Supplementary Methods

General Information.

$^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra were recorded on a Bruker Advance 400 MHz or 500 MHz NMR spectrometers at ambient temperature in CDCl$_3$. The chemical shifts are given in ppm relative to tetramethylsilane [$^1$H: $\delta =$ (SiMe$_4$) = 0.00 ppm] as an internal standard or relative to the resonance of the solvent [$^1$H: $\delta$ (CDCl$_3$) = 7.26, $^{13}$C: $\delta$ (CDCl$_3$) = 77.16 ppm]. Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), dd (doublet of doublets), dt (doublet of triplets), m (multiplets), etc. Coupling constants are reported as $J$ values in Hz. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF. HPLC was performed on Thermo UltiMate 3000. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system.

Unless otherwise stated, all reactions were set up on 10 mL reaction tube and carried out under nitrogen. NiBr$_2$•glyme was prepared according to the known procedure.$^1$ N-Methyl morpholine was purchased from Aladdin (purified by redistillation, 99.5%). All other solvents were purchased from Energy Chemical and used as received. Other commercial reagents were purchased from Sigma-Aldrich, Alfa Aesar, TCI, Strem, Acros, and Adamas-beta China and were used as received.

Reactions were monitored through thin layer chromatography [Merck 60 F254 precoated silica gel plate (0.2 mm thickness)]. Subsequent to elution, spots were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Other visualization methods include staining with a basic solution of potassium permanganate or acidic solution of ceric molybdate, followed by heating.
Carbamoyl chlorides \(1b, 1f, 1q\) are known compounds in the literature.\(^2\)

**Supplementary Figure 1. General procedure (A) for the preparation of carbamoyl chlorides.**

The carbamoyl chlorides were prepared according to the known procedure with slight modification.\(^2\)

**Step 1:** 2-Fluorobenzonitrile (1 equiv) was added to a 100 mL screw-cap vial equipped with a magnetic stir bar, then acetonitrile (0.5 M) and methylamine (15 equiv, 40% wt. in H\(_2\)O) were added, successively. The reaction was stirred at 90 °C for 12 h. After cooling to room temperature, the reaction was diluted with ethyl acetate and washed twice with water. The organic layer was dried over magnesium sulfate, filtered, and dried. The residue was purified by silica gel column chromatography in ethyl acetate/petroleum ether to give the desired aniline.

**Step 2:** The N-methyl aniline was stirred in THF (0.3 M) at 0 °C. Then Grignard reagent (3.0 M, 3 equiv) was added slowly. The reaction was heated to 80 °C for 6 h. After cooling to 0 °C, the reaction was quenched slowly with 2M aq. HCl. The imine hydrolysis was stirred at room temperature for 1 h. In some cases the imine hydrolysis required refluxing 4M HCl in EtOH overnight to convert to the corresponding ketones. The reaction was quenched with Na\(_2\)CO\(_3\) (aq.), then diluted with EtOAc and washed twice with water. The organic layer was dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography in ethyl acetate/petroleum ether to give the desired ketone.

**Step 3:** Potassium tert-butoxide (1.5 equiv) was added slowly to methyl triphenyl
phosphonium bromide (1.5 equiv) in THF (0.3 M) at 0 ºC. The suspension turned yellow upon addition of the base. The suspension was warmed to 40 ºC and stirred for 1 h. The reaction was cooled to 0 ºC and the 2-aminophenones were added in THF (10 mL). The reaction was warmed to 40 ºC again and stirred until consumption of starting material was observed by TLC (typically 2 h). Upon completion the reaction was filtered over a silica plug eluting with ethyl acetate. The crude styrene was concentrated under reduced pressure and used in next step without further purification.

Step 4: The methylated amine was dissolved in dichloromethane (0.3 M) and cooled to 0 ºC. Then pyridine (2 equiv) was added followed by triphosgene (0.4 equiv). The reaction was warmed to room temperature and stirred until completion indicated by TLC (typically 2 h). The reaction was quenched with 1 M HCl and extracted twice with dichloromethane. The organic layers were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The crude starting material was purified by silica gel column chromatography in ethyl acetate/petroleum ether to give the desired carbamoyl chloride.

**Supplementary Figure 2. General procedure (B) for the preparation of carbamoyl chlorides.**

![Chemical reaction](image)

Aminostyrenes (prepared from 2-aminobenzonitriles via General Procedure (A)) was dissolved in ethyl acetate (0.25 M). The aldehydes (1.5 equiv) were added followed by trifluoroacetic acid (2 equiv). The reaction was stirred for 30 minutes then sodium triacetoxyborohydride (2 equiv) was added. After stirring for 2 h the reaction was then quenched with 4 M aq. NaOH, diluted with ethyl acetate and washed twice with brine. The organic layer was dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography.

The alkylated amines were carried forward following General Procedure (A) to obtain
the carbamoyl chloride.

Methyl(2-(3-methylbut-1-en-2-yl)phenyl)carbamic chloride (1a).

Prepared following general procedure A. The crude product was purified by silica gel column chromatography (4% EtOAc in petroleum ether) to provide the title compound as a yellow solid in 69% yield. The product was isolated as a mixture of two rotamers. $^1$H NMR and $^{13}$C NMR data listed are for the major rotamer.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.46 – 7.11 (m, 4H), 5.25 (t, $J = 1.4$ Hz, 1H), 5.05 (s, 1H), 3.25 (s, 3H), 2.66 – 2.49 (m, 1H), 1.17 (d, $J = 6.7$ Hz, 3H), 1.01 (d, $J = 6.9$ Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 153.8, 149.7, 141.5, 140.2, 130.8, 129.0, 128.7, 128.2, 113.4, 39.9, 33.0, 22.6, 21.4.

(3-Methoxy-2-(prop-1-en-2-yl)phenyl)(methyl)carbamic chloride (1c).

Prepared following general procedure A. The crude product was purified by silica gel column chromatography (4% EtOAc in petroleum ether) to provide the title compound as a colorless oil in 57% yield. The product was isolated as a mixture of two rotamers. $^1$H NMR and $^{13}$C NMR data listed are for the major rotamer.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.42 – 7.12 (m, 4H), 5.32 – 5.13 (m, 1H), 5.06 (s, 1H), 3.25 (s, 3H), 2.51 – 2.26 (m, 2H), 1.08 (t, $J = 7.4$ Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 149.6, 148.4, 141.2, 140.2, 130.3, 128.9, 128.8, 128.2, 114.6, 40.0, 29.5, 12.6.

Methyl(2-(pent-1-en-2-yl)phenyl)carbamic chloride (1d).

Prepared following general procedure A. The crude product was purified by silica gel column chromatography (4% EtOAc in petroleum ether) to provide the title compound as a pale yellow oil in 44% yield.
The product was isolated as a mixture of two rotamers. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR data listed are for the major rotamer.

$^1\text{H}$ NMR (400 MHz, Chloroform-$d$) $\delta$ 7.46 – 7.10 (m, 4H), 5.24 (s, 1H), 5.05 (s, 1H), 3.26 (s, 3H), 2.44 – 2.25 (m, 2H), 1.53 – 1.36 (m, 2H), 0.93 (t, $J = 7.3$ Hz, 3H).

$^{13}\text{C}$ NMR (101 MHz, Chloroform-$d$) $\delta$ 149.6, 147.2, 141.0, 140.2, 130.5, 128.9, 128.8, 128.2, 115.8, 39.9, 38.7, 21.3, 13.7.

(2-(1-Cyclohexylvinyl)phenyl)(methyl)carbamic chloride (1e).

Prepared following general procedure A. The crude product was purified by silica gel column chromatography (4% EtOAc in petroleum ether) to provide the title compound as a colorless oil in 51% yield. The product was isolated as a mixture of two rotamers. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR data listed are for the major rotamer.

$^1\text{H}$ NMR (400 MHz, Chloroform-$d$) $\delta$ 7.42 – 7.13 (m, 4H), 5.21 (t, $J = 1.4$ Hz, 1H), 5.04 (s, 1H), 3.24 (s, 3H), 2.27 – 2.09 (m, 1H), 1.93 – 1.65 (m, 5H), 1.37 – 1.13 (m, 4H), 1.12 – 0.97 (m, 1H).

$^{13}\text{C}$ NMR (101 MHz, Chloroform-$d$) $\delta$ 153.1, 149.7, 141.6, 140.2, 130.9, 129.0, 128.6, 128.1, 113.6, 43.0, 39.9, 33.5, 31.9, 26.7, 26.6, 26.2.

Methyl(5-methyl-2-(3-methylbut-1-en-2-yl)phenyl)carbamic chloride (1g).

Prepared following general procedure A. The crude product was purified by silica gel column chromatography (4% EtOAc in petroleum ether) to provide the title compound as a pale yellow oil in 41% yield. The product was isolated as a mixture of two rotamers. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR data listed are for the major rotamer.

$^1\text{H}$ NMR (400 MHz, Chloroform-$d$) $\delta$ 7.20 – 6.93 (m, 3H), 5.22 (d, $J = 1.4$ Hz, 1H), 5.02 (d, $J = 1.0$ Hz, 1H), 3.23 (s, 3H), 2.67 – 2.48 (m, 1H), 2.37 (s, 3H), 1.16 (d, $J = 6.7$ Hz, 3H), 1.00 (d, $J = 6.9$ Hz, 3H).

$^{13}\text{C}$ NMR (101 MHz, Chloroform-$d$) $\delta$ 153.7, 149.7, 140.0, 138.4, 138.2, 130.6,
(5-Methoxy-2-(3-methylbut-1-en-2-yl)phenyl)(methyl)carbamic chloride (1h).

Prepared following general procedure A. The crude product was purified by silica gel column chromatography (8% EtOAc in petroleum ether) to provide the title compound as a yellow solid in 69% yield. The product was isolated as a mixture of two rotamers. $^1$H NMR and $^{13}$C NMR data listed are for the major rotamer.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.15 (d, $J = 8.5$ Hz, 1H), 6.90 (dd, $J = 8.6, 2.7$ Hz, 1H), 6.72 (d, $J = 2.6$ Hz, 1H), 5.21 (t, $J = 1.4$ Hz, 1H), 5.01 (t, $J = 1.0$ Hz, 1H), 3.83 (s, 3H), 3.23 (s, 3H), 2.62 – 2.46 (m, 1H), 1.16 (d, $J = 6.7$ Hz, 3H), 1.00 (d, $J = 6.9$ Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 159.1, 153.3, 149.6, 140.9, 133.7, 131.5, 114.4, 114.3, 113.2, 55.5, 39.8, 33.1, 22.6, 21.4.

(5-(Benzyl oxy)-2-(3-methylbut-1-en-2-yl)phenyl)(methyl)carbamic chloride (1i).

Prepared following general procedure A. The crude product was purified by silica gel column chromatography (8% EtOAc in petroleum ether) to provide the title compound as a pale yellow oil in 81% yield. The product was isolated as a mixture of two rotamers. $^1$H NMR and $^{13}$C NMR data listed are for the major rotamer.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.56 – 7.28 (m, 5H), 7.14 (d, $J = 8.5$ Hz, 1H), 6.97 (dd, $J = 8.6, 2.6$ Hz, 1H), 6.82 (dd, $J = 18.6, 2.6$ Hz, 1H), 5.21 (t, $J = 1.4$ Hz, 1H), 5.13 – 4.95 (m, 3H), 3.22 (s, 3H), 2.64 – 2.40 (m, 1H), 1.15 (d, $J = 6.7$ Hz, 3H), 1.00 (d, $J = 6.9$ Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 158.3, 153.3, 149.6, 140.9, 136.4, 134.0, 131.6, 128.7 (2C), 128.2, 127.6 (2C), 115.29, 115.28, 113.2, 70.4, 39.8, 33.2, 22.7, 21.5.
(5-Chloro-2-(3-methylbut-1-en-2-yl)phenyl)(methyl)carbamic chloride (1j).

Prepared following general procedure A. The crude product was purified by silica gel column chromatography (4% EtOAc in petroleum ether) to provide the title compound as a yellow solid in 72% yield. The product was isolated as a mixture of two rotamers. 

$^1$H NMR and $^{13}$C NMR data listed are for the major rotamer.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.40 – 7.05 (m, 3H), 5.27 (t, $J = 1.2$ Hz, 1H), 5.04 (s, 1H), 3.23 (s, 3H), 2.64 – 2.47 (m, 1H), 1.16 (d, $J = 6.7$ Hz, 3H), 1.01 (d, $J = 6.9$ Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 152.8, 149.3, 141.0, 140.1, 133.2, 131.9, 129.2, 129.0, 114.1, 39.8, 33.0, 22.5, 21.4.

Methyl(2-(3-methylbut-1-en-2-yl)-5-(trifluoromethyl)phenyl)carbamic chloride (1k).

Prepared following general procedure A. The crude product was purified by silica gel column chromatography (3% EtOAc in petroleum ether) to provide the title compound as a yellow oil in 51% yield. The product was isolated as a mixture of two rotamers. 

$^1$H NMR and $^{13}$C NMR data listed are for the major rotamer.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.70 – 7.32 (m, 3H), 5.33 (dd, $J = 1.6$, 0.8 Hz, 1H), 5.09 (s, 1H), 3.27 (s, 3H), 2.70 – 2.52 (m, 1H), 1.19 (d, $J = 6.7$ Hz, 3H), 1.02 (d, $J = 6.9$ Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 152.8, 149.2, 145.4, 140.5, 131.6, 130.7 (q, $J = 33.3$ Hz), 126.4 (q, $J = 3.8$ Hz), 125.5 (q, $J = 3.6$ Hz), 123.4 (q, $J = 272.4$ Hz), 114.6, 39.8, 32.8, 22.5, 21.3.

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ –62.55 (s, 3F).
(4-Chloro-2-(3-methylbut-1-en-2-yl)phenyl)(methyl)carbamic chloride (1l).

Prepared following general procedure A. The crude product was purified by silica gel column chromatography (4% EtOAc in petroleum ether) to provide the title compound as a yellow oil in 67% yield. The product was isolated as a mixture of two rotamers. 

$^1$H NMR and $^{13}$C NMR data listed are for the major rotamer.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.31 (dd, $J = 8.4$, 2.5 Hz, 1H), 7.23 (d, $J = 2.4$ Hz, 1H), 7.13 (d, $J = 8.4$ Hz, 1H), 5.28 (dd, $J = 1.6$, 0.9 Hz, 1H), 5.07 (d, $J = 0.9$ Hz, 1H), 3.22 (s, 3H), 2.67 – 2.47 (m, 1H), 1.17 (d, $J = 6.7$ Hz, 3H), 1.02 (d, $J = 6.9$ Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 152.8, 149.5, 143.2, 138.7, 134.4, 130.7, 130.4, 128.3, 114.3, 39.9, 32.8, 22.6, 21.3.

Methyl(2-(prop-1-en-2-yl)-5-(trifluoromethyl)phenyl)carbamic chloride (1m).

Prepared following general procedure A. The crude product was purified by silica gel column chromatography (4% EtOAc in petroleum ether) to provide the title compound as a yellow solid in 83% yield. The product was isolated as a mixture of two rotamers. 

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.66 – 7.56 (m, 1H), 7.53 – 7.48 (m, 1H), 7.45 (d, $J = 8.2$ Hz, 1H), 5.34 (t, $J = 1.5$ Hz, 1H), 5.10 (s, 1H), 3.29 (s, 3H), 2.12 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 149.1, 145.2, 141.3, 140.5, 130.8 (q, $J = 33.2$ Hz), 130.6, 126.2 (q, $J = 3.6$ Hz), 125.7 (q, $J = 3.5$ Hz), 123.3 (q, $J = 272.3$ Hz), 118.2, 39.9, 23.1.

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ –62.59 (s, 3F).

(3-Methoxy-2-(prop-1-en-2-yl)phenyl)(methyl)carbamic chloride (1n).

Prepared following general procedure A. The crude product was
purified by silica gel column chromatography (5% EtOAc in petroleum ether) to provide the title compound as a yellow solid in 55% yield. The product was isolated as a mixture of two rotamers. $^1$H NMR and $^{13}$C NMR data listed are for the major rotamer.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.29 (t, $J = 8.1$ Hz, 1H), 7.00 – 6.76 (m, 2H), 5.45 – 5.26 (m, 1H), 5.00 (s, 1H), 3.86 (s, 3H), 3.24 (s, 3H), 2.07 (s, 3H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 157.6, 149.5, 141.4, 139.2, 131.0, 128.6, 120.7, 116.7, 111.0, 56.0, 40.4, 23.1.

**Benzyl(2-(3-methylbut-1-en-2-yl)phenyl)carbamic chloride (1o).**

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.37 – 7.05 (m, 8H), 6.68 (d, $J = 8.9$ Hz, 1H), 5.43 – 5.24 (m, 2H), 5.12 (s, 1H), 4.15 (d, $J = 14.3$ Hz, 1H), 2.79 – 2.65 (m, 1H), 1.25 (d, $J = 6.7$ Hz, 3H), 1.03 (d, $J = 6.9$ Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 154.4, 150.2, 141.4, 137.9, 135.5, 131.2, 130.9, 129.3 (2C), 128.7, 128.5 (2C), 128.1, 127.5, 113.6, 55.3, 32.9, 23.0, 21.3.

**(4-Methoxybenzyl)(2-(3-methylbut-1-en-2-yl)phenyl)carbamic chloride (1p).**

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.31 (td, $J = 7.5$, 1.1 Hz, 1H), 7.24 (dd, $J =
7.7, 1.7 Hz, 1H), 7.13 (td, \( J = 7.7, 1.7 \) Hz, 1H), 7.06 (d, \( J = 8.6 \) Hz, 2H), 6.78 (d, \( J = 8.7 \) Hz, 2H), 6.65 (dd, \( J = 7.9, 1.3 \) Hz, 1H), 5.31 (s, 1H), 5.29 (d, \( J = 14.2 \) Hz, 1H), 5.11 (s, 1H), 4.08 (d, \( J = 14.2 \) Hz, 1H), 3.78 (s, 3H), 2.78 – 2.65 (m, 1H), 1.24 (d, \( J = 6.7 \) Hz, 3H), 1.02 (d, \( J = 6.9 \) Hz, 3H).

\(^{13}\text{C NMR (101 MHz, Chloroform-}d\text{)} \delta 159.4, 154.4, 150.0, 141.4, 137.9, 131.3, 130.8, 130.7 (2C), 128.6, 127.7, 127.5, 113.8 (2C), 113.6, 55.2, 54.8, 32.9, 23.0, 21.3.

Methyl(5-methyl-2-(prop-1-en-2-yl)phenyl)carbamic chloride (1r).

Prepared following general procedure A. The crude product was purified by silica gel column chromatography (4% EtOAc in petroleum ether) to provide the title compound as a yellow oil in 48% yield. The product was isolated as a mixture of two rotamers. \(^1\text{H NMR and}^{13}\text{C NMR data listed are for the major rotamer.}

\(^{1}\text{H NMR (400 MHz, Chloroform-}d\text{)} \delta 7.22 – 7.10 (m, 2H), 7.02 – 6.99 (m, 1H), 5.25 – 5.21 (m, 1H), 5.04 – 4.99 (m, 1H), 3.25 (s, 3H), 2.37 (s, 3H), 2.08 (s, 3H).

\(^{13}\text{C NMR (101 MHz, Chloroform-}d\text{)} \delta 149.6, 142.2, 139.9, 138.4, 138.3, 129.6, 129.5, 129.2, 116.5, 40.0, 23.5, 20.9.

(5-Methoxy-2-(prop-1-en-2-yl)phenyl)(methyl)carbamic chloride (1s).

Prepared following general procedure A. The crude product was purified by silica gel column chromatography (8% EtOAc in petroleum ether) to provide the title compound as a yellow solid in 79% yield. The product was isolated as a mixture of two rotamers. \(^1\text{H NMR and}^{13}\text{C NMR data listed are for the major rotamer.}

\(^{1}\text{H NMR (400 MHz, Chloroform-}d\text{)} \delta 7.23 (d, \( J = 8.5 \) Hz, 1H), 6.91 (dd, \( J = 8.6, 2.6 \) Hz, 1H), 6.72 (d, \( J = 2.6 \) Hz, 1H), 5.21 (t, \( J = 1.6 \) Hz, 1H), 5.00 (dd, \( J = 1.9, 1.0 \) Hz, 1H), 3.83 (s, 3H), 3.26 (s, 3H), 2.07 (s, 3H).

\(^{13}\text{C NMR (101 MHz, Chloroform-}d\text{)} \delta 159.2, 149.5, 141.8, 140.8, 133.6, 130.5, 116.4, 114.5, 114.1, 55.6, 39.8, 23.6.
(4-Chloro-2-(prop-1-en-2-yl)phenyl)(methyl)carbamic chloride (1t).

Prepared following general procedure A. The crude product was purified by silica gel column chromatography (4% EtOAc in petroleum ether) to provide the title compound as a yellow oil in 67% yield. The product was isolated as a mixture of two rotamers. 

$^1$H NMR and $^{13}$C NMR data listed are for the major rotamer.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.33 – 7.25 (m, 2H), 7.19 – 7.11 (m, 1H), 5.31 – 5.28 (m, 1H), 5.09 – 5.04 (m, 1H), 3.24 (s, 3H), 2.09 (s, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 149.3, 143.0, 141.3, 138.7, 134.6, 130.2, 129.8, 128.5, 117.8, 39.9, 23.1.

Benzy1(2-(prop-1-en-2-yl)phenyl)carbamic chloride (1u).

