, 154.3, 143.7, 143.6, 135.5, 132.6, 131.8, 129.3, 129.1, 128.5, 128.3, 128.2, 128.1, 126.4, 125.2, 123.3, 123.1, 121.9, 121.7, 112.4, 112.3, 107.0, 106.9, 67.1, 55.5, 53.7, 53.6, 52.3, 52.0, 36.4, 31.9, 31.2, 3.72, 26.7.

HRMS (positive ESI): Caled for C_{34}H_{33}N_3O_5 (M + H^+) 564.2493, found 564.2496.

*(E)-Dibutyl 2-(4-(3-methyl-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate*(3kc): purified using PE/EA (3:1) as an eluent, R_f = 0.28; yellow oil (81.4mg, 85%, E/Z > 20:1). \( ^1\)H NMR (600 MHz, CDCl_3) \( \delta \) 8.42- 8.38 (m, 2H), 6.92 (s, 1H), 6.85 (s, 1H), 6.65 (s, 1H), 6.57 – 5.58 (m, 1H), 5.45 – 5.33 (m, 1H), 4.40 (t, \( J = 4.4 \) Hz, 2H), 4.15 – 4.06 (m, 4H), 3.41 – 3.18 (m, 3H), 2.99 (t, \( J = 7.1 \) Hz, 2H), 2.65 – 2.55 (m, 2H), 2.30 (s, 3H), 1.62 – 1.55 (m, 4H), 1.40 – 1.30 (m, 4H), 0.90 (t, \( J = 7.1 \) Hz, 6H).

\( ^{13}\)C NMR (151 MHz, CDCl_3) \( \delta \) 161.6, 157.6, 140.0, 134.9, 133.9, 131.2, 130.2, 128.7, 127.0, 125.6, 123.1, 112.0, 65.2, 65.1, 53.3, 52.0, 36.8, 31.9, 31.6, 30.5, 29.9, 21.0, 19.0, 13.6. HRMS (positive ESI): Caled for C_{28}H_{37}N_3O_4 (M + H^+) 450.2857, found 450.2858.

*(E)-Dibutyl 2-(4-(6-chloro-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate*(3sc): purified using PE/EA (3:1) as an eluent, R_f = 0.29; yellow oil (73.9mg, 74%, E/Z = 11:1). \( ^1\)H NMR (600 MHz, CDCl_3) \( \delta \) 8.42 (d, \( J = 4.1 \) Hz, 2H\(_{[E]} + 2H_{[Z]}\)), 7.11 – 7.05 (m, H\(_{[E]} + H_{[Z]}\)), 7.02 (d, \( J = 7.8 \) Hz, H\(_{[E]} + H_{[Z]}\)), 6.76 – 6.60 (m, H\(_{[E]} + H_{[Z]}\)), 5.60 – 5.48 (m, H\(_{[E]} + H_{[Z]}\)), 5.31 – 5.23 (m, H\(_{[Z]}\)), 5.21 – 5.12 (m, H\(_{[E]}\)), 4.43 (t, \( J = 7.3 \) Hz, 2H\(_{[E]} + 2H_{[Z]}\)), 4.14 – 3.99 (m, 4H\(_{[E]} + 4H_{[Z]}\)), 3.50 (d, \( J = 6.2 \) Hz, 2H\(_{[Z]}\)), 3.45 (d, \( J = 6.0 \) Hz, 2H\(_{[E]}\)), 3.29 (t, \( J = 7.5 \) Hz, H\(_{[E]} + H_{[Z]}\)), 2.98 (t, \( J = 7.4 \) Hz, 2H\(_{[E]} + 2H_{[Z]}\)), 2.49 (t, \( J = 7.0 \) Hz, 2H\(_{[E]} + 2H_{[Z]}\)), 1.62 – 1.52 (m, 4H\(_{[E]} + 4H_{[Z]}\)), 1.40 – 1.28 (m, 4H\(_{[E]} + 4H_{[Z]}\)), 0.90 (t, \( J = 7.4 \) Hz, 6H\(_{[E]} + 6H_{[Z]}\)). \( ^{13}\)C NMR (151 MHz, CDCl_3) \( \delta \) 169.1, 161.4,
157.6, 144.4, 134.0, 133.7, 130.2, 130.1, 128.9, 126.6, 125.5, 125.0, 123.0, 112.7, 65.1, 54.0, 53.8, 52.2, 51.8, 34.4, 31.8, 30.5, 30.0, 29.6, 26.8, 19.0, 13.6. HRMS (positive ESI): Calcd for C_{27}H_{34}ClN_{3}O_{4} (M + H^+) 500.2311, found 500.2313.