Prepared following general procedure B. The crude product was purified by silica gel column chromatography (4% EtOAc in petroleum ether) to provide the title compound as a yellow oil in 52% yield. The product was isolated as a mixture of two rotamers. $^1$H NMR and $^{13}$C NMR data listed are for the major rotamer.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.36 – 7.24 (m, 5H), 7.23 – 7.07 (m, 3H), 6.71 (d, $J = 7.9$ Hz, 1H), 5.39 (d, $J = 14.3$ Hz, 1H), 5.34 – 5.25 (m, 1H), 5.14 (s, 1H), 4.10 (d, $J = 14.3$ Hz, 1H), 2.16 (s, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 150.2, 142.6, 141.1, 138.1, 135.4, 130.9, 129.8, 129.3 (2C), 128.9, 128.6 (2C), 128.2, 127.7, 117.2, 55.6, 23.4.
Alkyl halides 2f, 2g, 2h, 2i, 2j, 2l, 2m, 2n, 2ab, 2ad-ah are known compounds in the literature.

**Supplementary Figure 3. General procedure for the preparation of alkyl iodides.**

![General procedure for the preparation of alkyl iodides.](image)

The alkyl bromides (5 mmol, 1 equiv) and acetone (25 mL) were added to a 100 mL flask equipped with a magnetic stir bar, successively. After addition of NaI (1.80 g, 12 mmol, 2.4 equiv), the colorless solution turned yellow and a colorless precipitate was formed. The reaction mixture was then refluxed for 12 h. After cooling to room temperature, the mixture was filtered over a silica plug eluting with EtOAc. The solvent was concentrated under reduced pressure and the residue was purified through column chromatography on silica gel (ethyl acetate/petroleum ether) to give the corresponding iodides.

(2-(3-Iodoproxy)phenyl)methanol (2k).

![Image of (2-(3-Iodoproxy)phenyl)methanol](image)

The title compound was isolated as a colorless oil in 78% yield (1.14 g) through column chromatography on silica gel (40% EtOAc in petroleum ether).

\(^1\text{H NMR (400 MHz, Chloroform-}d\text{)} \delta 7.34 – 7.26 (m, 2H), 6.97 (t d, J = 7.5, 1.1 Hz, 1H), 6.91 (d d, J = 8.2, 1.0 Hz, 1H), 4.70 (s, 2H), 4.12 (t, J = 5.8 Hz, 2H), 3.37 (t, J = 6.7 Hz, 2H), 2.37 – 2.26 (m, 2H), 2.13 (s, 1H).

\(^1\text{C NMR (101 MHz, Chloroform-}d\text{)} 156.3, 129.2, 129.0, 128.8, 121.0, 111.2, 67.3, 61.8, 32.7, 2.2.

**Phenyl 6-iodohexanoate (2o).**

![Image of Phenyl 6-iodohexanoate](image)

The title compound was isolated as a colorless oil in 68% yield (1.08 g) through column chromatography on silica gel (10% EtOAc in petroleum ether).
$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.38 (t, $J = 7.9$ Hz, 2H), 7.23 (t, $J = 7.4$ Hz, 1H), 7.08 (d, $J = 7.7$ Hz, 2H), 3.22 (t, $J = 6.9$ Hz, 2H), 2.58 (t, $J = 7.4$ Hz, 2H), 1.89 (p, $J = 7.1$ Hz, 2H), 1.78 (p, $J = 7.5$ Hz, 2H), 1.59 – 1.48 (m, 2H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 172.0, 150.7, 129.5 (2C), 125.8, 121.6 (2C), 34.2, 33.1, 29.9, 23.9, 6.6.

3-Chlorophenyl 6-iodohexanoate (2p).

The title compound was isolated as a colorless oil in 65% yield (1.15 g) through column chromatography on silica gel (10% EtOAc in petroleum ether).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 7.31 (t, $J = 8.1$ Hz, 1H), 7.22 (ddd, $J = 8.1$, 2.0, 1.1 Hz, 1H), 7.13 (t, $J = 2.1$ Hz, 1H), 7.00 (ddd, $J = 8.1$, 2.2, 1.0 Hz, 1H), 3.22 (t, $J = 6.9$ Hz, 2H), 2.58 (t, $J = 7.4$ Hz, 2H), 1.95 – 1.83 (m, 2H), 1.83 – 1.72 (m, 2H), 1.61 – 1.49 (m, 2H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 171.5, 151.1, 134.7, 130.2, 126.1, 122.3, 120.0, 34.0, 33.0, 29.9, 23.9, 6.5.

3-(Dimethylamino)phenyl 6-iodohexanoate (2q).

The title compound was isolated as a colorless oil in 88% yield (1.59 g) through column chromatography on silica gel (10% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.23 (t, $J = 8.2$ Hz, 1H), 6.60 (ddd, $J = 8.4$, 2.5, 0.8 Hz, 1H), 6.47 – 6.37 (m, 2H), 3.24 (t, $J = 6.9$ Hz, 2H), 2.97 (s, 6H), 2.59 (t, $J = 7.5$ Hz, 2H), 1.97 – 1.87 (m, 2H), 1.85 – 1.74 (m, 2H), 1.62 – 1.54 (m, 2H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 172.1, 151.8, 151.7, 129.6, 109.9, 109.2, 105.4, 40.5 (2C), 34.2, 33.1, 30.0, 23.9, 6.6.
4-(Methylthio)phenyl 6-iodohexanoate (2r).

![Chemical Structure]

The title compound was isolated as a colorless oil in 84% yield (1.53 g) through column chromatography on silica gel (10% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-d) δ 7.30 – 7.24 (m, 2H), 7.05 – 6.98 (m, 2H), 3.21 (t, $J = 6.9$ Hz, 2H), 2.57 (t, $J = 7.4$ Hz, 2H), 2.47 (s, 3H), 1.94 – 1.83 (m, 2H), 1.82 – 1.72 (m, 2H), 1.60 – 1.47 (m, 2H).

$^{13}$C NMR (101 MHz, Chloroform-d) δ 171.9, 148.4, 135.6, 128.0 (2C), 122.0 (2C), 34.1, 33.1, 29.9, 23.8, 16.5, 6.6.

4-Hydroxyphenyl 6-iodohexanoate (2s).

![Chemical Structure]

The title compound was isolated as a colorless oil in 57% yield (0.95 g) through column chromatography on silica gel (30% EtOAc in petroleum ether).

$^1$H NMR (500 MHz, Chloroform-d) δ 6.97 – 6.86 (m, 2H), 6.80 – 6.68 (m, 2H), 5.21 (s, 1H), 3.21 (t, $J = 6.9$ Hz, 2H), 2.56 (t, $J = 7.4$ Hz, 2H), 1.95 – 1.84 (m, 2H), 1.83 – 1.72 (m, 2H), 1.59 – 1.47 (m, 2H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 172.8, 153.4, 144.0, 122.4 (2C), 116.0 (2C), 34.1, 33.0, 29.9, 23.8, 6.5.

4-((tert-Butyldimethylsilyl)oxy)phenyl 6-iodohexanoate (2t).

![Chemical Structure]

The title compound was isolated as a colorless oil in 72% yield (1.61 g) through column chromatography on silica gel (10% EtOAc in petroleum ether).

$^1$H NMR (500 MHz, Chloroform-d) δ 6.82 – 6.72 (m, 2H), 6.70 – 6.61 (m, 2H), 3.06 (t, $J = 6.9$ Hz, 2H), 2.40 (t, $J = 7.4$ Hz, 2H), 1.78 – 1.68 (m, 2H), 1.66 – 1.56 (m, 2H), 1.44 – 1.33 (m, 2H), 0.82 (s, 9H), 0.03 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 172.2, 153.2, 144.6, 122.2 (2C), 120.5 (2C),
The title compound was isolated as a colorless oil in 82% yield (1.65 g) through column chromatography on silica gel (10% EtOAc in petroleum ether).

**1H NMR (500 MHz, Chloroform-d)** \( \delta 7.23 \) (d, \( J = 8.5 \) Hz, 2H), \( 7.15 - 7.08 \) (m, 2H), 3.22 (t, \( J = 6.9 \) Hz, 2H), 2.59 (t, \( J = 7.4 \) Hz, 2H), 1.94 – 1.84 (m, 2H), 1.83 – 1.74 (m, 2H), 1.59 – 1.48 (m, 2H).

**13C NMR (126 MHz, Chloroform-d)** \( \delta 171.7, 148.9, 146.5, 122.9 \) (2C), 122.1 (2C), 120.4 (q, \( J = 256.8 \) Hz), 34.0, 33.0, 29.9, 23.8, 6.5.

**19F NMR (376 MHz, Chloroform-d)** \( \delta -58.13 \) (s, 3F).

The title compound was isolated as a colorless oil in 68% yield (1.31 g) through column chromatography on silica gel (10% EtOAc in petroleum ether).

**1H NMR (500 MHz, Chloroform-d)** \( \delta 7.69 - 7.60 \) (m, 2H), \( 7.25 - 7.18 \) (m, 2H), 3.22 (t, \( J = 6.9 \) Hz, 2H), 2.61 (t, \( J = 7.4 \) Hz, 2H), 1.95 – 1.84 (m, 2H), 1.84 – 1.73 (m, 2H), 1.60 – 1.49 (m, 2H).

**13C NMR (101 MHz, Chloroform-d)** \( \delta 171.4, 153.1, 128.1 \) (q, \( J = 32.9 \) Hz), 126.8 (q, \( J = 3.7 \) Hz, 2C), 123.9 (q, \( J = 271.9 \) Hz), 122.1 (2C), 34.1, 33.0, 29.9, 23.7, 6.5.

**19F NMR (376 MHz, Chloroform-d)** \( \delta -62.22 \) (s, 3F).
4-(tert-Butyl)phenyl 6-iodohexanoate (2w).

The title compound was isolated as a colorless oil in 78% yield (1.46 g) through column chromatography on silica gel (10% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.42 – 7.34 (m, 2H), 7.04 – 6.97 (m, 2H), 3.22 (t, $J$ = 7.0 Hz, 2H), 2.57 (t, $J$ = 7.4 Hz, 2H), 1.93 – 1.83 (m, 2H), 1.82 – 1.71 (m, 2H), 1.60 – 1.49 (m, 2H), 1.31 (s, 9H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 172.1, 148.6, 148.3, 126.3 (2C), 120.8 (2C), 34.5, 34.2, 33.1, 31.4 (3C), 29.9, 23.9, 6.6.

(E)-Hex-2-en-1-yl 6-iodohexanoate (2x).

The title compound was isolated as a colorless oil in 64% yield (1.04 g) through column chromatography on silica gel (10% EtOAc in petroleum ether).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 5.77 (dtt, $J$ = 14.9, 6.7, 1.3 Hz, 1H), 5.56 (dtt, $J$ = 15.6, 6.6, 1.5 Hz, 1H), 4.52 (dd, $J$ = 6.6, 0.7 Hz, 2H), 3.19 (t, $J$ = 7.0 Hz, 2H), 2.33 (t, $J$ = 7.5 Hz, 2H), 2.07 – 1.98 (m, 2H), 1.88 – 1.79 (m, 2H), 1.70 – 1.61 (m, 2H), 1.49 – 1.37 (m, 4H), 0.90 (t, $J$ = 7.4 Hz, 3H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 173.3, 136.5, 123.9, 65.3, 34.3, 34.1, 33.1, 30.0, 23.9, 22.1, 13.7, 6.6.
Supplementary Figure 4. Procedure for the preparation of ligand L12.

Step 1: The chiral ligand was prepared according to the known procedure with slight modification. To a dry 250 mL round bottom flask containing a stir bar was added 4-chloropicolinic acid (3.94 g, 25 mmol, 1 equiv). Under a N₂ atmosphere, CH₂Cl₂ (100 mL) was added via syringe, followed by N-methylmorpholine (2.91 g, 28.75 mmol, 1.15 equiv). The reaction mixture was cooled to 0 °C, before iso-butyl chloroformate (4.10 g, 30 mmol, 1.2 equiv) was added. The mixture was stirred for 20 min, and then (S)-tert-Leucinol (3.52 g, 30 mmol, 1.2 equiv) was added. The mixture was allowed to warm to r.t. and stirred overnight. Subsequently, the mixture was quenched with H₂O. The aqueous layer was extracted twice with CH₂Cl₂ and the combined organic phases were dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (50% EtOAc in petroleum ether) to provide S1 as a colorless oil in 63% yield (4.04 g).

Step 2: To a 100 mL screw-cap vial equipped with a magnetic stir bar was added S1 (3.85 g, 15 mmol, 1 equiv) and morpholine (15 mL), successively. The reaction mixture was stirred at 90 °C for 12 h. After cooling to room temperature, the reaction was diluted with EtOAc and washed twice with H₂O. The organic phase was then dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (60% EtOAc in petroleum ether) to give S2 as a colorless oil in 82% yield (3.78 g).

Step 3: To a dry 250 mL round-bottom flask containing a stir bar was added S2 (3.69 g, 12 mmol, 1 equiv). Under a N₂ atmosphere, CH₂Cl₂ (120 mL) was added via
syringe. The reaction mixture was cooled to –5 °C, and diethylaminosulfur trifluoride (2.71 g, 16.8 mmol, 1.4 equiv) was added. The reaction mixture was stirred for 2 h at this temperature, before K₂CO₃ (3.32 g, 24 mmol, 2.0 equiv) was added. The mixture was allowed to warm to r.t. and stirred for 3 h. Next, the reaction was quenched with H₂O carefully. The organic layer was washed with saturated aq. NaHCO₃ and brine, dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (70% EtOAc in petroleum ether + 1% NEt₃) to provide L12 as a colorless syrup in 69% yield (2.40 g).

$^1$H NMR (400 MHz, Chloroform-d) δ 8.37 (d, $J = 5.9$ Hz, 1H), 7.50 (d, $J = 2.7$ Hz, 1H), 6.72 (dd, $J = 5.9, 2.7$ Hz, 1H), 4.42 (dd, $J = 10.3, 8.7$ Hz, 1H), 4.29 (t, $J = 8.5$ Hz, 1H), 4.09 (dd, $J = 10.3, 8.3$ Hz, 1H), 3.92 – 3.79 (m, 4H), 3.45 – 3.31 (m, 4H), 0.97 (s, 9H).

$^{13}$C NMR (101 MHz, Chloroform-d) δ 163.1, 155.5, 150.3, 147.6, 109.4, 108.2, 76.4, 69.2, 66.4 (2C), 46.1 (2C), 34.0, 26.0 (3C).

HRMS (ESI) calcd for C₁₆H₂₄N₃O₂⁺ [(M+H)⁺] 290.1863, found 290.1859.
Supplementary Table 1. Optimization of reaction conditions for racemic variant of Ni-catalyzed carbo-acylation

| entry | precatalyst | ligand | solvent       | reductant | yield (%) |
|-------|-------------|--------|---------------|-----------|-----------|
| 1     | NiBr₂·glyme | L1     | DMA/NMM= 4:1  | Mn        | 90 (88%)  |
| 2     | NiBr₂·glyme | L13    | DMA/NMM= 4:1  | Mn        | trace     |
| 3     | NiBr₂·glyme | L14    | DMA/NMM= 4:1  | Mn        | 0         |
| 4     | NiBr₂·glyme | L15    | DMA/NMM= 4:1  | Mn        | 42        |
| 5     | NiBr₂       | L1     | DMA/NMM= 4:1  | Mn        | 0         |
| 6     | Ni(COD)₂    | L1     | DMA/NMM= 4:1  | Mn        | 77        |
| 7     | Ni(acac)₂   | L1     | DMA/NMM= 4:1  | Mn        | 0         |
| 8     | NiBr₂·glyme | L1     | DMA           | Mn        | 65        |
| 9     | NiBr₂·glyme | L1     | NMM           | Mn        | 0         |
| 10    | NiBr₂·glyme | L1     | THF           | Mn        | trace     |
| 11    | NiBr₂·glyme | L1     | DMF           | Mn        | 0         |
| 12    | NiBr₂·glyme | L1     | DMSO          | Mn        | 0         |
| 13    | NiBr₂·glyme | L1     | acetone       | Mn        | 0         |
| 14    | NiBr₂·glyme | -      | DMA/NMM= 4:1  | Mn        | trace     |
| 15    | NiBr₂·glyme | L1     | DMA/NMM= 4:1  | Mn        | 70        |
| 16    | NiBr₂·glyme | L1     | DMA/NMM= 4:1  | Mn        | 0         |
Supplementary Figure 5. General procedure for racemic variant of the Ni-catalyzed carbo-acylation

\[
\begin{align*}
&\text{Racemic 4-(\text{tert-Butyl})-2-(pyridin-2-yl)-4,5-dihydrooxazole (L1) (8.2 mg, 0.04 mmol, 20 mol%),} \\
&\text{carbamoyl chlorides 1 (if solid, 0.2 mmol, 1.0 equiv) and alkyl iodides 2}_a^b (if solid, 0.4 mmol, 2.0 equiv) \text{ were added to a reaction tube equipped with a stir bar.} \\
&\text{In a nitrogen-filled glovebox, NiBr}_2\text{-glyme (12.3 mg, 0.04 mmol, 20 mol%) and} \\
&\text{manganese dust (22 mg, 0.4 mmol, 2 equiv) were added to the mixture. The reaction} \\
&\text{tube was sealed and removed from the glovebox. Next, anhydrous DMA (1.2 mL) and} \\
&\text{N-methyl morpholine (0.3 mL) were added, followed by the addition of} \\
&\text{carbamoyl chlorides 1 (if liquid, 0.2 mmol, 1 equiv) and alkyl iodies 2}_a (if liquid, 0.4 mmol, 2.0 equiv) \text{ under the protection of nitrogen.} \\
&\text{Then the resulting mixture was stirred at the temperature specified below}^b \text{ for 24-96 h}^c. \\
&\text{The reaction was quenched with sat. aq. NH}_4\text{Cl solution (5 mL) and diluted with water (10 mL). The aqueous layer was extracted three times with EtOAc, and the combined organic layers were washed with brine (20 mL), dried over MgSO}_4, \text{ filtered, and concentrated under reduced pressure.} \\
&\text{The residue was purified through column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the desired product 3.} \\

[a] \text{Benzyl chlorides were used for 3aac-3aah.} \\

[b] 25 \degree C \text{ for 3ak, 3ap, 3aq, 3as, 3av-ax and 3aac-aah, 0 \degree C \text{ for 3aa-pa, 3ab-aj, 3al-ao, 3ar, 3at,} 3au \text{ and 3ay-aab.} } \\

[c] \text{Reaction time: 24 h for 3aa-ea, 3ga, 3ja, 3la, 3ab-ah, 3am, 3ay-aaa, 48 h for 3ha, 3ia, 3ka,} 3ma, 3na, 3ai-al, 3an-ax \text{ and 3aab-aah, 96 h for 3fa, 3oa and 3pa.}
3-Hexyl-3-isopropyl-1-methylindolin-2-one (3aa).

The title compound was isolated as a pale yellow oil in 88% yield (48.0 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether). For 1-mmol-scale reaction, the product was obtained in 85% yield (232.2 mg) starting the carbamoyl chloride 1a (237.7 mg).

\[ \text{\(^1\)H NMR (400 MHz, Chloroform-\text{d}) \delta 7.31 – 7.23 (m, 1H), 7.16 (ddd, } J = 7.4, 1.3, 0.6 \text{ Hz, 1H}, 7.05 (td, } J = 7.5, 1.0 \text{ Hz, 1H), 6.85 – 6.79 (m, 1H), 3.20 (s, 3H), 2.23 – 2.07 (m, 1H), 1.93 – 1.79 (m, 2H), 1.22 – 1.06 (m, 6H), 0.97 (d, } J = 7.0 \text{ Hz, 3H), 0.94 – 0.85 (m, 1H), 0.80 (t, } J = 7.0 \text{ Hz, 3H), 0.73 – 0.62 (m, 1H), 0.67 (d, } J = 6.8 \text{ Hz, 3H).} \]

\[ \text{\(^{13}\)C NMR (101 MHz, Chloroform-\text{d}) \delta 180.3, 144.4, 131.5, 127.5, 123.5, 122.1, 107.5, 56.5, 35.5, 35.3, 31.6, 29.6, 25.8, 24.4, 22.6, 17.4, 17.3, 14.0.} \]

HRMS (ESI) calcd for C\(_{18}\)H\(_{28}\)NO\(^+\) [(M+H\(^+\)] 274.2166, found 274.2166.

3-Hexyl-1,3-dimethylindolin-2-one (3ba).

The title compound was isolated as a pale yellow oil in 53% yield (26.1 mg) starting from the carbamoyl chloride 1b (41.9 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

\[ \text{\(^1\)H NMR (400 MHz, Chloroform-\text{d}) \delta 7.26 (t, } J = 7.7 \text{ Hz, 1H), 7.17 (d, } J = 7.3 \text{ Hz, 1H), 7.06 (t, } J = 7.5 \text{ Hz, 1H), 6.84 (d, } J = 7.7 \text{ Hz, 1H), 3.21 (s, 3H), 1.95 – 1.85 (m, 1H), 1.76 – 1.68 (m, 1H), 1.35 (s, 3H), 1.24 – 1.08 (m, 6H), 1.03 – 0.93 (m, 1H), 0.87 – 0.73 (m, 1H), 0.80 (t, } J = 6.9 \text{ Hz, 3H).} \]

\[ \text{\(^{13}\)C NMR (101 MHz, Chloroform-\text{d}) \delta 180.9, 143.3, 134.3, 127.6, 122.5, 122.4, 107.9, 48.5, 38.6, 31.5, 29.4, 26.1, 24.4, 23.8, 22.6, 14.0.} \]

HRMS (ESI) calcd for C\(_{16}\)H\(_{24}\)NO\(^+\) [(M+H\(^+\)] 246.1852, found 246.1852.

3-Hexyl-3-isopropyl-1-methylindolin-2-one (3ca).

The title compound was isolated as a pale yellow oil in 80% yield
(41.6 mg) starting from the carbamoyl chloride 1c (44.7 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.30 – 7.23 (m, 1H), 7.13 (d, $J = 7.2$ Hz, 1H), 7.07 (t, $J = 7.4$ Hz, 1H), 6.83 (d, $J = 7.8$ Hz, 1H), 3.21 (s, 3H), 1.96 – 1.83 (m, 2H), 1.82 – 1.66 (m, 2H), 1.22 – 1.07 (m, 6H), 1.00 – 0.90 (m, 1H), 0.85 – 0.72 (m, 1H), 0.80 (t, $J = 6.9$ Hz, 3H), 0.55 (t, $J = 7.3$ Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 180.2, 144.2, 132.4, 127.5, 122.6, 122.4, 107.7, 53.8, 37.8, 31.5, 31.0, 29.5, 26.0, 24.2, 22.6, 14.0, 8.6.

HRMS (ESI) calcd for C$_{17}$H$_{26}$NO $[(\text{M}+\text{H})^+]$ 260.2009, found 260.2009.

3-Hexyl-1-methyl-3-propyldolin-2-one (3da).

The title compound was isolated as a pale yellow oil in 74% yield (40.5 mg) starting from the carbamoyl chloride 1d (47.5 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.26 (t, $J = 7.6$ Hz, 1H), 7.14 (d, $J = 7.2$ Hz, 1H), 7.07 (t, $J = 7.4$ Hz, 1H), 6.83 (d, $J = 7.7$ Hz, 1H), 3.20 (s, 3H), 1.91 – 1.81 (m, 2H), 1.77 – 1.66 (m, 2H), 1.23 – 1.08 (m, 6H), 1.03 – 0.91 (m, 2H), 0.87 – 0.74 (m, 2H), 0.80 (t, $J = 6.8$ Hz, 3H), 0.76 (t, $J = 6.4$ Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 180.4, 144.0, 132.8, 127.5, 122.6, 122.3, 107.7, 53.3, 40.4, 38.1, 31.5, 29.5, 26.0, 24.1, 22.6, 17.5, 14.2, 14.0.

HRMS (ESI) calcd for C$_{18}$H$_{28}$NO $[(\text{M}+\text{H})^+]$ 274.2165, found 274.2165.

3-Cyclohexyl-3-hexyl-1-methylindolin-2-one (3ea).

The title compound was isolated as a pale yellow oil in 78% yield (49.0 mg) starting from the carbamoyl chloride 1e (55.4 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).
**1H NMR (400 MHz, Chloroform-d)** δ 7.28 – 7.23 (m, 1H), 7.16 (dd, J = 7.4, 1.2 Hz, 1H), 7.05 (td, J = 7.5, 1.0 Hz, 1H), 6.81 (dd, J = 7.8, 0.9 Hz, 1H), 3.19 (s, 3H), 1.89 – 1.69 (m, 5H), 1.63 – 1.53 (m, 2H), 1.48 – 1.41 (m, 1H), 1.25 – 1.06 (m, 9H), 1.05 – 0.86 (m, 2H), 0.79 (t, J = 7.0 Hz, 3H), 0.77 – 0.62 (m, 2H).

**13C NMR (101 MHz, Chloroform-d)** δ 180.4, 144.3, 132.1, 127.3, 123.5, 122.0, 107.5, 56.6, 45.4, 34.8, 31.5, 29.6, 27.4, 27.2, 26.7, 26.4, 26.3, 25.8, 24.1, 22.6, 14.0.

**HRMS (ESI)** calcd for C_{21}H_{32}N_{2}O + [(M+H)^+] 314.2478, found 314.2479.

3-Hexyl-1-methyl-3-phenylindolin-2-one (3fa).

The title compound was isolated as a pale yellow oil in 61% yield (37.5 mg) starting from the carbamoyl chloride 1f (54.3 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

**1H NMR (400 MHz, Chloroform-d)** δ 7.40 – 7.18 (m, 7H), 7.11 (td, J = 7.5, 1.1 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H), 3.22 (s, 3 H), 2.36 (td, J = 12.7, 4.4 Hz, 1H), 2.18 (td, J = 12.8, 4.2 Hz, 1H), 1.29 – 1.07 (m, 7H), 0.92 – 0.79 (m, 1H), 0.81 (t, J = 6.8 Hz, 3H).

**13C NMR (101 MHz, Chloroform-d)** δ 178.7, 144.0, 140.4, 132.4, 128.5 (2C), 128.1, 127.2, 126.9 (2C), 124.8, 122.6, 108.2, 56.8, 38.0, 31.5, 29.5, 26.4, 24.5, 22.6, 14.1.

**HRMS (ESI)** calcd for C_{21}H_{32}NO + [(M+H)^+] 308.2009, found 308.2008.

3-Hexyl-3-isopropyl-1,6-dimethylindolin-2-one (3ga).

The title compound was isolated as a pale yellow oil in 62% yield (35.6 mg) starting from the carbamoyl chloride 1g (50.3 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

**1H NMR (400 MHz, Chloroform-d)** δ 7.03 (d, J = 7.5 Hz, 1H), 6.85 (dd, J = 7.5, 1.5 Hz, 1H), 6.65 (d, J = 1.4 Hz, 1H), 3.18 (s, 3H), 2.39 (s, 3H), 2.12 (hept, J = 6.9 Hz,
$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.48 – 7.32 (m, 5H), 7.04 (d, $J = 8.1$ Hz, 1H), 6.63 (dd, $J = 8.2$, 2.3 Hz, 1H), 6.51 (d, $J = 2.3$ Hz, 1H), 5.07 (s, 2H), 3.16 (s, 3H), 2.16 – 2.05 (m, 1H), 1.90 – 1.76 (m, 2H), 1.23 – 1.08 (m, 6H), 0.97 (d, $J = 6.9$ Hz, 3H), 0.93 – 0.86 (m, 1H), 0.80 (t, $J = 7.0$ Hz, 3H), 0.76 – 0.68 (m, 1H), 0.66 (d, $J = 6.7$ Hz, 3H).

1ºC NMR (101 MHz, Chloroform-$d$) $\delta$ 180.6, 144.4, 137.4, 128.3, 123.2, 122.6, 108.5, 56.2, 35.5, 35.3, 31.6, 29.6, 25.8, 24.4, 22.6, 21.8, 17.5, 17.3, 14.0.

HRMS (ESI) calcd for C$_{19}$H$_{30}$NO$_2$+ [(M+H)$^+$] 304.2271, found 304.2270.

6-(Benzyloxy)-3-hexyl-3-isopropyl-1-methylindolin-2-one (3ia).

The title compound was isolated as a pale yellow oil in 85% yield (64.4 mg) starting from the carbamoyl chloride 1i (68.8 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.48 – 7.32 (m, 5H), 7.04 (d, $J = 8.1$ Hz, 1H), 6.63 (dd, $J = 8.2$, 2.3 Hz, 1H), 6.51 (d, $J = 2.3$ Hz, 1H), 5.07 (s, 2H), 3.16 (s, 3H), 2.16 – 2.05 (m, 1H), 1.90 – 1.76 (m, 2H), 1.23 – 1.08 (m, 6H), 0.97 (d, $J = 6.9$ Hz, 3H), 0.93 – 0.86 (m, 1H), 0.80 (t, $J = 7.0$ Hz, 3H), 0.76 – 0.68 (m, 1H), 0.66 (d, $J = 6.7$ Hz, 3H).
$^{13}$C NMR (101 MHz, Chloroform-$d$) δ 180.9, 159.0, 145.6, 136.9, 128.6 (2C), 128.1, 127.6 (2C), 124.0, 123.6, 106.6, 96.5, 70.3, 56.0, 35.6, 35.3, 31.6, 29.6, 25.8, 24.4, 22.6, 17.5, 17.3, 14.0.

HRMS (ESI) calcd for C$_{25}$H$_{34}$NO$_2$ $^{[}(\text{M}+\text{H})^{+}]$ 380.2584, found 380.2584.

6-Chloro-3-hexyl-3-isopropyl-1-methylindolin-2-one (3ja).

The title compound was isolated as a pale yellow oil in 65% yield (40.1 mg) starting from the carbamoyl chloride 1j (54.4 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-$d$) δ 7.07 (d, $J = 7.9$ Hz, 1H), 7.02 (dd, $J = 7.9$, 1.8 Hz, 1H), 6.82 (d, $J = 1.8$ Hz, 1H), 3.18 (s, 3H), 2.18 – 2.07 (m, 1H), 1.94 – 1.76 (m, 2H), 1.22 – 1.07 (m, 6H), 0.95 (d, $J = 6.9$ Hz, 3H), 0.92 – 0.85 (m, 1H), 0.80 (t, $J = 7.0$ Hz, 3H), 0.74 – 0.62 (m, 1H), 0.67 (d, $J = 6.7$ Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) δ 180.2, 145.6, 133.3, 129.8, 124.3, 121.9, 108.3, 56.3, 35.4, 35.3, 31.5, 29.5, 25.9, 24.4, 22.6, 17.4, 17.3, 14.0.

HRMS (ESI) calcd for C$_{18}$H$_{27}$ClNO $^{[}(\text{M}+\text{H})^{+}]$ 308.1776, found 308.1776.

3-Hexyl-3-isopropyl-1-methyl-6-(trifluoromethyl)indolin-2-one (3ka).

The title compound was isolated as a pale yellow oil in 77% yield (52.5 mg) starting from the carbamoyl chloride 1k (61.1 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-$d$) δ 7.29 – 7.24 (m, 1H), 7.21 – 7.16 (m, 1H), 6.95 (d, $J = 1.5$ Hz, 1H), 3.16 (s, 3H), 2.14 – 2.05 (m, 1H), 1.89 – 1.74 (m, 2H), 1.14 – 1.00 (m, 6H), 0.89 (d, $J = 6.9$ Hz, 3H), 0.86 – 0.78 (m, 1H), 0.73 (t, $J = 7.0$ Hz, 3H), 0.62 (d, $J = 6.8$ Hz, 3H), 0.60 – 0.51 (m, 1H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) δ 178.8, 143.9, 134.6, 129.0 (q, $J = 32.4$ Hz),
123.1 (q, J = 272.1 Hz), 122.5, 118.1 (q, J = 4.1 Hz), 103.2 (q, J = 3.7 Hz), 55.6, 34.4, 34.3, 30.5, 28.5, 24.9, 23.3, 21.5, 16.3, 16.2, 12.9.

\(^{19}\text{F NMR (471 MHz, Chloroform-}d\text{)} \delta -62.28 \text{ (s, 3F).}

\text{HRMS (ESI) calcd for C}_{19}\text{H}_{26}\text{F}_{3}\text{NONa}^+ [(M+Na)^+] 364.1859, found 364.1860.}

5-Chloro-3-hexyl-3-isopropyl-1-methylindolin-2-one (3la).

The title compound was isolated as a pale yellow oil in 64\% yield (39.5 mg) starting from the carbamoyl chloride \textit{II} (54.4 mg) through column chromatography on silica gel (10\% EtOAc in petroleum ether).

\(^{1}\text{H NMR (400 MHz, Chloroform-}d\text{)} \delta 7.25 \text{ (dd, } J = 8.2, 2.1 \text{ Hz, 1H), 7.14 \text{ (d, } J = 2.1 \text{ Hz, 1H), 6.75 \text{ (d, } J = 8.2 \text{ Hz, 1H), 3.18 \text{ (s, 3H), 2.13 \text{ (hept, } J = 6.9 \text{ Hz, 1H), 1.93 – 1.76 \text{ (m, 2H), 1.22 – 1.09 \text{ (m, 6H), 0.96 \text{ (d, } J = 6.9 \text{ Hz, 3H), 0.93 – 0.86 \text{ (m, 1H), 0.81 \text{ (t, } J = 7.0 \text{ Hz, 3H), 0.75 – 0.64 \text{ (m, 1H), 0.69 \text{ (d, } J = 6.8 \text{ Hz, 3H).}}}

\(^{13}\text{C NMR (101 MHz, Chloroform-}d\text{)} \delta 179.7, 142.9, 133.4, 127.5, 127.4, 123.9, 108.4, 56.8, 35.4, 35.4, 31.5, 29.6, 25.9, 24.4, 22.6, 17.4, 17.2, 14.0.

\text{HRMS (ESI) calcd for C}_{18}\text{H}_{27}\text{ClNO}^+ [(M+H)^+] 308.1776, found 308.1776.}

3-Hexyl-1,3-dimethyl-6-(trifluoromethyl)indolin-2-one (3ma).

The title compound was isolated as a pale yellow oil in 51\% yield (31.7 mg) starting from the carbamoyl chloride \textit{Im} (55.4 mg) through column chromatography on silica gel (10\% EtOAc in petroleum ether).

\(^{1}\text{H NMR (400 MHz, Chloroform-}d\text{)} \delta 7.35 \text{ (d, } J = 7.7 \text{ Hz, 1H), 7.26 \text{ (d, } J = 7.5 \text{ Hz, 1H), 7.04 \text{ (s, 1H), 3.25 \text{ (s, 3H), 1.92 \text{ (td, } J = 12.8, 4.6 \text{ Hz, 1H), 1.74 \text{ (td, } J = 12.9, 4.4 \text{ Hz, 1H), 1.37 \text{ (s, 3H), 1.24 – 1.09 \text{ (m, 6H), 1.02 – 0.91 \text{ (m, 1H), 0.86 – 0.75 \text{ (m, 1H), 0.81 \text{ (t, } J = 6.9 \text{ Hz, 3H).}}}

\(^{13}\text{C NMR (101 MHz, Chloroform-}d\text{)} \delta 180.5, 143.9, 138.2, 130.2 \text{ (q, } J = 32.3 \text{ Hz),}}
124.1 (q, $J = 272.6$ Hz), 122.6, 119.5 (q, $J = 4.1$ Hz), 104.6 (q, $J = 3.9$ Hz), 48.6, 38.4, 31.5, 29.3, 26.3, 24.4, 23.6, 22.5, 14.0.

$^{19}$F NMR (471 MHz, Chloroform-$d$) $\delta$ –62.26 (s, 3F).

HRMS (ESI) calcd for C$_{17}$H$_{23}$F$_{3}$NO$^+$ [(M+H)$^+$] 314.1726, found 314.1732.

3-Hexyl-4-methoxy-1,3-dimethylindolin-2-one (3na).

The title compound was isolated as a pale yellow oil in 91% yield (49.8 mg) starting from the carbamoyl chloride 1n (47.9 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.22 (t, $J = 8.1$ Hz, 1H), 6.62 (d, $J = 8.5$ Hz, 1H), 6.50 (d, $J = 7.8$ Hz, 1H), 3.84 (s, 3H), 3.19 (s, 3H), 2.13 – 2.03 (m, 1H), 1.88 – 1.78 (m, 1H), 1.40 (s, 3H), 1.21 – 1.09 (m, 6H), 0.92 – 0.84 (m, 1H), 0.80 (t, $J = 7.0$ Hz, 3H), 0.77 – 0.67 (m, 1H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 181.3, 156.0, 144.5, 128.7, 119.4, 105.7, 101.3, 55.3, 49.2, 36.1, 31.5, 29.3, 26.3, 24.9, 22.5, 22.0, 14.0.

HRMS (ESI) calcd for C$_{17}$H$_{26}$NO$_2$$^+$ [(M+H)$^+$] 276.1958, found 276.1959.

1-Benzyl-3-hexyl-3-isopropylindolin-2-one (3oa).

The title compound was isolated as a pale yellow oil in 45% yield (31.5 mg) starting from the carbamoyl chloride 1o (62.8 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.35 – 7.22 (m, 5H), 7.20 – 7.11 (m, 2H), 7.01 (t, $J = 7.6$ Hz, 1H), 6.72 (d, $J = 7.7$ Hz, 1H), 4.99 – 4.83 (m, 2H), 2.25 – 2.14 (m, 1H), 1.98 – 1.82 (m, 2H), 1.23 – 1.06 (m, 6H), 1.04 – 0.93 (m, 1H), 0.99 (d, $J = 7.0$ Hz, 3H), 0.81 (t, $J = 6.9$ Hz, 3H), 0.77 – 0.64 (m, 1H), 0.74 (d, $J = 6.7$ Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 180.3, 143.5, 136.3, 131.6, 128.6 (2C),
127.49 (2C), 127.47, 127.38, 123.5, 122.1, 108.6, 56.3, 43.6, 35.9, 35.5, 31.6, 29.6, 24.5, 22.5, 17.6, 17.5, 14.1.

HRMS (ESI) calcd for C24H32NO+ [(M+H)+] 350.2478, found 350.2478.

3-Hexyl-3-isopropyl-1-(4-methoxybenzyl)indolin-2-one (3pa).

The title compound was isolated as a pale yellow oil in 51% yield (38.8 mg) starting from the carbamoyl chloride 1p (68.8 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

\(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.25 (d, \(J = 8.0\) Hz, 2H), 7.18 – 7.12 (m, 2H), 7.00 (t, \(J = 7.5\) Hz, 1H), 6.82 (d, \(J = 8.2\) Hz, 2H), 6.75 (d, \(J = 7.9\) Hz, 1H), 4.91 – 4.79 (m, 2H), 3.77 (s, 3H), 2.24 – 2.13 (m, 1H), 1.97 – 1.81 (m, 2H), 1.22 – 1.06 (m, 6H), 1.02 – 0.92 (m, 1H), 0.98 (d, \(J = 7.0\) Hz, 3H), 0.80 (t, \(J = 7.0\) Hz, 3H), 0.75 – 0.59 (m, 1H), 0.72 (d, \(J = 6.8\) Hz, 3H).

\(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 180.3, 159.0, 143.6, 131.6, 128.9 (2C), 128.5, 127.4, 123.5, 122.0, 114.0 (2C), 108.6, 56.2, 55.2, 43.1, 35.8, 35.5, 31.6, 29.6, 24.5, 22.5, 17.6, 17.4, 14.0.

HRMS (ESI) calcd for C25H34NO2+ [(M+H)+] 380.2584, found 380.2584.

3-Isopropyl-1-methyl-3-propylindolin-2-one (3ab).

The title compound was isolated as a pale yellow oil in 67% yield (31.1 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.26 (td, \(J = 7.7, 1.3\) Hz, 1H), 7.17 (dd, \(J = 7.4, 1.3, 0.5\) Hz, 1H), 7.05 (td, \(J = 7.5, 1.1\) Hz, 1H), 6.82 (dt, \(J = 7.8, 0.7\) Hz, 1H), 3.20 (s, 3H), 2.20 – 2.08 (m, 1H), 1.93 – 1.78 (m, 2H), 1.02 – 0.89 (m, 1H), 0.97 (d, \(J = 6.9\) Hz, 3H), 0.77 (t, \(J = 6.9\) Hz, 3H), 0.75 – 0.64 (m, 1H), 0.68 (d, \(J = 6.8\) Hz, 3H).
**13C NMR (101 MHz, Chloroform-d)**  δ 180.3, 144.3, 131.5, 127.5, 123.5, 122.0, 107.5, 56.5, 37.7, 35.3, 25.8, 17.8, 17.4, 17.3, 14.3.

**HRMS (ESI)** calcd for C_{15}H_{22}NO^+ [(M+H)^+] 232.1696, found 232.1696.

**3-Isopropyl-1-methyl-3-nonylindolin-2-one (3ac).**

![3-Isopropyl-1-methyl-3-nonylindolin-2-one](image)

The title compound was isolated as a pale yellow oil in 75% yield (47.2 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

**1H NMR (400 MHz, Chloroform-d)**  δ 7.26 (td, J = 7.6, 1.3 Hz, 1H), 7.16 (dd, J = 7.4, 1.2 Hz, 1H), 7.04 (td, J = 7.5, 1.0 Hz, 1H), 6.82 (d, J = 7.7 Hz, 1H), 3.20 (s, 3H), 2.14 (hept, J = 6.9 Hz, 1H), 1.93 – 1.79 (m, 2H), 1.28 – 1.06 (m, 12H), 0.99 – 0.87 (m, 1H), 0.97 (d, J = 6.9 Hz, 3H), 0.85 (t, J = 7.0 Hz, 3H), 0.75 – 0.62 (m, 1H), 0.68 (d, J = 6.7 Hz, 3H).

**13C NMR (101 MHz, Chloroform-d)**  δ 180.3, 144.3, 131.5, 127.5, 123.5, 122.1, 107.5, 56.4, 35.5, 35.3, 31.8, 30.0, 29.5, 29.4, 29.2, 25.8, 24.5, 22.7, 17.4, 17.3, 14.1.