*(E)-Ethyl 6-(1-(pyrimidin-2-yl)indolin-7-yl)hex-4-enoate 4*: purified using PE/EA (3:1) as an eluent, R_f = 0.40; yellow oil (58.1 mg, 86%). ^1^H NMR (400 MHz, CDCl_3) δ 8.43 (t, J = 4.1 Hz, 2H), 7.13 – 6.98 (m, 3H), 6.70 – 6.66 (m, 1H), 5.60 – 5.52 (m, 1H), 5.45 – 5.34 (m, 1H), 4.48 – 4.34 (m, 2H), 4.11 (q, J = 7.1 Hz, 2H), 3.27 (d, J = 6.8 Hz, 2H), 3.05 (t, J = 7.7 Hz, 2H), 2.37 – 2.26 (m, 4H), 1.23 (t, J = 7.1 Hz, 3H). ^1^C NMR (151 MHz, CDCl_3) δ 173.2, 161.3, 157.6, 142.3, 134.73, 130.7, 129.8, 129.5, 128.3, 124.1, 122.3, 112.2, 60.3, 53.3, 37.0, 34.3, 29.9, 27.9, 14.2. HRMS (positive ESI): Calcd for C_{20}H_{24}N_{2}O_{2} (M + H^+) 338.1683, found 338.1686.

*(E)-2-(4-(1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonic acid 5*: purified using DCM/MeOH (4:1) (1% HAc) as an eluent, R_f = 0.42; gray solid (63.9 mg, 90%); Mp: 162.1–164.6 °C. ^1^H NMR (400 MHz, CDCl_3) δ 8.43 (dd, J = 4.8, 1.8 Hz, 2H), 7.10 (d, J = 6.8 Hz, 1H), 7.07 – 6.85 (m, 2H), 6.81 (m, 1H), 5.61 – 5.49 (m, 1H), 5.34 (m, 1H), 4.93 (s, 4H), 4.34 (m, 2H), 3.32 – 3.18 (m, 3H), 3.01 (t, J = 7.6 Hz, 2H), 2.47 (d, J = 6.9 Hz, 2H). ^1^C NMR (101 MHz, CDCl_3) δ 172.7, 162.4, 159.0, 143.5, 136.3, 132.3, 131.7, 129.5, 128.6, 127.4, 125.4, 123.4, 113.8, 54.8, 38.2, 33.0, 32.9, 30.7, 27.9. HRMS (positive ESI): Calcd for C_{19}H_{19}N_{2}O_{4}(M + H^+) 354.1449, found 354.1452.

*(E)-Diethyl -2-(4-(1-(pyrimidin-2-yl)indolin-7-yl)but-2-enoyl)malonate 6*: purified using PE/EA (6:1) as an eluent, R_f = 0.28; yellow oil (32.0 mg, 38%). ^1^H NMR (400 MHz, CDCl_3) δ 8.19 (d, J = 4.7 Hz, 2H), 7.42 (d, J = 7.8 Hz, 1H), 7.19 (d, J = 7.3 Hz, 1H), 7.03 (t, J = 7.6 Hz, 1H), 7.03 (t, J = 7.6 Hz, 1H), 6.56 (t, J = 4.5 Hz, 1H), 6.32 (dd, J = 20.9, 3.1 Hz, 2H), 4.44 (m, 3H), 4.20 (m, 4H), 3.14 (t, J = 7.9 Hz, 2H), 1.27 (t, J = 7.0 Hz, 6H). ^1^C NMR (101 MHz, CDCl_3) δ 166.2, 160.1, 156.6, 153.6, 144.1, 140.3, 135.2, 126.7, 124.1, 123.3, 120.0, 112.3, 110.7, 107.3, 62.0, 52.3, 52.0, 29.2, 14.0. HRMS (positive ESI): Calcd for C_{23}H_{25}N_{3}O_{5}(M + H^+) 424.1867, found 424.1873.

*Diethyl 2-(4-(1-(pyrimidin-2-yl)indolin-7-yl)butyl)malonate 7*: purified using PE/EA (5:1) as an eluent, R_f = 0.35; yellow oil (69.1 mg, 84%). ^1^H NMR (400 MHz, CDCl_3) δ 8.41 (t, J = 4.5 Hz, 2H), 7.12 – 6.96 (m, 3H), 6.68 (t, J =
4.8 Hz, H), 4.40 (dd, J = 9.9, 5.4 Hz, 2H), 4.20 – 4.10 (m, 4H), 3.28 – 3.17 (m, H), 3.03 (t, J = 7.6 Hz, 2H), 2.62 – 2.52 (m, 2H), 1.82 (m, 2H), 1.61 (m, 2H), 1.23 (mt, 8H). 