**HRMS (ESI)** calcd for C_{21}H_{34}NO^+ [(M+H)^+] 316.2635, found 316.2635.

**3-(4-Chlorobutyl)-3-isopropyl-1-methylindolin-2-one (3ad).**

![3-(4-Chlorobutyl)-3-isopropyl-1-methylindolin-2-one](image)

The title compound was isolated as a pale yellow oil in 68% yield (38.1 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

**1H NMR (400 MHz, Chloroform-d)**  δ 7.28 (td, J = 7.7, 1.3 Hz, 1H), 7.17 (ddd, J = 7.4, 1.4, 0.6 Hz, 1H), 7.06 (td, J = 7.5, 1.0 Hz, 1H), 6.84 (d, J = 7.7 Hz, 1H), 3.44 – 3.32 (m, 2H), 3.21 (s, 3H), 2.15 (hept, J = 6.9 Hz, 1H), 1.97 – 1.82 (m, 2H), 1.73 – 1.55 (m, 2H), 1.09 – 1.00 (m, 1H), 0.97 (d, J = 7.0 Hz, 3H), 0.93 – 0.83 (m, 1H), 0.68 (d, J = 6.7 Hz, 3H).
$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 179.9, 144.3, 130.9, 127.7, 123.5, 122.2, 107.7, 56.2, 44.5, 35.3, 34.6, 32.8, 25.8, 21.9, 17.4, 17.2.

HRMS (ESI) calcd for C$_{16}$H$_{23}$ClNO$^+$ [(M+H)$^+$] 280.1463, found 280.1472.

3-(4-Fluorobutyl)-3-isopropyl-1-methylindolin-2-one (3ae).

The title compound was isolated as a pale yellow oil in 71\% yield (37.3 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (10\% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.28 (td, $J$ = 7.6, 1.3 Hz, 1H), 7.17 (dd, $J$ = 7.5, 1.2 Hz, 1H), 7.06 (td, $J$ = 7.5, 1.0 Hz, 1H), 6.83 (d, $J$ = 7.7 Hz, 1H), 4.41 – 4.17 (m, 2H), 3.20 (s, 3H), 2.15 (hept, $J$ = 7.0 Hz, 1H), 1.98 – 1.85 (m, 2H), 1.70 – 1.47 (m, 2H), 1.09 – 0.93 (m, 1H), 0.97 (d, $J$ = 7.0 Hz, 3H) 0.90 – 0.79 (m, 1H), 0.68 (d, $J$ = 6.8 Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 180.0, 144.3, 131.0, 127.7, 123.5, 122.2, 107.7, 83.8 (d, $J$ = 164.6 Hz), 56.3, 35.4, 35.1, 30.6 (d, $J$ = 19.6 Hz), 25.9, 20.4 (d, $J$ = 5.5 Hz), 17.4, 17.3.

$^{19}$F NMR (471 MHz, Chloroform-$d$) $\delta$ –223.09 (s, 1F).

HRMS (ESI) calcd for C$_{16}$H$_{23}$FNO$^+$ [(M+H)$^+$] 264.1758, found 264.1766.

6-(3-Isopropyl-1-methyl-2-oxoindolin-3-yl)hexanenitrile (3af).

The title compound was isolated as a pale yellow oil in 92\% yield (52.3 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (20\% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.25 – 7.17 (m, 1H), 7.09 (dd, $J$ = 7.4, 1.2 Hz, 1H), 6.99 (td, $J$ = 7.5, 1.0 Hz, 1H), 6.77 (dd, $J$ = 7.8, 0.9 Hz, 1H), 3.13 (s, 3H), 2.14 (t, $J$ = 7.1 Hz, 2H), 2.11 – 2.00 (m, 1H), 1.88 – 1.74 (m, 2H), 1.50 – 1.39 (m, 2H), 1.31 – 1.20 (m, 2H), 0.93 – 0.82 (m, 1H), 0.90 (d, $J$ = 7.0 Hz, 3H), 0.73 – 0.62 (m, 1H), 0.60
(d, J = 6.8 Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) δ 180.0, 144.3, 131.0, 127.7, 123.4, 122.2, 119.6, 107.7, 56.3, 35.4, 34.9, 28.8, 25.8, 25.0, 23.6, 17.4, 17.2, 17.0.

HRMS (ESI) calcd for C$_{18}$H$_{25}$N$_{2}$O$^+$ [(M+H)$^+$] 285.1961, found 285.1966.

3-(3-(1,3-Dioxolan-2-yl)propyl)-3-isopropyl-1-methylindolin-2-one (3ag).

The title compound was isolated as a pale yellow oil in 73% yield (44.4 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (15% EtOAc in petroleum ether).

$^1$H NMR (500 MHz, Chloroform-d) δ 7.26 (td, J = 7.7, 1.3 Hz, 1H), 7.16 (dd, J = 7.5, 1.2 Hz, 1H), 7.04 (td, J = 7.5, 1.0 Hz, 1H), 6.84 – 6.79 (m, 1H), 4.68 (t, J = 4.9 Hz, 1H), 3.93 – 3.82 (m, 2H), 3.80 – 3.71 (m, 2H), 3.19 (s, 3H), 2.20 – 2.10 (m, 1H), 1.98 – 1.87 (m, 2H), 1.63 – 1.53 (m, 1H), 1.53 – 1.44 (m, 1H), 1.12 – 1.01 (m, 1H), 0.96 (d, J = 6.9 Hz, 3H), 0.93 – 0.80 (m, 1H), 0.68 (d, J = 6.7 Hz, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 178.0, 144.3, 131.1, 127.6, 123.5, 122.1, 107.6, 104.4, 64.8, 64.7, 56.3, 35.4 (2C), 34.1, 25.9, 19.3, 17.4, 17.3.

HRMS (ESI) calcd for C$_{18}$H$_{26}$NO$_3$+$^+$ [(M+H)$^+$] 304.1907, found 304.1909.

3-Isopropyl-3-(4-(4-methoxyphenoxy)butyl)-1-methylindolin-2-one (3ah).

The title compound was isolated as a pale yellow oil in 96% yield (71.0 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-d) δ 7.27 (t, J = 7.8 Hz, 1H), 7.16 (d, J = 7.3 Hz, 1H), 7.05 (t, J = 7.5 Hz, 1H), 6.82 (d, J = 7.8 Hz, 1H), 6.81 – 6.69 (m, 4H), 3.82 – 3.68 (m, 2H), 3.74 (s, 3H), 3.20 (s, 3H), 2.20 – 2.10 (m, 1H), 2.00 – 1.86 (m, 2H), 1.73 – 1.54 (m, 2H), 1.15 – 1.03 (m, 1H), 0.97 (d, J = 6.9 Hz, 3H), 0.94 – 0.81 (m, S31)
1H), 0.68 (d, J = 6.7 Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-\textit{d}) $\delta$ 180.1, 153.6, 153.1, 144.3, 131.1, 127.6, 123.5, 122.2, 115.4 (2C), 114.5 (2C), 107.7, 68.2, 56.4, 55.7, 35.4, 35.2, 29.6, 25.9, 21.1, 17.4, 17.3.

HRMS (ESI) calcd for C$_{23}$H$_{29}$NO$_3$Na$^+$ [(M+Na)$^+$] 390.2040, found 390.2045.

3-Isopropyl-1-methyl-3-(4-(4-(methylsulfonyl)phenoxy)butyl)indolin-2-one (3ai). The title compound was isolated as a pale yellow oil in 88% yield (73.3 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (50% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-\textit{d}) $\delta$ 7.81 (dd, J = 8.8, 1.9 Hz, 2H), 7.28 (dd, J = 8.0, 5.8, 1.7 Hz, 1H), 7.17 (d, J = 7.4 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.91 (dd, J = 8.8, 1.9 Hz, 2H), 6.84 (d, J = 7.8 Hz, 1H), 3.88 (t, J = 6.7 Hz, 2H), 3.21 (s, 3H), 3.01 (s, 3H), 2.23 – 2.07 (m, 1H), 2.05 – 1.87 (m, 2H), 1.79 – 1.61 (m, 2H), 1.16 – 1.04 (m, 1H), 0.98 (d, J = 6.9 Hz, 3H), 0.94 – 0.80 (m, 1H), 0.68 (d, J = 6.7 Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-\textit{d}) $\delta$ 180.0, 163.1, 144.3, 131.9, 131.0, 129.5 (2C), 127.7, 123.5, 122.2, 114.9 (2C), 107.7, 68.1, 56.3, 44.9, 35.4, 35.0, 29.2, 25.9, 21.0, 17.4, 17.3.

HRMS (ESI) calcd for C$_{23}$H$_{30}$NO$_4$S$^+$ [(M+H)$^+$] 416.1890, found 416.1892.

3-Isopropyl-1-methyl-3-(4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)butyl)indolin-2-one (3aj). The title compound was isolated as a pale yellow oil in 62% yield (57.1 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (20% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-\textit{d}) $\delta$ 7.73 – 7.66 (m, 2H), 7.27 (td, J = 7.7, 1.3 Hz,
1H) 7.16 (ddd, J = 7.4, 1.3, 0.6 Hz, 1H), 7.05 (td, J = 7.5, 1.0 Hz, 1H), 6.82 (dt, J = 7.7, 0.7 Hz, 1H), 6.80–6.74 (m, 2H), 3.90–3.76 (m, 2H), 3.20 (s, 3H), 2.21–2.10 (m, 1H), 2.01–1.88 (m, 2H), 1.74–1.57 (m, 2H), 1.32 (s, 12H), 0.97 (d, J = 6.9 Hz, 3H), 0.92–0.83 (m, 1H), 0.68 (d, J = 6.7 Hz, 3H).

\(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 180.0, 161.5, 144.3, 136.4 (2C), 131.1, 127.6, 123.5, 122.2, 113.8 (2C), 107.6, 83.5 (2C), 67.3, 56.4, 35.4, 35.1, 29.4, 25.8, 24.9 (4C), 21.1, 17.4, 17.3.

HRMS (ESI) calcd for C\(_{28}\)H\(_{38}\)BNO\(_{4}\)Na\(^+\) [(M+Na)\(^+\)] 486.2786, found 486.2793.

3-(4-((2-(Hydroxymethyl)phenoxy)butyl)-3-isopropyl-1-methylindolin-2-one (3ak). The title compound was isolated as a pale yellow oil in 78% yield (57.4 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (60% EtOAc in petroleum ether).

\(^{1}\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.31–7.13 (m, 4H), 7.05 (t, J = 7.5 Hz, 1H), 6.89 (t, J = 7.4 Hz, 1H), 6.83 (d, J = 7.7 Hz, 1H), 6.76 (d, J = 8.2 Hz, 1H), 4.55 (s, 2H), 3.93–3.80 (m, 2H), 3.19 (s, 3H), 2.61–2.32 (brs, 1H), 2.20–2.08 (m, 1H), 2.05–1.85 (m, 2H), 1.75–1.59 (m, 2H), 1.16–1.03 (m, 1H), 0.98 (d, J = 6.9 Hz, 3H), 0.96–0.83 (m, 1H), 0.68 (d, J = 6.7 Hz, 3H).

\(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 180.2, 156.7, 144.3, 131.1, 129.3, 128.8 (2C), 127.7, 123.5, 122.3 120.5, 111.1, 107.8, 67.3, 61.8, 56.5, 35.4, 35.0, 29.3, 25.9, 21.1, 17.4, 17.3.

HRMS (ESI) calcd for C\(_{23}\)H\(_{29}\)NO\(_{3}\)Na\(^+\) [(M+Na)\(^+\)] 390.2040, found 390.2046.

4-(4-(3-Isopropyl-1-methyl-2-oxoindolin-3-yl)butoxy)benzaldehyde (3al). The title compound was isolated as a pale yellow oil in 92% yield (67.4 mg) starting from the carbamoyl chloride 1a
(47.5 mg) through column chromatography on silica gel (30% EtOAc in petroleum ether).

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 9.86 (s, 1H), 7.79 (d, \(J = 8.4\) Hz, 2H), 7.33 – 7.24 (m, 1H), 7.17 (d, \(J = 7.3\) Hz, 1H), 7.09 – 7.02 (m, 1H), 6.89 (d, \(J = 8.3\) Hz, 2H), 6.84 (d, \(J = 7.7\) Hz, 1H), 3.96 – 3.83 (m, 2H), 3.20 (s, 3H), 2.20 – 2.10 (m, 1H), 2.04 – 1.88 (m, 2H), 1.76 – 1.60 (m, 2H), 1.18 – 1.03 (m, 1H), 0.98 (d, \(J = 6.9\) Hz, 3H), 0.94 – 0.85 (m, 1H), 0.69 (d, \(J = 6.7\) Hz, 3H).

\(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 190.8, 180.2, 164.1, 144.3, 132.0 (2C), 131.0, 129.7, 127.7, 123.5, 122.2, 114.7 (2C), 107.7, 68.0, 56.4, 35.4, 35.1, 29.3, 25.9, 21.1, 17.4, 17.3.

HRMS (ESI) calcd for C\(_{23}\)H\(_{28}\)NO\(_3\) \([(M+H)^+]\) 366.2064, found 366.2081.

3-(6-(4-Acetylphenoxy)hexyl)-3-isopropyl-1-methylindolin-2-one (3am).

The title compound was isolated as a pale yellow oil in 88% yield (71.5 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (20% EtOAc in petroleum ether).

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.96 – 7.86 (m, 2H), 7.31 – 7.23 (m, 1H), 7.16 (dd, \(J = 7.4\), 1.2 Hz, 1H), 7.05 (td, \(J = 7.5\), 1.0 Hz, 1H), 6.90 – 6.80 (m, 3H), 3.93 (t, \(J = 6.5\) Hz, 2H), 3.20 (s, 3H), 2.55 (s, 3H), 2.17 – 2.09 (m, 1H), 1.95 – 1.80 (m, 2H), 1.71 – 1.64 (m, 2H), 1.33 – 1.23 (m, 4H), 1.02 – 0.90 (m, 1H), 0.97 (d, \(J = 7.0\) Hz, 3H), 0.80 – 0.70 (m, 1H), 0.67 (d, \(J = 6.7\) Hz, 3H).

\(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 196.8, 180.2, 163.0, 144.3, 131.3, 130.6 (2C), 130.1, 127.5, 123.4, 122.1, 114.1 (2C), 107.6, 68.1, 56.4, 35.4, 35.3, 29.6, 29.0, 26.3, 25.8, 25.7, 24.3, 17.4, 17.3.

HRMS (ESI) calcd for C\(_{26}\)H\(_{33}\)NO\(_3\)Na\(^+\) \([(M+Na)^+]\) 430.2353, found 430.2359.
2-(5-(3-Isopropyl-1-methyl-2-oxoindolin-3-yl)pentyl)isoindoline-1,3-dione (3an).

The title compound was isolated as a pale yellow oil in 90% yield (72.6 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (40% EtOAc in petroleum ether).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 7.82 (dd, $J = 5.4$, 3.0 Hz, 2H), 7.70 (dd, $J = 5.5$, 3.0 Hz, 2H), 7.25 (td, $J = 7.7$, 1.2 Hz, 1H), 7.15 (dd, $J = 7.3$, 1.2 Hz, 1H), 7.03 (td, $J = 7.5$, 1.0 Hz, 1H), 6.81 (d, $J = 7.8$ Hz, 1H), 3.56 (t, $J = 7.1$ Hz, 2H), 3.19 (s, 3H), 2.17 – 2.07 (m, 1H), 1.92 – 1.80 (m, 2H), 1.57 – 1.47 (m, 2H), 1.29 – 1.17 (m, 2H), 1.00 – 0.90 (m, 1H), 0.95 (d, $J = 7.0$ Hz, 3H), 0.78 – 0.69 (m, 1H), 0.66 (d, $J = 6.8$ Hz, 3H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 180.1, 168.4 (2C), 144.3, 133.8 (2C), 132.1 (2C), 131.2, 127.6, 123.5, 123.1 (2C), 122.1, 107.6, 56.3, 38.0, 35.3, 35.2, 28.3, 27.1, 25.8, 24.1, 17.4, 17.3.

HRMS (ESI) calcd for C$_{25}$H$_{29}$N$_2$O$_3$ $^+$ [(M+H)$^+$] 405.2173, found 405.2184.

Phenyl 7-(3-isopropyl-1-methyl-2-oxoindolin-3-yl)heptanoate (3ao).

The title compound was isolated as a pale yellow oil in 94% yield (73.8 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (15% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.39 – 7.31 (m, 2H), 7.29 – 7.24 (m, 1H), 7.23 – 7.14 (m, 2H), 7.08 – 7.01 (m, 3H), 6.82 (dt, $J = 7.7$, 0.7 Hz, 1H), 3.19 (s, 3H), 2.46 (t, $J = 7.5$ Hz, 2H), 2.14 (hept, $J = 6.8$ Hz, 1H), 1.95 – 1.81 (m, 2H), 1.67 – 1.57 (m, 2H), 1.32 – 1.16 (m, 4H), 1.03 – 0.90 (m, 1H), 0.97 (d, $J = 6.9$ Hz, 3H), 0.79 – 0.65 (m, 1H), 0.68 (d, $J = 6.8$ Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 180.2, 172.2, 150.7, 144.4, 131.3, 129.4 (2C), 127.6, 125.7, 123.5, 122.1, 121.6 (2C), 107.6, 56.4, 35.4, 35.3, 34.3, 29.6, 28.8, 25.8, 24.8, 24.3, 17.4, 17.3.
HRMS (ESI) calcd for C_{25}H_{32}NO_{3}^+ [(M+H)^+] 394.2377, found 394.2383.

3-Chlorophenyl 7-(3-isopropyl-1-methyl-2-oxoindolin-3-yl)heptanoate (3ap).

The title compound was isolated as a pale yellow oil in 76% yield (65.1 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (15% EtOAc in petroleum ether).

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 7.32–7.25 (m, 2H), 7.22–7.15 (m, 2H), 7.09 (t, $J = 2.1$ Hz, 1H), 7.05 (td, $J = 7.5$, 1.0 Hz, 1H), 6.96 (ddd, $J = 8.1$, 2.2, 1.0 Hz, 1H), 6.83 (d, $J = 7.7$ Hz, 1H), 3.20 (s, 3H), 2.46 (t, $J = 7.5$ Hz, 2H), 2.18–2.10 (m, 1H), 1.95–1.82 (m, 2H), 1.65–1.58 (m, 2H), 1.30–1.15 (m, 4H), 1.01–0.91 (m, 1H), 0.97 (d, $J = 6.9$ Hz, 3H), 0.78–0.69 (m, 1H), 0.68 (d, $J = 6.7$ Hz, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 180.2, 171.8, 151.2, 144.4, 134.6, 131.3, 130.1, 127.6, 126.0, 123.5, 122.3, 122.1, 120.0, 107.6, 56.4, 35.4, 35.3, 34.2, 29.5, 28.8, 25.8, 24.7, 24.3, 17.4, 17.3.

HRMS (ESI) calcd for C_{25}H_{31}ClNO_{3}^+ [(M+H)^+] 428.1987, found 428.1996.

3-(Dimethylamino)phenyl 7-(3-isopropyl-1-methyl-2-oxoindolin-3-yl)heptanoate (3aq).

The title compound was isolated as a pale yellow oil in 79% yield (69.0 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (15% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.26 (t, $J = 4.2$ Hz, 1H), 7.22–7.14 (m, 2H), 7.05 (t, $J = 7.5$ Hz, 1H), 6.82 (d, $J = 7.7$ Hz, 1H), 6.56 (dd, $J = 8.4$, 2.3 Hz, 1H), 6.42–6.31 (m, 2H), 3.20 (s, 3H), 2.93 (s, 6H), 2.45 (t, $J = 7.5$ Hz, 2H), 2.18–2.10 (m, 1H), 1.95–1.81 (m, 2H), 1.65–1.56 (m, 2H), 1.30–1.16 (m, 4H), 0.96–0.89 (m, 1H), 0.97 (d, $J = 6.9$ Hz, 3H), 0.78–0.64 (m, 1H), 0.67 (d, $J = 6.7$ Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 180.2, 172.4, 151.8, 151.6, 144.3, 131.3,
129.6, 127.5, 123.5, 122.1, 109.8, 109.3, 107.6, 105.4, 56.4, 40.5 (2C), 35.36, 35.35, 34.4, 29.6, 28.9, 25.8, 24.9, 24.3, 17.4, 17.3.

**HRMS (ESI)** calcd for C_{27}H_{37}N_{2}O_{3}^+ [(M+H)^+] 437.2799, found 437.2798.

4-(Methylthio)phenyl 7-(3-isopropyl-1-methyl-2-oxoindolin-3-yl)heptanoate (3ar).

The title compound was isolated as a pale yellow oil in 93% yield (81.9 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (15% EtOAc in petroleum ether).

**{H NMR (400 MHz, Chloroform-d)}** δ 7.26 (dd, J = 8.7, 2.8 Hz, 3H), 7.16 (d, J = 7.3 Hz, 1H), 7.05 (t, J = 7.4 Hz, 1H), 6.98 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 7.7 Hz, 1H), 3.20 (s, 3H), 2.46 (d, J = 6.3 Hz, 5H), 2.19 – 2.10 (m, 1H), 1.94 – 1.80 (m, 2H), 1.66 – 1.56 (m, 2H), 1.29 – 1.18 (m, 4H), 1.01 – 0.88 (m, 1H), 0.97 (d, J = 6.9 Hz, 3H), 0.78 – 0.64 (m, 1H), 0.67 (d, J = 6.7 Hz, 3H).

**{C NMR (101 MHz, Chloroform-d)}** δ 180.2, 172.2, 148.4, 144.3, 135.5, 131.3, 128.0 (2C), 127.6, 123.5, 122.11, 122.06 (2C), 107.6, 56.4, 35.4, 35.3, 34.2, 29.5, 28.8, 25.8, 24.8, 24.3, 17.4, 17.3, 16.5.

**HRMS (ESI)** calcd for C_{26}H_{34}NO_{3}S^+ [(M+H)^+] 440.2254, found 440.2261.

4-Hydroxyphenyl 7-(3-isopropyl-1-methyl-2-oxoindolin-3-yl)heptanoate (3as).