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 169.5, 161.4, 157.6, 142.4, 134.8, 132.5, 128.0, 124.3, 122.1, 112.2, 61.2, 53.4, 52.0, 33.5, 29.9, 28.6, 27.4, 14.1. HRMS (positive ESI): Calcd for C\(_{23}\)H\(_{29}\)N\(_3\)O\(_4\) (M + H\(^+\)) 412.2231, found 412.2235.

**Diethyl 2-(4-(1-(pyrimidin-2-yI)-1H-indol-7-yl)butyl)malonate 8:**

purified using PE/EA (5:1) as an eluent, R\(_f\) = 0.33; yellow oil (73.7 mg, 90%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 8.68 (d, J = 4.8 Hz, 2H), 7.70 (d, J = 3.5 Hz, 1H), 7.41 (d, J = 7.5 Hz, 1H), 7.11 – 7.03 (m, 3H), 6.62 (t, J = 6.8 Hz, 1H), 4.14 – 3.95 (m, 4H), 3.11 (t, J = 7.5 Hz, 1H), 2.86 – 2.79 (m, 2H), 1.64 (m, 2H), 1.35 (m, 2H), 1.16 (t, J = 7.1 Hz, 6H), 1.08 – 1.00 (m, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 169.5, 158.3, 133.8, 132.2, 130.0, 128.6, 125.6, 122.3, 119.1, 117.5, 107.0, 61.2, 51.9, 34.8, 29.3, 28.6, 27.3, 14.1. HRMS (positive ESI): Calcd for C\(_{23}\)H\(_{27}\)N\(_3\)O\(_4\) (M + H\(^+\)) 410.2075, found 410.2073.

**Ethyl 6-(1-(pyrimidin-2-yI)-1H-indol-7-yl)hexanoate 9:**

purified using PE/EA (5:1) as an eluent, R\(_f\) = 0.28; yellow oil (55.3 mg, 82%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.77 (d, J = 4.8 Hz, 2H), 7.77 (d, J = 3.6 Hz, 1H), 7.49 (dd, J = 7.4, 1.5 Hz, 1H), 7.16 (m, 3H), 6.70 (t, J = 4.8 Hz, 1H), 4.09 (q, J = 7.1 Hz, 2H), 2.95 – 2.85 (m, 2H), 2.15 (t, J = 7.6 Hz, 2H), 1.41 (m, 4H), 1.23 (t, J = 7.1 Hz, 3H), 1.15 – 1.05 (m, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 173.7, 158.3, 133.8, 132.2, 130.0, 128.8, 125.6, 122.3, 119.0, 117.4, 107.1, 60.2, 34.9, 34.2, 29.3, 29.1, 24.8, 14.3. HRMS (positive ESI): Calcd for C\(_{23}\)H\(_{27}\)N\(_3\)O\(_2\) (M + H\(^+\)) 338.1863, found 338.1865.
NMR Spectra

Figure S3. $^1$H NMR spectrum of compound 3aa

Figure S4. $^{13}$C NMR spectrum of compound 3aa
**Figure S5.** $^1$H-$^1$H-COSY spectrum of compound 3aa

**Figure S6.** HMQC spectrum of compound 3aa
Figure S7. $^1$H NMR spectrum of compound 3ba

Figure S8. $^{13}$C NMR spectrum of compound 3ba
Figure S9. $^1$H NMR spectrum of compound 3ca

Figure S10. $^{13}$C NMR spectrum of compound 3ca
Figure S11. $^1$H NMR spectrum of compound 3da

Figure S12. $^{13}$C NMR spectrum of compound 3da
Figure S13. $^1$H NMR spectrum of compound 3ea

Figure S14. $^{13}$C NMR spectrum of compound 3ea
Figure S15. $^1$H NMR spectrum of compound 3fa

Figure S16. $^{13}$C NMR spectrum of compound 3fa
Figure S17. $^1$H NMR spectrum of compound 3ga

Figure S18. $^{13}$C NMR spectrum of compound 3ga
Figure S19. $^1$H NMR spectrum of compound 3ha

Figure S20. $^{13}$C NMR spectrum of compound 3ha
Figure S21. $^1$H NMR spectrum of compound 3ia

Figure S22. $^{13}$C NMR spectrum of compound 3ia
Figure S23. $^1$H NMR spectrum of compound 3ja

Figure S24. $^{13}$C NMR spectrum of compound 3ja
Figure S25. $^1$H NMR spectrum of compound 3ka

Figure S26. $^{13}$C NMR spectrum of compound 3ka
Figure S27. $^1$H NMR spectrum of compound 3la