The title compound was isolated as a pale yellow oil in 64% yield (52.4 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (40% EtOAc in petroleum ether).

**{H NMR (400 MHz, Chloroform-d)}** δ 7.32 – 7.23 (m, 1H), 7.17 (d, J = 7.4 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H), 6.92 – 6.73 (m, 5H), 6.55 – 6.24 (brs, 1H), 3.22 (s, 3H), 2.42 (t, J = 7.6 Hz, 2H), 2.20 – 2.10 (m, 1H), 1.96 – 1.81 (m, 2H), 1.65 – 1.52 (m, 2H), 1.27 – 1.14 (m, 4H), 1.02 – 0.86 (m, 1H), 0.98 (d, J = 6.9 Hz, 3H), 0.77 – 0.60 (m,
1H), 0.66 (d, J = 6.7 Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) δ 180.8, 172.9, 153.8, 144.2, 143.8, 131.3, 127.6, 123.5, 122.4, 122.3 (2C), 116.0 (2C), 107.8, 56.7, 35.4, 35.3, 34.2, 29.5, 28.8, 26.0, 24.8, 24.3, 17.4, 17.3.

HRMS (ESI) calcd for C$_{25}$H$_{31}$NO$_4$Na$^+$ [(M+Na)$^+$] 432.2145, found 432.2147.

4-((tert-Butyldimethylsilyl)oxy)phenyl
7-(3-isopropyl-1-methyl-2-oxoindolin-3-yl)heptanoate (3at).

The title compound was isolated as a pale yellow oil in 86% yield (90.1 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (15% EtOAc in petroleum ether).

$^1$H NMR (500 MHz, Chloroform-$d$) δ 7.31 – 7.23 (m, 1H), 7.16 (d, J = 7.3 Hz, 1H), 7.05 (t, J = 7.5 Hz, 1H), 6.89 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 7.8 Hz, 1H), 6.79 (d, J = 8.4 Hz, 2H), 3.20 (s, 3H), 2.43 (t, J = 7.5 Hz, 2H), 2.20 – 2.08 (m, 1H), 1.96 – 1.79 (m, 2H), 1.66 – 1.55 (m, 2H), 1.29 – 1.15 (m, 4H), 1.02 – 0.81 (m, 1H), 0.97 (s, 9H), 0.96 (d, J = 6.9 Hz, 3H), 0.78 – 0.65 (m, 1H), 0.67 (d, J = 6.7 Hz, 3H), 0.18 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) δ 180.2, 172.5, 153.1, 144.7, 144.3, 131.3, 127.5, 123.5, 122.2 (2C), 122.1, 120.5 (2C), 107.6, 56.4, 35.4, 35.3, 34.2, 29.6, 28.8, 25.8, 25.7 (3C), 24.9, 24.3, 18.2, 17.4, 17.3, −4.5 (2C).

HRMS (ESI) calcd for C$_{31}$H$_{46}$NO$_4$Si$^+$ [(M+H)$^+$] 524.3191, found 524.3200.

4-(Trifluoromethoxy)phenyl
7-(3-isopropyl-1-methyl-2-oxoindolin-3-yl)heptanoate (3au).

The title compound was isolated as a colorless oil in 72% yield (69.1 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (15% EtOAc in petroleum ether).
\(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.27 (td, \(J = 7.7, 1.3\) Hz, 1H), 7.24 – 7.18 (m, 2H), 7.16 (dd, \(J = 7.4, 1.3\) Hz, 1H), 7.11 – 7.01 (m, 3H), 6.85 – 6.80 (m, 1H), 3.20 (s, 3H), 2.47 (t, \(J = 7.5\) Hz, 2H), 2.19 – 2.10 (m, 1H), 1.95 – 1.81 (m, 2H), 1.67 – 1.57 (m, 2H), 1.30 – 1.16 (m, 4H), 1.02 – 0.90 (m, 1H), 0.97 (d, \(J = 6.9\) Hz, 3H), 0.79 – 0.70 (m, 1H), 0.68 (d, \(J = 6.8\) Hz, 3H).

\(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 180.2, 171.9, 148.9, 146.4 (q, \(J = 1.6\) Hz), 144.4, 131.3, 127.6, 123.5, 122.9 (2C), 122.12, 122.07 (2C), 120.4 (q, \(J = 258.3\) Hz), 107.6, 56.4, 35.4, 35.3, 34.2, 29.5, 28.8, 25.8, 24.7, 24.3, 17.4, 17.3.

HRMS (ESI) calcd for C\(_{26}\)H\(_{31}\)F\(_3\)N\(_4\)O\(_3\)\(^+\) [(M+H)\(^+\)] 478.2200, found 478.2208.

\(^{19}\)F NMR (376 MHz, Chloroform-\(d\)) \(\delta\) –58.12 (s, 3F).

4-(Trifluoromethyl)phenyl 7-(3-isopropyl-1-methyl-2-oxoindolin-3-yl)heptanoate (3av).

The title compound was isolated as a pale yellow oil in 78% yield (72.0 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (15% EtOAc in petroleum ether).

\(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.63 (d, \(J = 8.6\) Hz, 2H), 7.27 (td, \(J = 7.7, 1.2\) Hz, 1H), 7.22 – 7.13 (m, 3H), 7.05 (td, \(J = 7.5, 1.0\) Hz, 1H), 6.83 (d, \(J = 7.8\) Hz, 1H), 3.20 (s, 3H), 2.49 (t, \(J = 7.5\) Hz, 2H), 2.14 (hept, \(J = 6.8\) Hz, 1H), 1.96 – 1.80 (m, 2H), 1.67 – 1.59 (m, 2H), 1.28 – 1.19 (m, 4H), 1.01 – 0.90 (m, 1H), 0.97 (d, \(J = 6.9\) Hz, 3H), 0.79 – 0.69 (m, 1H), 0.68 (d, \(J = 6.7\) Hz, 3H).

\(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 180.2, 171.7, 153.2, 144.4, 131.3, 128.0 (q, \(J = 33.1\) Hz), 127.6, 126.8 (q, \(J = 3.6\) Hz, 2C), 123.9 (q, \(J = 272.0\) Hz), 123.5, 122.12, 122.09 (2C), 107.6, 56.4, 35.4, 35.3, 34.2, 29.5, 28.8, 25.8, 24.7, 24.3, 17.4, 17.3.

HRMS (ESI) calcd for C\(_{26}\)H\(_{31}\)F\(_3\)N\(_4\)O\(_3\)\(^+\) [(M+H)\(^+\)] 462.2251, found 462.2261.

\(^{19}\)F NMR (376 MHz, Chloroform-\(d\)) \(\delta\) –62.21 (s, 3F).
4-(tert-Butyl)phenyl 7-(3-isopropyl-1-methyl-2-oxoindolin-3-yl)heptanoate (3aw).

The title compound was isolated as a pale yellow oil in 80% yield (71.7 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.36 (d, $J = 8.5$ Hz, 2H), 7.27 (td, $J = 7.7$, 1.2 Hz, 1H), 7.16 (d, $J = 7.3$ Hz, 1H), 7.09 – 7.01 (m, 1H), 6.96 (d, $J = 8.5$ Hz, 2H), 6.82 (d, $J = 7.7$ Hz, 1H), 3.20 (s, 3H), 2.45 (t, $J = 7.5$ Hz, 2H), 2.20 – 2.09 (m, 1H), 1.95 – 1.80 (m, 2H), 1.65 – 1.56 (m, 2H), 1.31 (s, 9H), 1.27 – 1.15 (m, 4H), 1.00 – 0.86 (m, 1H), 0.97 (d, $J = 6.9$ Hz, 3H), 0.77 – 0.62 (m, 1H), 0.68 (d, $J = 6.7$ Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 180.2, 172.4, 148.5, 148.3, 144.3, 131.3, 127.6, 126.3 (2C), 123.5, 122.1, 120.9 (2C), 107.6, 56.4, 35.4, 35.3, 34.5, 34.3, 31.4 (3C), 29.6, 28.8, 25.9, 24.9, 24.3, 17.4, 17.3.

HRMS (ESI) calcd for C$_{29}$H$_{40}$NO$_3$ $\left[(M+H)^+\right]$ 450.3003, found 450.3012.

(E)-Hex-2-en-1-yl 7-(3-isopropyl-1-methyl-2-oxoindolin-3-yl)heptanoate (3ax).

The title compound was isolated as a pale yellow oil in 92% yield (73.5 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (15% EtOAc in petroleum ether).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 7.31 – 7.23 (m, 1H), 7.15 (dd, $J = 7.3$, 1.2 Hz, 1H), 7.05 (td, $J = 7.5$, 1.0 Hz, 1H), 6.85 – 6.78 (m, 1H), 5.74 (dtt, $J = 14.8$, 6.7, 1.2 Hz, 1H), 5.54 (dtt, $J = 15.6$, 6.5, 1.5 Hz, 1H), 4.48 (dd, $J = 6.5$, 1.1 Hz, 2H), 3.20 (s, 3H), 2.22 (t, $J = 7.5$ Hz, 2H), 2.18 – 2.09 (m, 1H), 2.06 – 1.98 (m, 2H), 1.92 – 1.79 (m, 2H), 1.53 – 1.45 (m, 2H), 1.45 – 1.35 (m, 2H), 1.25 – 1.10 (m, 4H), 0.96 (d, $J = 6.9$ Hz, 3H), 0.94 – 0.85 (m, 1H), 0.89 (t, $J = 7.4$ Hz, 3H), 0.74 – 0.64 (m, 1H), 0.67 (d, $J = 6.8$ Hz, 3H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 180.2, 173.6, 144.3, 136.3, 131.4, 127.5, 124.0, 123.5, 122.1, 107.6, 65.1, 56.4, 35.4 (2C), 34.31, 34.25, 29.6, 28.9, 25.8, 24.9, 24.3, 22.1, 17.4, 17.3, 13.7.
HRMS (ESI) calcd for C_{25}H_{38}NO_{3}^+ [(M+H)^+] 400.2846, found 400.2851.

5-(3-Isopropyl-1-methyl-2-oxoindolin-3-yl)pentyl acetate (3ay).

The title compound was isolated as a pale yellow oil in 92% yield (58.3 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (15% EtOAc in petroleum ether).

^1H NMR (400 MHz, Chloroform-d) δ 7.31 – 7.24 (m, 1H), 7.16 (d, J = 7.3 Hz, 1H), 7.05 (t, J = 7.5 Hz, 1H), 6.83 (d, J = 7.7 Hz, 1H), 3.93 (t, J = 6.7 Hz, 2H), 3.20 (s, 3H), 2.14 (hept, J = 6.6 Hz, 1H), 1.99 (s, 3H), 1.94 – 1.76 (m, 2H), 1.52 – 1.42 (m, 2H), 1.31 – 1.15 (m, 2H), 1.04 – 0.86 (m, 1H), 0.97 (d, J = 6.9 Hz, 3H), 0.79 – 0.59 (m, 1H), 0.67 (d, J = 6.8 Hz, 3H).

^13C NMR (101 MHz, Chloroform-d) δ 180.1, 171.2, 144.3, 131.2, 127.6, 123.4, 122.1, 107.6, 64.5, 56.3, 35.4, 35.3, 28.3, 26.3, 25.8, 24.2, 21.0, 17.4, 17.3.

HRMS (ESI) calcd for C_{19}H_{28}NO_{3}^+ [(M+H)^+] 318.2064, found 318.2073.

3-(Cyclohexylmethyl)-3-isopropyl-1-methylindolin-2-one (3az).

The title compound was isolated as a pale yellow oil in 77% yield (43.7 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

^1H NMR (400 MHz, Chloroform-d) δ 7.31 – 7.21 (m, 1H), 7.14 (ddd, J = 7.4, 1.3, 0.6 Hz, 1H), 7.03 (td, J = 7.5, 1.0 Hz, 1H), 6.82 (dt, J = 7.8, 0.8 Hz, 1H), 3.20 (s, 3H), 2.12 – 2.01 (m, 1H), 1.93 – 1.81 (m, 2H), 1.54 – 1.33 (m, 4H), 1.14 – 1.06 (m, 1H), 1.03 – 0.78 (m, 5H), 0.92 (d, J = 6.9 Hz, 3H), 0.74 – 0.61 (m, 1H), 0.65 (d, J = 6.8, 0.8 Hz, 3H).

^13C NMR (101 MHz, Chloroform-d) δ 180.4, 144.2, 131.5, 127.4, 123.9, 121.9, 107.6, 55.5, 42.5, 36.9, 34.8, 34.6, 33.8, 26.2, 26.1, 26.1, 25.9, 17.2, 17.1.

S41
HRMS (ESI) calcd for C\textsubscript{19}H\textsubscript{28}NO\textsuperscript{+} [(M+H)\textsuperscript{+}] 286.2165, found 286.2173.

3-Isopropyl-1-methyl-3-((tetrahydro-2H-pyran-4-yl)methyl)indolin-2-one (3aaa).

The title compound was isolated as a pale yellow oil in 80% yield (46.1 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (15% EtOAc in petroleum ether).

\textsuperscript{1}H NMR (400 MHz, Chloroform-d) \( \delta \) 7.28 (t, \( J = 6.5 \) Hz, 1H), 7.16 (d, \( J = 7.3 \) Hz, 1H), 7.05 (t, \( J = 7.5 \) Hz, 1H), 6.83 (d, \( J = 7.7 \) Hz, 1H), 3.76 (dd, \( J = 9.0, 5.9 \) Hz, 1H), 3.71 – 3.62 (m, 1H), 3.21 (s, 3H), 3.15 – 2.99 (m, 2H), 2.13 – 2.03 (m, 1H), 1.99 – 1.86 (m, 2H), 1.32 – 1.21 (m, 2H), 1.20 – 1.09 (m, 1H), 1.09 – 0.97 (m, 1H), 0.95 (d, \( J = 6.9 \) Hz, 3H), 0.92 – 0.85 (m, 1H), 0.64 (d, \( J = 6.7 \) Hz, 3H).

\textsuperscript{13}C NMR (101 MHz, Chloroform-d) \( \delta \) 180.1, 144.1, 131.1, 127.7, 123.9, 122.1, 107.7, 67.8, 67.7, 55.3, 42.1, 36.8, 34.2, 33.7, 32.3, 25.9, 17.2, 17.1.

HRMS (ESI) calcd for C\textsubscript{18}H\textsubscript{26}NO\textsuperscript{2+} [(M+H\textsuperscript{+})] 288.1958, found 288.1958.

3-Isopropyl-3-(4-(4-methoxyphenyl)-2-methylbutyl)-1-methylindolin-2-one (3aabb).

The title compound was isolated as a pale yellow oil in 68% yield (49.8 mg, dr = 2:1) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (15% EtOAc in petroleum ether).

\textsuperscript{1}H NMR (400 MHz, Chloroform-d) \( \delta \) (mixture of two diastereomers) 7.32 – 7.21 (m, 1H), 7.17 – 6.70 (m, 7H), 3.77 (s, 3H), 3.15 (s, 3H), 2.52 – 2.24 (m, 2H), 2.14 – 1.98 (m, 2H), 1.91 – 1.79 (m, 1H), 1.44 – 1.30 (m, 0.67H), 1.21 – 1.09 (m, 1.33H), 1.06 – 0.82 (m, 4H), 0.76 – 0.58 (m, 5H), 0.53 (d, \( J = 6.3 \) Hz, 1H).

\textsuperscript{13}C NMR (101 MHz, Chloroform-d) \( \delta \) (major diastereomer) 180.4, 157.5, 144.3, 134.6, 131.1, 129.1 (2C), 127.5, 124.0, 121.9, 113.6 (2C), 107.7, 55.7, 55.3, 41.7, 40.1, 36.8, 32.1, 29.6, 25.9, 20.2, 17.3, 17.1.
$^{13}$C NMR (101 MHz, Chloroform-$d$) δ (minor diastereomer) 180.2, 157.4, 144.2, 134.9, 131.3, 129.2 (2C), 127.5, 124.1, 121.9, 113.6 (2C), 107.6, 55.7, 55.3, 42.2, 39.4, 36.9, 31.8, 29.9, 25.9, 20.9, 17.3, 17.1.

HRMS (ESI) calcd for C$_{24}$H$_{32}$NO$_2^+$ [(M+H)$^+$] 366.2428, found 366.2436.

3-Isopropyl-1-methyl-3-phenylindolin-2-one (3aac).

The title compound was isolated as a pale yellow oil in 71% yield (41.7 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-$d$) δ 7.31 (t, $J = 7.7$ Hz, 1H), 7.26 – 7.17 (m, 3H), 7.16 – 7.06 (m, 3H), 7.03 (d, $J = 7.5$ Hz, 2H), 6.86 (d, $J = 7.8$ Hz, 1H), 3.21 (s, 3H), 2.33 – 2.07 (m, 4H), 2.06 – 1.92 (m, 1H), 0.98 (d, $J = 6.9$ Hz, 3H), 0.70 (d, $J = 6.7$ Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) δ 179.8, 144.5, 141.8, 130.9, 128.34 (2C), 128.25 (2C), 127.8, 125.8, 123.5, 122.3, 107.7, 56.4, 37.6, 35.4, 31.0, 25.9, 17.4, 17.3.

HRMS (ESI) calcd for C$_{20}$H$_{23}$NO Na$^+$ [(M+Na)$^+$] 316.1672, found 316.1678.

3-Isopropyl-3-(4-methoxyphenethyl)-1-methylindolin-2-one (3aad).

The title compound was isolated as a pale yellow oil in 56% yield (36.1 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (15% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-$d$) δ 7.30 (td, $J = 7.7$, 1.3 Hz, 1H), 7.22 (dd, $J = 7.3$, 1.2 Hz, 1H), 7.09 (td, $J = 7.5$, 1.0 Hz, 1H), 6.94 (dt, $J = 8.6$, 2.3 Hz, 2H), 6.85 (d, $J = 7.7$ Hz, 1H), 6.75 (dt, $J = 8.7$, 2.4 Hz, 2H), 3.75 (s, 3H), 3.21 (s, 3H), 2.28 – 2.14 (m, 3H), 2.13 – 2.02 (m, 1H), 1.99 – 1.88 (m, 1H), 0.98 (d, $J = 6.9$ Hz, 3H), 0.69 (d, $J = 6.8$ Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) δ 179.8, 157.7, 144.5, 133.9, 130.9, 129.2 (2C), 127.7, 123.5, 122.3, 113.7 (2C), 107.7, 56.4, 55.2, 37.8, 35.5, 30.0, 25.9, 17.4, 17.3.
HRMS (ESI) calcd for C_{21}H_{25}NO_{2}Na^{+} [(M+Na)^{+}] 324.1958, found 324.1966.

4-(2-(3-Isopropyl-1-methyl-2-oxoindolin-3-yl)ethyl)phenyl acetate (3aae).

The title compound was isolated as a white solid in 74% yield (52.1 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (15% EtOAc in petroleum ether).

^1H NMR (400 MHz, Chloroform-d) δ 7.30 (t, J = 7.7 Hz, 1H), 7.21 (d, J = 7.4 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H), 7.01 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 8.0 Hz, 2H), 6.85 (d, J = 7.8 Hz, 1H), 3.20 (s, 3H), 2.33 – 2.05 (m, 4H), 2.26 (s, 3H), 2.05 – 1.93 (m, 1H), 0.98 (d, J = 6.8 Hz, 3H), 0.69 (d, J = 6.7 Hz, 3H).

^13C NMR (101 MHz, Chloroform-d) δ 179.7, 169.7, 148.7, 144.4, 139.3, 130.8, 129.3 (2C), 127.8, 123.5, 122.3, 121.2 (2C), 107.8, 56.3, 37.4, 35.5, 30.4, 25.9, 21.2, 17.4, 17.3.

HRMS (ESI) calcd for C_{22}H_{26}NO_{3}^{+} [(M+H)^{+}] 352.1907, found 352.1911.

3-(3-Chlorophenethyl)-3-isopropyl-1-methylindolin-2-one (3aaf).

The title compound was isolated as a pale yellow oil in 59% yield (38.5 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

^1H NMR (400 MHz, Chloroform-d) δ 7.31 (t, J = 7.7 Hz, 1H), 7.21 (d, J = 7.4 Hz, 1H), 7.16 – 7.05 (m, 3H), 6.98 (s, 1H), 6.92 (d, J = 7.1 Hz, 1H), 6.86 (d, J = 7.8 Hz, 1H), 3.21 (s, 3H), 2.30 – 1.91 (m, 5H), 0.98 (d, J = 6.9 Hz, 3H), 0.69 (d, J = 6.6 Hz, 3H).

^13C NMR (101 MHz, Chloroform-d) δ 179.6, 144.4, 143.7, 133.9, 130.6, 129.5, 128.5, 127.9, 126.6, 126.0, 123.5, 122.4, 107.8, 56.2, 37.1, 35.5, 30.8, 25.9, 17.4, 17.2.
HRMS (ESI) calcd for C_{20}H_{23}ClNO^{+} [(M+H)^{+}] 328.1463, found 328.1469.

3-(4-Chloro-3-methoxyphenethyl)-3-isopropyl-1-methylindolin-2-one (3aag).