Figure S28. $^{13}$C NMR spectrum of compound 3la
Figure S29. $^1$H NMR spectrum of compound 3ma

Figure S30. $^{13}$C NMR spectrum of compound 3ma
**Figure S31.** $^1$H NMR spectrum of compound 3na

**Figure S32.** $^{13}$C NMR spectrum of compound 3na
Figure S33. $^1$H NMR spectrum of compound 3oa

Figure S34. $^{13}$C NMR spectrum of compound 3oa
Figure S35. $^1$H NMR spectrum of compound 3pa

Figure S36. $^{13}$C NMR spectrum of compound 3pa
Figure S37. $^1$H NMR spectrum of compound 3qa

Figure S38. $^{13}$C NMR spectrum of compound 3qa
Figure S39. $^1$H NMR spectrum of compound 3ra

Figure S40. $^{13}$C NMR spectrum of compound 3ra
Figure S41. $^1$H NMR spectrum of compound 3sa

Figure S42. $^{13}$C NMR spectrum of compound 3sa
Figure S43. $^1$H NMR spectrum of compound 3ta

Figure S44. $^{13}$C NMR spectrum of compound 3ta
Figure S45. $^1$H NMR spectrum of compound 3ua

Figure S46. $^{13}$C NMR spectrum of compound 3ua
Figure S47. $^1$H NMR spectrum of compound 3va

Figure S48. $^{13}$C NMR spectrum of compound 3va
Figure S49. $^1$H NMR spectrum of compound 3wa

Figure S50. $^{13}$C NMR spectrum of compound 3wa
Figure S51. $^1$H NMR spectrum of compound 3xa

Figure S52. $^{13}$C NMR spectrum of compound 3xa
Figure S53. $^1$H NMR spectrum of compound 3ya

Figure S54. $^{13}$C NMR spectrum of compound 3ya
Figure S55. $^1$H NMR spectrum of compound 3za

Figure S56. $^{13}$C NMR spectrum of compound 3za
**Figure S57.** $^1$H NMR spectrum of compound 3a’a

**Figure S58.** $^{13}$C NMR spectrum of compound 3a’a
Figure S59. $^1$H NMR spectrum of compound 3b’a

Figure S60. $^{13}$C NMR spectrum of compound 3b’a
Figure S61. $^1$H NMR spectrum of compound 3ab

Figure S62. $^{13}$C NMR spectrum of compound 3ab
Figure S63. $^1$H NMR spectrum of compound 3ac

Figure S64. $^{13}$C NMR spectrum of compound 3ac
Figure S65. $^1$H NMR spectrum of compound 3ad

Figure S66. $^{13}$C NMR spectrum of compound 3ad
Figure S67. $^1$H NMR spectrum of compound 3ae

Figure S68. $^{13}$C NMR spectrum of compound 3ae
Figure S69. $^1$H NMR spectrum of compound 3af

Figure S70. $^{13}$C NMR spectrum of compound 3af
Figure S71. $^1$H NMR spectrum of compound 3ag

Figure S72. $^{13}$C NMR spectrum of compound 3ag
Figure S73. $^1$H NMR spectrum of compound 3ah

Figure S74. $^{13}$C NMR spectrum of compound 3ah
Figure S75. $^1$H NMR spectrum of compound 3ai

Figure S76. $^{13}$C NMR spectrum of compound 3ai
Figure S77. $^1$H NMR spectrum of compound 3aj

Figure S78. $^{13}$C NMR spectrum of compound 3aj
Figure S79. $^1$H NMR spectrum of compound 3ak

Figure S80. $^{13}$C NMR spectrum of compound 3ak
Figure S81. $^1$H NMR spectrum of compound 3fe

Figure S82. $^{13}$C NMR spectrum of compound 3fe
Figure S83. $^1$H NMR spectrum of compound 3kc

Figure S84. $^{13}$C NMR spectrum of compound 3kc
Figure S85. $^1$H NMR spectrum of compound 3sc

Figure S86. $^{13}$C NMR spectrum of compound 3sc
Figure S87. $^1$H NMR spectrum of compound 5

Figure S88. $^{13}$C NMR spectrum of compound 5
Figure S89. $^1$H NMR spectrum of compound 6

Figure S90. $^{13}$C NMR spectrum of compound 6
Figure S91. $^1$H NMR spectrum of compound 7

Figure S92. $^{13}$C NMR spectrum of compound 7
Figure S93. $^1$H NMR spectrum of compound 8

Figure S94. $^{13}$C NMR spectrum of compound 8
Figure S95. $^1$H NMR spectrum of compound 9

Figure S96. $^{13}$C NMR spectrum of compound 9