The title compound was isolated as a white solid in 71% yield (50.5 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (15% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.31 (td, $J = 7.7$, 1.3 Hz, 1H), 7.23 (ddd, $J = 7.4$, 1.3, 0.6 Hz, 1H), 7.17 (d, $J = 8.0$ Hz, 1H), 7.10 (td, $J = 7.5$, 1.0 Hz, 1H), 6.86 (dt, $J = 7.9$, 0.8 Hz, 1H), 6.60 – 6.51 (m, 2H), 3.84 (s, 3H), 3.20 (s, 3H), 2.29 – 2.07 (m, 4H), 2.05 – 1.95 (m, 1H), 0.98 (d, $J = 6.9$ Hz, 3H), 0.69 (d, $J = 6.7$ Hz, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 179.7, 154.6, 144.5, 141.8, 130.7, 129.8, 127.9, 123.6, 122.3, 121.1, 119.7, 117.2, 107.8, 56.3, 37.3, 35.5, 31.0, 25.9, 17.4, 17.3.

HRMS (ESI) calcd for C_{21}H_{24}ClNO_{2}Na^{+} [(M+Na)^{+}] 380.1388, found 380.1395.

3-(2-(Benzo[d][1,3]dioxol-5-yl)ethyl)-3-isopropyl-1-methylindolin-2-one (3aah).

The title compound was isolated as a pale yellow oil in 56% yield (38.0 mg) starting from the carbamoyl chloride 1a (47.5 mg) through column chromatography on silica gel (15% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.30 (td, $J = 7.7$, 1.3 Hz, 1H), 7.21 (d, $J = 7.3$ Hz, 1H), 7.09 (t, $J = 7.5$ Hz, 1H), 6.85 (d, $J = 7.7$ Hz, 1H), 6.65 (d, $J = 7.9$ Hz, 1H), 6.52 (d, $J = 1.5$ Hz, 1H), 6.46 (dd, $J = 8.0$, 1.6 Hz, 1H), 5.88 (s, 2H), 3.22 (s, 3H), 2.27 – 2.12 (m, 3H), 2.10 – 2.02 (m, 1H), 1.95 – 1.87 (m, 1H), 0.98 (d, $J = 6.9$ Hz, 3H), 0.68 (d, $J = 6.7$ Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 179.8, 147.4, 145.6, 144.4, 135.7, 130.9, 127.8, 123.5, 122.3, 121.0, 108.9, 108.0, 107.7, 100.7, 56.3, 37.9, 35.5, 30.7, 25.9, 17.4, 17.2.
HRMS (ESI) calcd for C$_{21}$H$_{24}$NO$_3$\(^+\) [(M+H)$^+$] 338.1751, found 338.1758.
Supplementary Table 2. Ni-Precatalyst Screening for asymmetric carbo-acylation[a-c]

| entry | precatalyst              | yield (%) | ee (%) |
|-------|--------------------------|-----------|--------|
| 1     | NiBr$_2$·glyme           | 29        | 26     |
| 2     | NiBr$_2$·diglyme         | 28        | 25     |
| 3     | NiBr$_2$                | 0         | -      |
| 4     | Ni$_2$                   | trace     | -      |
| 5     | NiCl$_2$·glyme           | 28        | 26     |
| 6     | Ni(OTf)$_2$              | 0         | -      |
| 7     | Ni(acac)$_2$             | 0         | -      |
| 8     | NiCl$_2$                | 0         | -      |
| 9     | Ni(cod)$_2$              | 28        | 24     |

[a] Reactions were performed on a 0.2 mmol scale of the carbamoyl chloride 1f using 2.0 equiv of n-pentyl iodide (2a), 10 mol% Ni-precatalyst, 15 mol% ligand L15, 2.0 equiv of Zn as reductant in 1.5 mL EtOH at room temperature for 12 h, [b] NMR-yields using CH$_2$Br$_2$ as an internal standard, [c] Enantiomeric Excesses were determined by HPLC analysis on chiral stationary phase.

Supplementary Table 3. Ligand Screening for asymmetric carbo-acylation[a-c]

| entry | ligand | yield (%) | ee (%) |
|-------|--------|-----------|--------|
| 1     | L1     | 9         | 71     |
| 2     | L16    | 0         | -      |
Reactions were performed on a 0.2 mmol scale of the carbamoyl chloride 1f using 2.0 equiv of n-pentyl iodide (2a), 10 mol% NiBr$_2$•glyme, 15 mol% ligand L$_1$, 2.0 equiv of Zn as reductant in 1.5 mL solvent at room temperature for 12 h, [b] NMR-yields using CH$_2$Br$_2$ as an internal standard, [c] Enantiomeric Excesses were determined by HPLC analysis on chiral stationary phase.

Supplementary Table 4. Solvent screening with Zn as reductant for asymmetric carbo-acylation [a-c]

| entry | solvent     | yield (%) | ee (%) |
|-------|-------------|-----------|--------|
| 1     | THF         | trace     | -      |
| 2     | PhOMe       | 0         | -      |
| 3     | MeCN        | trace     | -      |
| 4     | DMAc        | 14        | 60     |
| 5     | DMF         | trace     | -      |
| 6     | NMP         | 20        | 53     |
| 7     | MeOH        | trace     | -      |

[a] Reactions were performed on a 0.2 mmol scale of the carbamoyl chloride 1f using 2.0 equiv of n-pentyl iodide (2a), 10 mol% NiBr$_2$•glyme, 15 mol% ligand L$_1$, 2.0 equiv of Zn as reductant in 1.5 mL solvent at room temperature for 12 h, [b] NMR-yields using CH$_2$Br$_2$ as an internal standard, [c] Enantiomeric Excesses were determined by HPLC analysis on chiral stationary phase.
Supplementary Table 5. Solvent screening with Mn as reductant for asymmetric carbo-acylation \[^{[a-c]}\]

| entry | solvent\(^a\) | yield (%) | ee (%) |
|-------|----------------|-----------|--------|
| 1     | THF            | trace     | -      |
| 2     | Et\(_2\)O      | 0         | -      |
| 3     | PhOMe          | 0         | -      |
| 4     | MTBE\(^c\)     | 0         | -      |
| 5     | CPME\(^d\)     | 0         | -      |
| 6     | MeCN           | trace     | -      |
| 7     | DMF            | trace     | -      |
| 8     | DMA            | 50        | 64     |
| 9     | DMPU           | 0         | -      |
| 10    | NMP            | 20        | 54     |
| 11    | MeOH           | trace     | -      |
| 12    | EtOH           | 11        | 73     |

\[^{[a]}\] Reactions were performed on a 0.2 mmol scale of the carbamoyl chloride \(1f\) using 2.0 equiv of \(n\)-pentyl iodide (2a), 10 mol\% NiBr\(_2\)-glyme, 15 mol\% ligand L1, 2.0 equiv of Mn as reductant in 1.5 mL solvent at room temperature for 12 h. \[^{[b]}\] NMR yields using CH\(_2\)Br\(_2\) as an internal standard. \[^{[c]}\] Enantiomeric Excesses were determined by HPLC analysis on chiral stationary phase.

Supplementary Table 6. Additive screening for asymmetric carbo-acylation \[^{[a-c]}\]

| entry | additive | yield (%) | ee (%) |
|-------|----------|-----------|--------|
| 1     | KI       | 37        | 64     |
| 2     | KBr      | 19        | 65     |
| 3     | KF       | 28        | 63     |
| 4     | CsF      | trace     | -      |
| 5     | DMBA\(^d\) | trace     | -      |
| 6     | 4 Å MS   | 58        | 64     |
| 7     | MgCl\(_2\) | trace    | -      |
Supplementary Table 7. Further ligand screening for asymmetric carbo-acylation [a-c]

| Ligand | ee (%) |
|--------|--------|
| L3     | 19%, 33% ee |
| L4     | 50%, 66% ee |
| L5     | 55%, 63% ee |
| L6     | 44%, 67% ee |
| L7     | 47%, 57% ee |
| L8     | trace, n.d. |
| L9     | 29%, 48% ee |
| L10    | 50%, 71% ee |
| L11    | trace, n.d. |
| L12    | 64%, 85% ee |
| L25    | trace, n.d. |
| L26    | 19%, 12% ee |
| L27    | trace, n.d. |
| L28    | trace, n.d. |
| L29    | 0%, n.d. |
| L30    | 0%, n.d. |
| L31    | 50%, 65% ee |
| L32    | 49%, 66% ee |
| L33    | 27%, 61% ee |
| L34    | 64%, 84% ee |
| L35    | 58%, 83% ee |
| L36    | 60%, 79% ee |
| L37    | 61%, 84% ee |
| L38    | 60%, 83% ee |
| L39    | 62%, 82% ee |

[a] Reactions were performed on a 0.2 mmol scale of the carbamoyl chloride If using 2.0 equiv of n-pentyl iodide (2a), 10 mol% NiBr2•glyme, 15 mol% ligand L1, 2.0 equiv of Mn as reductant and 1.0 equiv of additive in 1.5 mL DMA at room temperature for 12 h, [b] NMR-yields using CH2Br2 as an internal standard, [c] Enantiomeric Excesses were determined by HPLC analysis on chiral stationary phase.
Supplementary Table 8. Co-solvent and concentration screening for asymmetric carbo-acylation \[^{[a-d]}\]

| entry | Solvent                | yield (%) | ee (%) |
|-------|------------------------|-----------|--------|
| 1     | DMA/NMM = 9:1 (0.13 M) | 20        | -      |
| 2     | DMA/NMM = 4:1 (0.13 M) | 45        | 87     |
| 3     | DMA/NMM = 3:1 (0.13 M) | 32        | 87     |
| 4     | DMA/NMM = 4:1 (0.2 M)  | 33        | 87     |
| 5     | DMA/NMM = 4:1 (0.4 M)  | 29        | 87     |

\[^{[e]}\] Reaction performed with 1.0 equiv of ZnI\(_2\).

Supplementary Table 9. Further optimization of the catalyst loading for asymmetric carbo-acylation \[^{[a-c]}\]

| entry | catalyst (x mol%) | ligand (y mol%) | yield (%) | ee (%) |
|-------|-------------------|-----------------|-----------|--------|
| 1     | 15                | 20              | 55        | 88     |
| 2     | 10                | 20              | 21        | 87     |
| 3     | 20                | 20              | 61        | 88     |
| 4\[^{[d]}\] | 20             | 20              | 65 (61\(^{[e]}\)) | 88 |

\[^{[a]}\] Reactions were performed on a 0.2 mmol scale of the carbamoyl chloride \(\text{If}\) using 2.0 equiv of \(n\)-pentyl iodide (2a), 10 mol\% NiBr\(_2\)-glyme, 15 mol\% ligand L14, 2.0 equiv of Mn as reductant in 1.5 mL DMA/NMM at 10 °C for 72 h, \[^{[b]}\] NMR-yields using CH\(_2\)Br\(_2\) as an internal standard, \[^{[c]}\] Enantiomeric Excesses were determined by HPLC analysis on chiral stationary phase, \[^{[d]}\] Reaction time: 96 h, \[^{[e]}\] Yield of the isolated product.
Supplementary Figure 6. General procedure for asymmetric Ni-Catalyzed carbo-acylation

\[
\begin{align*}
\text{(S)-4-(2-((\text{tert-Butyl})-4,5-dihydrooxazol-2-yl)pyridin-4-yl)morpholine (L12) (11.6 mg, 0.04 mmol, 20 mol%)},
\text{ carbamoyl chlorides 1 (if solid, 0.2 mmol, 1 equiv) and alkyl iodides 2}^{[a]} \text{ (if solid, 0.4 mmol, 2.0 equiv) were added to a reaction tube equipped with a stir bar. In a nitrogen-filled glovebox, NiBr}_2\text{-glyme (12.3 mg, 0.04 mmol, 20 mol%) and manganese dust (22 mg, 0.4 mmol, 2 equiv) were added to the mixture. The reaction tube was sealed and removed from the glovebox. Next, anhydrous DMAc (1.2 mL) and N-methyl morpholine (0.3 mL) were added, followed by the addition of carbamoyl chlorides 1 (if liquid, 0.2 mmol, 1 equiv) and alkyl iodides 2}^{[a]} \text{ (if liquid, 0.4 mmol, 2.0 equiv) under the protection of nitrogen. Then the resulting mixture was stirred at the temperature specified below}^{[b]} \text{ for 24-96 h}^{[c]}. 
\text{The reaction was quenched with sat. aq. NH}_4\text{Cl solution (5 mL) and diluted with water (10 mL). The aqueous layer was extracted three times with EtOAc, and the combined organic layers were washed with brine (20 mL), dried over MgSO}_4\text{, filtered, and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the desired product 3.}
\end{align*}
\]

\[a\] Benzyl chloride was used for 3bac,

\[b\] 25 °C for 3bx and 3bac, 10 °C for 3ba-da, 3fa, 3ma, 3qa-ua, 3bd, 3bf, 3bi, 3bk-bm, 3bo, 3br, 3bv and 3by-baa,

\[c\] 24 h for 3bac, 48 h for 3ba-da, 3ma, 3ra-ua, 3bd, 3bf, 3bi, 3bk-bm, 3bo, 3br, 3bv and 3bx-baa, 96 h for 3fa and 3qa.
(S)-3-Hexyl-1,3-dimethylindolin-2-one (3ba).

The title compound was isolated as a pale yellow oil in 61% yield (30.1 mg, 85% ee) starting from the carbamoyl chloride 1b (41.9 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether). For 1-mmol-scale reaction, the product was obtained in 58% yield (142.2 mg, 85% ee) starting the carbamoyl chloride 1b (209.7 mg).

\[ \text{\(^1H\) NMR (400 MHz, Chloroform-} \text{d}) \delta \]

(Needs to be filled in with the actual NMR data)

\[ \text{\(^{13}C\) NMR (101 MHz, Chloroform-} \text{d}) \delta \]

(Needs to be filled in with the actual NMR data)

\[ \text{HRMS (ESI) calcd for C}_{16}\text{H}_{24}\text{NO}\text{\[^{(M+H)}\] = 246.1852, found 246.1852.} \]

\[ \text{HPLC-Data: CHIRALPAK AD-H, 25 °C, \text{PrOH-hexanes 1.5/98.5, 1 mL/min, 254 nm, } t_R(\text{major}) = 8.3 \text{ min, } t_R(\text{minor}) = 9.1 \text{ min.}} \]

(S)-3-Ethyl-3-hexyl-1-methylindolin-2-one (3ca).

The title compound was isolated as a pale yellow oil in 85% yield (44.4 mg, 65% ee) starting from the carbamoyl chloride 1c (44.7 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

\[ \text{\(^1H\) NMR (400 MHz, Chloroform-} \text{d}) \delta \]

(Needs to be filled in with the actual NMR data)

\[ \text{\(^{13}C\) NMR (101 MHz, Chloroform-} \text{d}) \delta \]

(Needs to be filled in with the actual NMR data)

\[ \text{HRMS (ESI) calcd for C}_{17}\text{H}_{26}\text{NO}\text{\[^{(M+H)}\] = 260.2009, found 260.2009.} \]
**HPLC-Data:** CHIRALPAK IC, 25 °C, iPrOH-hexanes 20/80, 1 mL/min, 254 nm, \( t_R\) (major) = 5.0 min, \( t_R\) (minor) = 6.2 min.

(S)-3-Hexyl-1-methyl-3-propylindolin-2-one (3da).

The title compound was isolated as a pale yellow oil in 80% yield (43.6 mg, 63% ee) starting from the carbamoyl chloride 1d (47.5 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

\(^1\)H NMR (400 MHz, Chloroform-d) \( \delta \) 7.26 (t, \( J = 7.6 \) Hz, 1H), 7.14 (d, \( J = 7.2 \) Hz, 1H), 7.07 (t, \( J = 7.4 \) Hz, 1H), 6.83 (d, \( J = 7.7 \) Hz, 1H), 3.20 (s, 3H), 1.91 – 1.81 (m, 2H), 1.77 – 1.66 (m, 2H), 1.23 – 1.08 (m, 6H), 1.03 – 0.91 (m, 2H), 0.87 – 0.74 (m, 2H), 0.80 (t, \( J = 6.8 \) Hz, 3H), 0.76 (t, \( J = 6.4 \) Hz, 3H).

\(^{13}\)C NMR (101 MHz, Chloroform-d) \( \delta \) 180.4, 144.0, 132.8, 127.5, 122.6, 122.3, 107.7, 53.3, 40.4, 38.1, 31.5, 29.5, 26.0, 24.1, 22.6, 17.5, 14.2, 14.0.

HRMS (ESI) calcd for C\(_{18}\)H\(_{28}\)NO\(^+\) [(M+H)\(^+\)] 274.2165, found 274.2165.

**HPLC-Data:** CHIRALPAK IC, 25 °C, iPrOH-hexanes 20/80, 1 mL/min, 254 nm, \( t_R\) (major) = 4.6 min, \( t_R\) (minor) = 5.3 min.

(R)-3-Hexyl-1-methyl-3-phenylindolin-2-one (3fa).

The title compound was isolated as a pale yellow oil in 61% yield (37.6 mg, 88% ee) starting from the carbamoyl chloride 1f (54.3 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

\(^1\)H NMR (400 MHz, Chloroform-d) \( \delta \) 7.40 – 7.18 (m, 7H), 7.11 (td, \( J = 7.5 \), 1.1 Hz, 1H), 6.90 (d, \( J = 7.8 \) Hz, 1H), 3.22 (s, 3 H), 2.36 (td, \( J = 12.7 \), 4.4 Hz, 1H), 2.18 (td, \( J = 12.8 \), 4.2 Hz, 1H), 1.29 – 1.07 (m, 7H), 0.92 – 0.79 (m, 1H), 0.81 (t, \( J = 6.8 \) Hz, 3H).

\(^{13}\)C NMR (101 MHz, Chloroform-d) \( \delta \) 178.7, 144.0, 140.4, 132.4, 128.5 (2C), 128.1, 127.2, 126.9 (2C), 124.8, 122.6, 108.2, 56.8, 38.0, 31.5, 29.5, 26.4, 24.5, 22.6, 14.1.
HRMS (ESI) calcd for C_{21}H_{26}NO^+ [(M+H)^+] 308.2009, found 308.2008.

**HPLC-Data:** CHIRALPAK AD-H, 25 °C, iPrOH-hexanes 15/85, 1 mL/min, 254 nm, 
$tr_{(major)} = 5.6$ min, $tr_{(minor)} = 6.2$ min.

**(R)-3-Hexyl-3-(4-methoxyphenyl)-1-methylindolin-2-one (3qa).**

The title compound was isolated as a pale yellow oil in 52% yield (35.2 mg, 89% ee) starting from the carbamoyl chloride 1q (60.4 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-d) δ 7.33 (td, $J = 7.7$, 1.3 Hz, 1H), 7.28 (d, $J = 2.2$ Hz, 1H), 7.26 (d, $J = 1.7$ Hz, 1H), 7.22 (dd, $J = 7.5$, 0.6 Hz, 1H), 7.11 (td, $J = 7.5$, 1.1 Hz, 1H), 6.90 (d, $J = 7.8$ Hz, 1H), 6.84 – 6.78 (m, 2H), 3.76 (s, 3H), 3.21 (s, 3H), 2.32 (td, $J = 12.7$, 4.4 Hz, 1H), 2.14 (td, $J = 12.8$, 4.2 Hz, 1H), 1.28 – 1.06 (m, 7H), 0.93 – 0.77 (m, 1H), 0.81 (t, $J = 6.9$ Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) δ 179.0, 158.7, 144.0, 132.6, 132.5, 128.0 (2C), 124.7, 122.5, 113.8 (3C), 108.2, 56.1, 55.3, 38.1, 31.5, 29.5, 26.3, 24.5, 22.6, 14.0.

HRMS (ESI) calcd for C_{22}H_{28}NO_2^+ [(M+H)+] 338.2115, found 338.2123.

**HPLC-Data:** CHIRALPAK IC, 25 °C, iPrOH-hexanes 30/70, 1 mL/min, 254 nm, 
$tr_{(major)} = 13.1$ min, $tr_{(minor)} = 8.5$ min.

**(S)-3-Hexyl-1,3-dimethyl-6-(trifluoromethyl)indolin-2-one (3ma).**

The title compound was isolated as a pale yellow oil in 50% yield (31.3 mg, 82% ee) starting from the carbamoyl chloride 1m (55.4 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-d) δ 7.35 (d, $J = 7.7$ Hz, 1H), 7.26 (d, $J = 7.5$ Hz, 1H), 7.04 (s, 1H), 3.25 (s, 3H), 1.92 (td, $J = 12.8$, 4.6 Hz, 1H), 1.74 (td, $J = 12.9$, 4.4 Hz, 1H), 1.37 (s, 3H), 1.24 – 1.09 (m, 6H), 1.02 – 0.91 (m, 1H), 0.86 – 0.75 (m, 1H),
0.81 (t, J = 6.9 Hz, 3H).

\(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 180.5, 143.9, 138.2, 130.2 (q, \(J = 32.3\) Hz), 124.1 (q, \(J = 272.6\) Hz), 122.6, 119.5 (q, \(J = 4.1\) Hz), 104.6 (q, \(J = 3.9\) Hz), 48.6, 38.4, 31.5, 29.3, 26.3, 24.4, 23.6, 22.5, 14.0.

\(^{19}\)F NMR (471 MHz, Chloroform-\(d\)) \(\delta\) −62.26 (s, 3F).

HRMS (ESI) calcd for C\(_{17}\)H\(_{23}\)F\(_3\)NO\(^+\) [(M+H\(^+\)] 314.1726, found 314.1732.

HPLC-Data: CHIRALPAK AD-H, 25 °C, \(^{1}\)PrOH-hexanes 1/99, 1 mL/min, 254 nm, 
\(t_R\) (major) = 5.6 min, \(t_R\) (minor) = 6.3 min.

\((S)-3\)-Hexyl-1,3,6-trimethylindolin-2-one (3ra).

The title compound was isolated as a pale yellow oil in 65% yield (33.8 mg, 84% ee) starting from the carbamoyl chloride \(\text{Ir}\) (44.7 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

\(^{1}\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.04 (dd, \(J = 7.5, 1.4\) Hz, 1H), 6.88 (d, \(J = 7.4\) Hz, 1H), 6.67 (s, 1H), 3.19 (s, 3H), 2.39 (s, 3H), 1.86 (tdd, \(J = 12.2, 4.7, 1.4\) Hz, 1H), 1.70 (tdd, \(J = 13.2, 4.5, 1.4\) Hz, 1H), 1.32 (s, 3H), 1.22 – 1.08 (m, 6H), 1.04 – 0.93 (m, 1H), 0.89 – 0.77 (m, 1H), 0.81 (td, \(J = 6.9, 1.5\) Hz, 3H).

\(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 181.2, 143.4, 137.6, 131.4, 122.9, 122.2, 108.8, 48.3, 38.6, 31.6, 29.4, 26.1, 24.4, 23.9, 22.6, 21.8, 14.0.

HRMS (ESI) calcd for C\(_{17}\)H\(_{26}\)NO\(^+\) [(M+H\(^+\)] 260.2009, found 260.2008.

HPLC-Data: CHIRALPAK AD-H, 25 °C, \(^{1}\)PrOH-hexanes 2/98, 1 mL/min, 254 nm, 
\(t_R\) (major) = 5.8 min, \(t_R\) (minor) = 6.3 min.

\((S)-3\)-Hexyl-6-methoxy-1,3-dimethylindolin-2-one (3sa).

The title compound was isolated as a pale yellow oil in 55% yield (30.3 mg, 83% ee) starting from the carbamoyl chloride \(\text{Is}\) (47.9 mg) through column chromatography on
silica gel (15% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.05 (d, $J = 8.1$ Hz, 1H), 6.56 (dd, $J = 8.1$, 2.3 Hz, 1H), 6.43 (d, $J = 2.3$ Hz, 1H), 3.83 (s, 3H), 3.19 (s, 3H), 1.85 (ddd, $J = 13.3$, 12.1, 4.8 Hz, 1H), 1.68 (ddd, $J = 13.3$, 12.2, 4.5 Hz, 1H), 1.32 (s, 3H), 3.83 (s, 3H), 3.19 (s, 3H), 1.85 (ddd, $J = 13.3$, 12.1, 4.8 Hz, 1H), 1.68 (ddd, $J = 13.3$, 12.2, 4.5 Hz, 1H), 1.32 (s, 3H), 1.24 – 1.07 (m, 6H), 1.00 – 0.90 (m, 1H), 0.89 – 0.77 (m, 1H), 0.81 (t, $J = 16.9$ Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 181.5, 159.8, 144.5, 126.3, 122.9, 106.1, 95.9, 55.5, 48.0, 38.7, 31.5, 29.4, 26.1, 24.4, 23.9, 22.6, 14.0.

HRMS (ESI) calcd for C$_{17}$H$_{26}$NO$_2$ $[(M+H)^+]$ 276.1958, found 276.1961.

HPLC-Data: CHIRALPAK IB, 25 ºC, $i$PrOH-hexanes 3/97, 1 mL/min, 254 nm, $t_R$(major) = 5.1 min, $t_R$(minor) = 6.6 min.

(S)-5-Chloro-3-hexyl-1,3-dimethylindolin-2-one (3ta).

The title compound was isolated as a pale yellow oil in 56% yield (31.2 mg, 80% ee) starting from the carbamoyl chloride 1t (48.8 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.24 (dd, $J = 8.2$, 2.1 Hz, 1H), 7.14 (d, $J = 2.1$ Hz, 1H), 6.76 (d, $J = 8.2$ Hz, 1H), 3.20 (s, 3H), 1.89 (td, $J = 12.9$, 4.7 Hz, 1H), 1.69 (td, $J = 12.9$, 4.4 Hz, 1H), 1.34 (s, 3H), 1.23 – 1.08 (m, 6H), 1.02 – 0.88 (m, 1H), 0.87 – 0.74 (m, 1H), 0.82 (t, $J = 6.9$ Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 180.3, 141.9, 136.1, 127.8, 127.5, 123.0, 108.8, 48.8, 38.5, 31.5, 29.4, 26.2, 24.4, 23.7, 22.6, 14.0.

HRMS (ESI) calcd for C$_{16}$H$_{23}$ClNO$^+$ [(M+H)$^+$] 280.1463, found 280.1473.

HPLC-Data: CHIRALPAK AD-H, 25 ºC, $i$PrOH-hexanes 2/98, 1 mL/min, 254 nm, $t_R$(major) = 5.8 min, $t_R$(minor) = 6.4 min.

(S)-1-Benzyl-3-hexyl-3-methylindolin-2-one (3ua).

The title compound was isolated as a pale yellow oil in 51%
yield (32.9 mg, 80% ee) starting from the carbamoyl chloride 1u (57.0 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 7.33 – 7.21 (m, 5H), 7.19 – 7.11 (m, 2H), 7.02 (t, $J = 7.4$ Hz, 1H), 6.71 (d, $J = 7.8$ Hz, 1H), 4.99 (d, $J = 15.7$ Hz, 1H), 4.84 (d, $J = 15.6$ Hz, 1H), 1.96 (td, $J = 12.9$, 4.7 Hz, 1H), 1.77 (td, $J = 12.8$, 4.3 Hz, 1H), 1.40 (s, 3H), 1.22 – 1.10 (m, 6H), 1.09 – 1.00 (m, 1H), 0.89 – 0.77 (m, 1H), 0.81 (t, $J = 6.9$ Hz, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 181.0, 142.4, 136.2, 134.3, 128.7 (2C), 127.52, 127.49, 127.3 (2C), 122.6, 122.4, 109.0, 48.5, 43.6, 38.7, 31.5, 29.4, 24.6, 24.2, 22.5, 14.0.

HRMS (ESI) calcd for C$_{22}$H$_{27}$NONa$^+$ [(M+Na)$^+$] 344.1985, found 344.1985.

HPLC-Data: CHIRALPAK AD-H, 25 °C, iPrOH-hexanes 10/90, 1 mL/min, 254 nm, $t_R$(major) = 5.8 min, $t_R$(minor) = 7.3 min.

(S)-3-(4-Chlorobutyl)-1,3-dimethylindolin-2-one (3bd).

The title compound was isolated as a pale yellow oil in 62% yield (31.1 mg, 82% ee) starting from the carbamoyl chloride 1b (41.9 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.28 (td, $J = 7.6$, 1.3 Hz, 1H), 7.18 (dd, $J = 7.4$, 1.3 Hz, 1H), 7.08 (td, $J = 7.5$, 1.0 Hz, 1H), 6.85 (dt, $J = 7.7$, 0.7 Hz, 1H), 3.40 (td, $J = 6.8$, 1.7 Hz, 2H), 3.22 (s, 3H), 1.91 (td, $J = 12.8$, 5.0 Hz, 1H), 1.76 (td, $J = 12.5$, 4.6 Hz, 1H), 1.71 – 1.58 (m, 2H), 1.36 (s, 3H), 1.17 – 0.95 (m, 2H).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 180.6, 143.3, 133.8, 127.8, 122.6, 122.5, 108.0, 48.3, 44.5, 37.6, 32.6, 26.2, 23.8, 22.0.

HRMS (ESI) calcd for C$_{14}$H$_{19}$CINO$^+$ [(M+H)$^+$] 252.1150, found 252.1157.

HPLC-Data: CHIRALPAK AD-H, 25 °C, iPrOH-hexanes 2/98, 1 mL/min, 254 nm, $t_R$(major) = 11.3 min, $t_R$(minor) = 12.5 min.
(S)-6-(1,3-Dimethyl-2-oxoindolin-3-yl)hexanenitrile (3bf).

The title compound was isolated as a pale yellow oil in 63% yield (32.3 mg, 81% ee) starting from the carbamoyl chloride 1b (41.9 mg) through column chromatography on silica gel (20% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-d) δ 7.28 (td, $J = 7.7$, 1.3 Hz, 1H), 7.16 (ddd, $J = 7.3$, 1.4, 0.6 Hz, 1H), 7.08 (td, $J = 7.5$, 1.0 Hz, 1H), 6.85 (dt, $J = 7.8$, 0.8 Hz, 1H), 3.22 (s, 3H), 2.23 (t, $J = 7.1$ Hz, 2H), 1.92 (ddd, $J = 13.3$, 12.1, 4.8 Hz, 1H), 1.73 (ddd, $J = 13.3$, 12.2, 4.5 Hz, 1H), 1.58 – 1.47 (m, 2H), 1.40 – 1.28 (m, 2H), 1.35 (s, 3H), 1.07 – 0.95 (m, 1H), 0.92 – 0.82 (m, 1H).

$^{13}$C NMR (101 MHz, Chloroform-d) δ 180.6, 143.3, 133.9, 127.8, 122.6, 122.4, 119.6, 108.0, 48.3, 38.0, 28.6, 26.2, 25.0, 23.9, 23.7, 17.0.

HPLC-Data: CHIRALPAK AD-H, 25 °C, iPrOH-hexanes 10/90, 1 mL/min, 254 nm, $t_R$(major) = 9.2 min, $t_R$(minor) = 9.8 min.

HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{21}\text{N}_2\text{O}^+ [(\text{M}+\text{H})^+]$ 257.1648, found 257.1653.

(S)-1,3-Dimethyl-3-(4-(4-(methylsulfonyl)phenoxy)butyl)indolin-2-one (3bi).

The title compound was isolated as a pale yellow oil in 73% yield (56.5 mg, 86% ee) starting from the carbamoyl chloride 1b (41.9 mg) through column chromatography on silica gel (50% EtOAc in petroleum ether).

$^1$H NMR (500 MHz, Chloroform-d) δ 7.85 – 7.79 (m, 2H), 7.28 (td, $J = 7.7$, 1.1 Hz, 1H), 7.18 (d, $J = 7.1$ Hz, 1H), 7.08 (t, $J = 7.5$ Hz, 1H), 6.94 – 6.90 (m, 2H), 6.86 (d, $J = 7.8$ Hz, 1H), 3.89 (t, $J = 6.5$ Hz, 2H), 3.22 (s, 3H), 3.02 (s, 3H), 1.98 (td, $J = 12.7$, 4.7 Hz, 1H), 1.81 (td, $J = 12.8$, 4.4 Hz, 1H), 1.75 – 1.60 (m, 2H), 1.37 (s, 3H), 1.20 – 1.11 (m, 1H), 1.09 – 0.98 (m, 1H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 180.6, 163.1, 143.3, 133.9, 132.0, 129.5 (2C), 127.8, 122.6, 122.5, 114.9 (2C), 108.1, 68.0, 48.4, 44.9, 38.1, 29.0, 26.2, 23.9, 21.1.

HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{25}\text{NO}_4\text{SSNa}^+ [(\text{M}+\text{Na})^+]$ 410.1397, found 410.1403.
HPLC-Data: CHIRALPAK AD-H, 25 °C, iPrOH-hexanes 40/60, 1 mL/min, 254 nm, $t_R$(major) = 9.8 min, $t_R$(minor) = 8.6 min.

(S)-3-(4-(2-(Hydroxymethyl)phenoxy)butyl)-1,3-dimethylindolin-2-one (3bk).

The title compound was isolated as a pale yellow oil in 46% yield (31.2 mg, 83% ee) starting from the carbamoyl chloride 1b (41.9 mg) through column chromatography on silica gel (60% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.30 – 7.15 (m, 4H), 7.07 (td, $J$ = 7.5, 1.0 Hz, 1H), 6.91 (td, $J$ = 7.4, 1.1 Hz, 1H), 6.85 (dt, $J$ = 7.7, 0.7 Hz, 1H), 6.78 (dd, $J$ = 8.2, 1.0 Hz, 1H), 4.56 (s, 2H), 3.96 – 3.85 (m, 2H), 3.21 (s, 3H), 2.39 – 2.09 (brs, 1H), 2.08 – 1.94 (m, 1H), 1.85 – 1.76 (m, 1H), 1.76 – 1.60 (m, 2H), 1.37 (s, 3H), 1.21 – 1.11 (m, 1H), 1.10 – 0.98 (m, 1H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 180.7, 156.7, 143.3, 133.9, 129.2, 128.9 (2C), 127.8, 122.6, 122.4, 120.6, 111.1, 108.1, 67.3, 62.0, 48.5, 38.0, 29.2, 26.2, 23.8, 21.1.

HRMS (ESI) calcd for C$_{21}$H$_{25}$NO$_3$Na$^+$ [(M+Na)$^+$] 362.1727, found 362.1732.

HPLC-Data: CHIRALPAK IC, 25 °C, iPrOH-hexanes 50/50, 1 mL/min, 254 nm, $t_R$(major) = 7.4 min, $t_R$(minor) = 8.5 min.

(S)-4-(4-(1,3-Dimethyl-2-oxoindolin-3-yl)butoxy)benzaldehyde (3bl).

The title compound was isolated as a pale yellow oil in 63% yield (42.5 mg, 85% ee) starting from the carbamoyl chloride 1b (41.9 mg) through column chromatography on silica gel (30% EtOAc in petroleum ether).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 9.86 (s, 1H), 7.82 – 7.75 (m, 2H), 7.32 – 7.24 (m, 1H), 7.18 (d, $J$ = 7.1 Hz, 1H), 7.07 (t, $J$ = 7.5 Hz, 1H), 6.90 (d, $J$ = 8.5 Hz, 2H), 6.85 (d, $J$ = 7.7 Hz, 1H), 3.91 (td, $J$ = 6.5, 2.7 Hz, 2H), 3.22 (s, 3H), 1.98 (td, $J$ = 12.7, 4.8 Hz, 1H), 1.81 (td, $J$ = 12.8, 4.4 Hz, 1H), 1.75 – 1.62 (m, 2H), 1.37 (s, 3H), 1.21 –
1.11 (m, 1H), 1.10 – 0.97 (m, 1H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) δ 190.8, 180.6, 164.1, 143.3, 133.9, 132.0 (2C), 129.8, 127.8, 122.6, 122.5, 114.7 (2C), 108.0, 67.9, 48.4, 38.1, 29.1, 26.2, 23.9, 21.1.

HRMS (ESI) calcd for C$_{22}$H$_{24}$NO$_3$ $[(M+H)^+]$ 338.1751, found 338.1752.

HPLC-Data: CHIRALPAK AD-H, 25 °C, iPrOH-hexanes 20/80, 1 mL/min, 254 nm, $t_R$(major) = 9.8 min, $t_R$(minor) = 11.2 min.

(S)-3-(6-(4-Acetylphenoxy)hexyl)-1,3-dimethylindolin-2-one (3bm).

The title compound was isolated as a pale yellow oil in 74% yield (55.9 mg, 85% ee) starting from the carbamoyl chloride 1b (41.9 mg) through column chromatography on silica gel (20% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-$d$) δ 7.94 – 7.88 (m, 2H), 7.27 (td, $J = 7.7$, 1.3 Hz, 1H), 7.17 (ddd, $J = 7.3$, 1.4, 0.6 Hz, 1H), 7.07 (td, $J = 7.5$, 1.0 Hz, 1H), 6.89 – 6.82 (m, 3H), 3.93 (t, $J = 6.5$ Hz, 2H), 3.21 (s, 3H), 2.55 (s, 3H), 1.99 – 1.84 (m, 1H), 1.79 – 1.62 (m, 3H), 1.42 – 1.30 (m, 2H), 1.35 (s, 3H), 1.27 – 1.18 (m, 2H), 1.07 – 0.94 (m, 1H), 0.93 – 0.81 (m, 1H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) δ 196.8, 180.8, 163.1, 143.3, 134.2, 130.6 (2C), 130.1, 127.7, 122.45, 122.46, 114.1 (2C), 107.9, 68.1, 48.4, 38.4, 29.4, 29.0, 26.4, 26.1, 25.7, 24.4, 23.9.

HRMS (ESI) calcd for C$_{24}$H$_{30}$NO$_3$ $[(M+H)^+]$ 380.2220, found 380.2225.

HPLC-Data: CHIRALPAK AD-H, 25 °C, iPrOH-hexanes 20/80, 1 mL/min, 254 nm, $t_R$(major) = 11.0 min, $t_R$(minor) = 11.9 min.
Phenyl (S)-7-(1,3-dimethyl-2-oxoindolin-3-yl)heptanoate (3bo).

The title compound was isolated as a pale yellow oil in 67% yield (48.8 mg, 84% ee) starting from the carbamoyl chloride 1b (41.9 mg) through column chromatography on silica gel (15% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-$d$) δ 7.36 (t, $J = 7.7$ Hz, 2H), 7.29 – 7.24 (m, 1H), 7.21 (t, $J = 7.4$ Hz, 1H), 7.17 (d, $J = 7.3$ Hz, 1H), 7.09 – 7.01 (m, 3H), 6.84 (d, $J = 7.8$ Hz, 1H), 3.21 (s, 3H), 2.47 (t, $J = 7.5$ Hz, 2H), 1.91 (td, $J = 12.7$, 4.7 Hz, 1H), 1.73 (td, $J = 12.8$, 4.4 Hz, 1H), 1.67 – 1.57 (m, 2H), 1.35 (s, 3H), 1.32 – 1.15 (m, 4H), 1.07 – 0.94 (m, 1H), 0.92 – 0.77 (m, 1H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) δ 180.8, 172.2, 150.7, 143.3, 134.2, 129.4 (2C), 127.7, 125.7, 122.48, 122.46, 121.6 (2C), 107.9, 48.4, 38.4, 34.3, 29.4, 28.8, 26.1, 24.8, 24.3, 23.9.

HRMS (ESI) calcd for C$_{23}$H$_{28}$NO$_3^+$ [(M+H)$^+$] 366.2064, found 366.2069.

HPLC-Data: CHIRALPAK AD-H, 25 °C, iPrOH-hexanes 10/90, 1 mL/min, 254 nm, $t_R$(major) = 9.6 min, $t_R$(minor) = 10.4 min.

4-(Methylthio)phenyl (S)-7-(1,3-dimethyl-2-oxoindolin-3-yl)heptanoate (3br).

The title compound was isolated as a pale yellow oil in 75% yield (61.6 mg, 84% ee) starting from the carbamoyl chloride 1b (41.9 mg) through column chromatography on silica gel (20% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-$d$) δ 7.29 – 7.22 (m, 3H), 7.17 (dd, $J = 7.3$, 1.2 Hz, 1H), 7.06 (td, $J = 7.5$, 1.1 Hz, 1H), 7.01 – 6.93 (m, 2H), 6.84 (dt, $J = 7.7$, 0.7 Hz, 1H), 3.21 (s, 3H), 2.46 (s, 3H), 2.46 (t, $J = 7.5$ Hz, 2H), 1.90 (td, $J = 12.8$, 4.7 Hz, 1H), 1.73 (td, $J = 12.8$, 4.4 Hz, 1H), 1.67 – 1.57 (m, 2H), 1.35 (s, 3H), 1.31 – 1.16 (m, 4H), 1.07 – 0.94 (m, 1H), 0.91 – 0.78 (m, 1H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) δ 180.8, 172.2, 148.5, 143.3, 135.5, 134.2, 128.0 (2C), 127.7, 122.48, 122.46, 122.1 (2C), 107.9, 48.4, 38.4, 34.2, 29.3, 28.8, 26.1, 24.8, 24.3, 23.9, 16.5.
HRMS (ESI) calcd for C_{24}H_{30}NO_{3}S\^+ [(M+H)^+] 412.1941, found 412.1948.

HPLC-Data: CHIRALPAK AD-H, 25 °C, \textsuperscript{1}PrOH-hexanes 20/80, 1 mL/min, 254 nm, \( t_R \) (major) = 9.2 min, \( t_R \) (minor) = 9.9 min.

4-(Trifluoromethyl)phenyl (S)-7-(1,3-dimethyl-2-oxoindolin-3-yl)heptanoate (3bv).

The title compound was isolated as a pale yellow oil in 59% yield (51.1 mg, 85% ee) starting from the carbamoyl chloride 1b (41.9 mg) through column chromatography on silica gel (15% EtOAc in petroleum ether).

\( ^1\text{H} \text{NMR} \quad (500 \text{ MHz}, \text{Chloroform-d}) \quad \delta \quad 7.56 \text{ (d, } J = 8.4 \text{ Hz, 2H)}, \quad 7.23 - 7.16 \text{ (m, 1H)}, \quad 7.13 - 7.07 \text{ (m, 3H)}, \quad 6.99 \text{ (t, } J = 7.5 \text{ Hz, 1H)}, \quad 6.77 \text{ (d, } J = 7.7 \text{ Hz, 1H)}, \quad 3.14 \text{ (s, 3H)}, \quad 2.42 \text{ (t, } J = 7.5 \text{ Hz, 2H)}, \quad 1.84 \text{ (td, } J = 12.8, 4.6 \text{ Hz, 1H)}, \quad 1.66 \text{ (td, } J = 12.8, 4.4 \text{ Hz, 1H)}, \quad 1.60 - 1.52 \text{ (m, 2H)}, \quad 1.28 \text{ (s, 3H)}, \quad 1.24 - 1.11 \text{ (m, 4H)}, \quad 0.98 - 0.87 \text{ (m, 1H)}, \quad 0.84 - 0.73 \text{ (m, 1H)}.

\( ^{13}\text{C} \text{NMR} \quad (126 \text{ MHz}, \text{Chloroform-d}) \quad \delta \quad 180.8, \quad 171.7, \quad 153.2, \quad 143.3, \quad 134.2, \quad 128.0 \text{ (q, } J = 32.7 \text{ Hz)}, \quad 127.7, \quad 126.8 \text{ (q, } J = 4.0 \text{ Hz, 2C}), \quad 123.9 \text{ (q, } J = 272.3 \text{ Hz)}, \quad 122.48, \quad 122.45, \quad 122.1 \text{ (2C)}, \quad 107.9, \quad 48.4, \quad 38.4, \quad 34.2, \quad 29.3, \quad 28.7, \quad 26.1, \quad 24.7, \quad 24.3, \quad 23.9.

\( ^{19}\text{F} \text{NMR} \quad (376 \text{ MHz, Chloroform-d}) \quad \delta \quad -62.21 \text{ (s, 3F)}.

HRMS (ESI) calcd for C_{24}H_{27}F_{3}NO_{3}^+ [(M+H)^+] 434.1938, found 434.1942.

HPLC-Data: CHIRALPAK AD-H, 25 °C, \textsuperscript{1}PrOH-hexanes 10/90, 1 mL/min, 254 nm, \( t_R \) (major) = 8.2 min, \( t_R \) (minor) = 8.9 min.

(E)-Hex-2-en-1-yl (S)-7-(1,3-dimethyl-2-oxoindolin-3-yl)heptanoate (3bx).

The title compound was isolated as a pale yellow oil in 71% yield (52.6 mg, 85% ee) starting from the carbamoyl chloride 1b (41.9 mg) through column chromatography on silica gel (15% EtOAc in
petroleum ether).

\(^{1}H\) NMR (500 MHz, Chloroform-\(d\)) \(\delta 7.30 - 7.23 \) (m, 1H), 7.16 (d, \(J = 7.3\) Hz, 1H), 7.06 (t, \(J = 7.4\) Hz, 1H), 6.84 (d, \(J = 7.7\) Hz, 1H), 5.74 (dt, \(J = 14.7, 6.7\) Hz, 1H), 5.54 (dt, \(J = 14.3, 6.6\) Hz, 1H), 4.48 (d, \(J = 6.5\) Hz, 2H), 3.21 (s, 3H), 2.22 (t, \(J = 7.5\) Hz, 2H), 1.88 (td, \(J = 12.8, 4.6\) Hz, 1H), 1.71 (td, \(J = 12.9, 4.4\) Hz, 1H), 1.55 – 1.45 (m, 2H), 1.45 – 1.36 (m, 2H), 1.34 (s, 3H), 1.23 – 1.11 (m, 4H), 1.01 – 0.93 (m, 1H), 0.89 (t, \(J = 7.4\) Hz, 3H), 0.85 – 0.75 (m, 1H).

\(^{13}C\) NMR (126 MHz, Chloroform-\(d\)) \(\delta 180.8, 173.6, 143.3, 136.3, 134.2, 127.6, 124.0, 122.5\) (2C), 107.9, 65.1, 48.4, 38.5, 34.31, 34.25, 29.4, 28.9, 26.1, 24.9, 24.3, 23.8, 22.1, 13.7.

HRMS (ESI) calcd for C\(_{23}\)H\(_{34}\)NO\(_{3}\) \([\text{M+H}]^+\) 372.2533, found 372.2536.

HPLC-Data: CHIRALPAK AD-H, 25 °C, \(\text{iPrOH-hexanes} 10/90\), 1 mL/min, 254 nm, \(t_R\)(major) = 5.4 min, \(t_R\)(minor) = 5.8 min.

((S))-5-(1,3-dimethyl-2-oxoindolin-3-yl)pentyl acetate (3by).

The title compound was isolated as a pale yellow oil in 56% yield (32.2 mg, 84% ee) starting from the carbamoyl chloride 1b (41.9 mg) through column chromatography on silica gel (20% EtOAc in petroleum ether).

\(^{1}H\) NMR (400 MHz, Chloroform-\(d\)) \(\delta 7.31 - 7.24 \) (m, 1H), 7.16 (ddd, \(J = 7.4, 1.3, 0.6\) Hz, 1H), 7.07 (td, \(J = 7.5, 1.0\) Hz, 1H), 6.85 (dt, \(J = 7.7, 0.8\) Hz, 1H), 3.94 (t, \(J = 6.7\) Hz, 2H), 3.22 (s, 3H), 2.00 (s, 3H), 1.90 (td, \(J = 12.5, 4.7\) Hz, 1H), 1.73 (td, \(J = 12.5, 4.6\) Hz, 1H), 1.52 – 1.43 (m, 2H), 1.35 (s, 3H), 1.29 – 1.13 (m, 2H), 1.08 – 0.95 (m, 1H), 0.90 – 0.79 (m, 1H).

\(^{13}C\) NMR (101 MHz, Chloroform-\(d\)) \(\delta 180.7, 171.1, 143.3, 134.1, 127.7, 122.5, 122.4, 107.9, 64.4, 48.4, 38.3, 28.3, 26.11, 26.05, 24.2, 23.8, 21.0.

HRMS (ESI) calcd for C\(_{17}\)H\(_{24}\)NO\(_{3}\) \([\text{M+H}]^+\) 290.1751, found 290.1756.

HPLC-Data: CHIRALPAK IC, 25 °C, \(\text{iPrOH-hexanes} 40/60\), 1 mL/min, 254 nm, \(t_R\)(major) = 11.1 min, \(t_R\)(minor) = 12.6 min.
(S)-3-(Cyclohexylmethyl)-1,3-dimethylindolin-2-one (3bz).

The title compound was isolated as a pale yellow oil in 53% yield (27.3 mg, 84% ee) starting from the carbamoyl chloride 1b (41.9 mg) through column chromatography on silica gel (10% EtOAc in petroleum ether).

$^1$H NMR (500 MHz, Chloroform-$d$) δ 7.30 – 7.23 (m, 1H), 7.16 (d, $J = 7.3$ Hz, 1H), 7.06 (t, $J = 7.5$ Hz, 1H), 6.85 (d, $J = 7.7$ Hz, 1H), 3.22 (s, 3H), 1.93 (dd, $J = 14.0, 7.0$ Hz, 1H), 1.73 (dd, $J = 14.0, 5.2$ Hz, 1H), 1.56 – 1.43 (m, 3H), 1.39 – 1.30 (m, 1H), 1.31 (s, 3H), 1.24 – 1.17 (m, 1H), 1.02 – 0.89 (m, 4H), 0.87 – 0.80 (m, 1H), 0.79 – 0.70 (m, 1H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) δ 181.2, 143.1, 134.4, 127.5, 122.7, 122.3, 108.0, 47.9, 45.4, 34.8, 34.5, 33.5, 26.22, 26.18, 26.1 (2C), 26.0.

HRMS (ESI) calcd for C$_{17}$H$_{24}$NO + [(M+H)$^+$] 258.1852, found 258.1856.

HPLC-Data: CHIRALPAK AD-H, 25 °C, $^4$PrOH-hexanes 2/98, 1 mL/min, 254 nm, $t_R$(major) = 8.5 min, $t_R$(minor) = 9.3 min.

(S)-1,3-Dimethyl-3-((tetrahydro-2H-pyran-4-yl)methyl)indolin-2-one (3baa).

The title compound was isolated as a pale yellow oil in 49% yield (25.5 mg, 83% ee) starting from the carbamoyl chloride 1b (41.9 mg) through column chromatography on silica gel (15% EtOAc in petroleum ether).

$^1$H NMR (400 MHz, Chloroform-$d$) δ 7.28 (t, $J = 7.7$ Hz, 1H), 7.17 (d, $J = 7.3$ Hz, 1H), 7.07 (t, $J = 7.5$ Hz, 1H), 6.86 (d, $J = 7.7$ Hz, 1H), 3.81 – 3.65 (m, 2H), 3.23 (s, 3H), 3.17 – 3.02 (m, 2H), 2.00 (dd, $J = 14.1, 5.6$ Hz, 1H), 1.78 (dd, $J = 14.1, 4.9$ Hz, 1H), 1.34 (s, 3H), 1.28 – 0.96 (m, 5H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) δ 180.8, 143.0, 134.1, 127.8, 122.7, 122.5, 108.1, 67.72, 67.69, 47.7, 44.9, 34.0, 33.4, 32.2, 26.3, 26.1.

HRMS (ESI) calcd for C$_{16}$H$_{22}$NO$_2$ + [(M+H)$^+$] 260.1645, found 260.1651.

HPLC-Data: CHIRALPAK AD-H, 25 °C, $^4$PrOH-hexanes 10/90, 1 mL/min, 254 nm,
$t_R$(major) = 6.7 min, $t_R$(minor) = 7.2 min.

(S)-1,3-Dimethyl-3-phenethylindolin-2-one (3bac).

The title compound was isolated as a pale yellow oil in 50% yield (26.6 mg, 85% ee) starting from the carbamoyl chloride 1b (41.9 mg) through column chromatography on silica gel (15% EtOAc in petroleum ether).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 7.30 (t, $J = 7.7$ Hz, 1H), 7.24 – 7.17 (m, 3H), 7.15 – 7.08 (m, 2H), 7.02 (d, $J = 7.4$ Hz, 2H), 6.87 (d, $J = 7.7$ Hz, 1H), 3.21 (s, 3H), 2.34 – 2.22 (m, 2H), 2.17 – 2.08 (m, 1H), 2.06 – 1.97 (m, 1H), 1.39 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 180.4, 143.5, 141.4, 133.8, 128.31 (2C), 128.26 (2C), 127.9, 125.9, 122.6, 122.5, 108.0, 48.4, 40.3, 31.0, 26.2, 24.0.

HRMS (ESI) calcd for C$_{18}$H$_{20}$NO$^+$ [(M+H)$^+$] 266.1539, found 266.1542.

HPLC-Data: CHIRALCEL OD-H, 25 °C, iPrOH-hexanes 10/90, 1 mL/min, 254 nm, $t_R$(major) = 7.6 min, $t_R$(minor) = 6.1 min.
Supplementary Figure 7. Coupling reaction of carbamate 4 with \( n \)-pentyl iodide (2a)

\[
\begin{align*}
\text{L12} & \quad (8.2 \text{ mg, 0.04 mmol, 20 mol\%}) \quad \text{and methyl methyl(2-(3-methylbut-1-en-2-yl)phenyl)carbamate (4)} \quad (46.7 \text{ mg, 0.2 mmol, 1 equiv}) \quad \text{were added to a reaction tube equipped with a stir bar. In a nitrogen-filled glovebox, NiBr}_2 \cdot \text{glyme (12.3 mg, 0.04 mmol, 20 mol\%)} \quad \text{and manganese dust (22 mg, 0.4 mmol, 2 equiv) were added to the mixture. The reaction tube was sealed and removed from the glovebox. Next, anhydrous DMAc (1.2 mL) and N-methyl morpholine (0.3 mL) were added, followed by the addition of 1-iodopentane 2a (79.2 mg, 0.4 mmol, 2.0 equiv) under the protection of nitrogen. Then the resulting mixture was stirred at 25 °C for 24 h. The reaction was quenched with sat. aq. NH}_4\text{Cl solution (5 mL) and diluted with water (10 mL). The aqueous layer was extracted three times with EtOAc, and the combined organic layers were washed with brine (20 mL), dried over MgSO}_4, filtered, and concentrated under reduced pressure. No reaction occurred to the carbamate 4 according to TLC analysis.}
\end{align*}
\]

Supplementary Figure 8. Stoichiometric reaction of the carbamoyl chloride 1c with Ni(COD)\(_2\)

\[
\begin{align*}
\text{L12} & \quad (57.9 \text{ mg, 0.2 mmol, 1 equiv}) \quad \text{and the carbamic chloride 1c (44.7 mg, 0.2 mmol, 1 equiv}) \quad \text{were added to a reaction tube equipped with a stir bar. Next, anhydrous DMAc (1.2 mL) and N-methyl morpholine (0.3 mL) were added under the protection of nitrogen. Subsequently, the reaction mixture was brought into a nitrogen-filled glovebox, and Ni(COD)\(_2\) (55 mg, 0.2 mmol, 1 equiv) was added to the mixture. The}
\end{align*}
\]
reaction tube was sealed and removed from the glovebox. After the resulting mixture was stirred at 25 °C for 1 h, the reaction was quenched with sat. aq. NH₄Cl solution (5 mL) and diluted with water (10 mL). The aqueous layer was extracted three times with EtOAc, and the combined organic layers were washed with brine (20 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford the desired product (R)-3-ethyl-1,3-dimethylindolin-2-one (6) in 49% yield (18.5 mg, 60% ee).

(R)-3-ethyl-1,3-dimethylindolin-2-one (6)

\[ ^1H \text{NMR (500 MHz, Chloroform-}d) \delta 7.27 (t, J = 7.7 \text{ Hz, 1H}), 7.17 (d, J = 7.3 \text{ Hz, 1H}), 7.07 (t, J = 7.4 \text{ Hz, 1H}), 6.84 (d, J = 7.8 \text{ Hz, 1H}), 3.22 (s, 3H), 1.93 (dq, J = 14.5, 7.4 \text{ Hz, 1H}), 1.77 (dq, J = 14.5, 7.4 \text{ Hz, 1H}), 1.35 (s, 3H), 0.59 (t, J = 7.4 \text{ Hz, 3H}). \]

\[ ^{13}C \text{NMR (126 MHz, Chloroform-}d) \delta 180.8, 143.5, 134.0, 127.6, 122.5, 122.4, 107.8, 49.0, 31.5, 26.1, 23.3, 8.9. \]

HRMS (ESI) calcd for C₁₂H₁₆NO \[(\text{M+H})^+\] 190.1226, found 190.1226.

HPLC-Data: CHIRALCEL OJ-H, 25 °C, iPrOH-hexanes 2/98, 1 mL/min, 254 nm, \( t_R \) (major) = 7.2 min, \( t_R \) (minor) = 7.7 min.

Supplementary Figure 9. Coupling reaction of the carbamoyl chloride 7 with \( n \)-pentyl iodide (2a)

\[
\begin{align*}
\text{7} & \quad \text{NiBr}_2\text{-glyme (20 mol\%)} \\
\text{Me} & \quad \text{L1 (20 mol\%)} \\
\text{N} & \quad \text{DMAc/NMM = 4:1 (0.13 M)} \\
+ \quad \text{Mn (2 equiv)} \\
\text{Me} & \quad \text{2a (2 equiv)} \\
\text{25 °C, 24 h} & \quad \rightarrow \\
\text{8} & \quad \text{NiBr}_2\text{-glyme (20 mol\%)}
\end{align*}
\]

Racemic L1 (8.2 mg, 0.04 mmol, 20 mol%) and methyl(phenyl)carbamic chloride (7) (33.9 mg, 0.2 mmol, 1 equiv) were added to a reaction tube equipped with a stir bar and brought into a nitrogen-filled glovebox. NiBr₂ • glyme (12.3 mg, 0.04 mmol, 20 mol%) and manganese dust (22 mg, 0.4 mmol, 2 equiv) were added to the mixture. The reaction tube was sealed and removed from the glovebox. Next, anhydrous DMAc (1.2 mL) and N-methyl morpholine (0.3 mL) were added, followed by the
addition of 1-iodopentane 2a (79.2 mg, 0.4 mmol, 2.0 equiv) under the protection of nitrogen. After the resulting mixture was stirred at 25 °C for 24 h, the reaction was quenched with sat. aq. NH₄Cl solution (5 mL) and further diluted with water (10 mL). The aqueous layer was extracted three times with EtOAc, and the combined organic layers were washed with brine (20 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure. The formation of the cross-coupling product 8 was not observed.

Supplementary Figure 10. Radical clock experiment of the carbamoyl chloride 1a with 6-iodohex-1-ene (2ai)

Racemic L1 (20 mol%) and the carbamic chloride 1a (47.5 mg, 0.2 mmol, 1 equiv) were added to a reaction tube equipped with a stir bar and brought into a nitrogen-filled glovebox. NiBr₂ · glyme (12.3 mg, 0.04 mmol, 20 mol%) and manganese dust (22 mg, 0.4 mmol, 2 equiv) were added to the mixture. The reaction tube was sealed and removed from the glovebox. Next, anhydrous DMAC (1.2 mL) and N-methyl morpholine (0.3 mL) were added, followed by the addition of 6-iodohex-1-ene 2ai (84.0 mg, 0.4 mmol, 2.0 equiv) under the protection of nitrogen. After the resulting mixture was stirred at 25 °C for 24 h, the reaction was quenched with sat. aq. NH₄Cl solution (5 mL) and further diluted with water (10 mL). The aqueous layer was extracted three times with EtOAc, and the combined organic layers were washed with brine (20 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford 3-(2-cyclopentylethyl)-3-isopropyl-1-methyl indolin-2-one (3aai) as a pale yellow oil in 22% yield (12.6 mg).

¹H NMR (500 MHz, Chloroform-d) δ 7.30 – 7.24 (m, 1H), 7.16 (d, J = 7.4 Hz, 1H), 7.05 (t, J = 7.5 Hz, 1H), 6.82 (d, J = 7.7 Hz, 1H), 3.20 (s, 3H), 2.20 – 2.06 (m, 1H), 1.95 – 1.79 (m, 3H), 1.71 – 1.55 (m, 2H), 1.53 – 1.38 (m, 2H), 1.25 – 1.08 (m, 3H),
1.04 – 0.81 (m, 2H), 0.96 (d, J = 6.8 Hz, 3H), 0.77 – 0.62 (m, 1H), 0.67 (d, J = 6.6 Hz, 3H).

**HRMS (ESI)** calcd for C_{19}H_{27}NONa^{+} [(M+Na)^{+}] 308.1985, found 308.1992.

Supplementary Figure 11. Determination of the Absolute Configuration of the Carbo-Acylation Products

The carbamoyl chloride 1b was subjected to the alkyl-carbamoylation with benzyl chloride under the standard reaction conditions, affording the oxindole 3bac as the product. It is known in the literature that the compound 3bac with S-configuration can be synthesized through Pd-catalyzed asymmetric alkenylation of an oxindole followed by hydrogenation.\(^\text{[11]}\) The absolute configuration of compound 3bac prepared using our method was determined to be S through comparison of the HPLC data with these reported in the literature.\(^\text{[a]}\) The absolute stereochemistry of all the other alkyl-carbamoylation products were assigned assuming a common reaction pathway.

\[^{[\text{a}]}\text{Our HPLC-Data: CHIRALCEL OD-H, 25 °C, iPrOH-hexanes 10/90, 1 mL/min, 254 nm, t}_R(\text{major}) = 7.6 \text{ min, } t_R(\text{minor}) = 6.1 \text{ min.} \]

\[^{[\text{a}]}\text{Reported HPLC-Data: CHIRALCEL OD-H, 25 °C, iPrOH-hexanes 10/90, 1 mL/min, 254 nm, t}_R(\text{major}) = 7.4 \text{ min, } t_R(\text{minor}) = 6.1 \text{ min.} \]
Supplementary Figure 12

Integration Results

| No. | Peak Name | Retention Time | Area  | Height | Relative Area | Relative Height | Amount |
|-----|-----------|----------------|-------|--------|---------------|-----------------|--------|
| 1   |           | 8.100 min      | 150.363 | 907.371 | 49.84 %       | 53.85 %         | n.a.   |
| 2   |           | 8.857 min      | 151.309 | 777.644 | 59.16 %       | 46.15 %         | n.a.   |
| Total|           |                | 301.662 | 1685.016 | 100.00 %      | 100.00 %        | n.a.   |

Integration Results

| No. | Peak Name | Retention Time | Area  | Height | Relative Area | Relative Height | Amount |
|-----|-----------|----------------|-------|--------|---------------|-----------------|--------|
| 1   |           | 8.267 min      | 117.707 | 719.163 | 92.46 %       | 93.99 %         | n.a.   |
| 2   |           | 9.133 min      | 9.595  | 46.794 | 7.54 %        | 6.11 %          | n.a.   |
| Total|           |                | 127.302 | 765.958 | 100.00 %      | 100.00 %        | n.a.   |
Supplementary Figure 13
Supplementary Figure 14.
Supplementary Figure 15.

### Integration Results

| No. | Peak Name | Retention Time (min) | Area (mAU*min) | Height (mAU) | Relative Area (%) | Relative Height (%) | Amount |
|-----|-----------|----------------------|----------------|--------------|-------------------|---------------------|--------|
| 1   |           | 5.647                | 48,400         | 415.955      | 50.03             | 52.81               | n.a.   |
| 2   |           | 6.187                | 48,340         | 371.624      | 49.97             | 47.19               | n.a.   |
| Total|           |                      |                | 96,740       |                   |                     |        |

### Integration Results

| No. | Peak Name | Retention Time (min) | Area (mAU*min) | Height (mAU) | Relative Area (%) | Relative Height (%) | Amount |
|-----|-----------|----------------------|----------------|--------------|-------------------|---------------------|--------|
| 1   |           | 5.620                | 38,111         | 328.646      | 93.67             | 94.45               | n.a.   |
| 2   |           | 6.166                | 2,411          | 19,301       | 6.13              | 6.55                | n.a.   |
| Total|           |                      |                | 40,598       |                   |                     |        |
Supplementary Figure 16.
Supplementary Figure 17.
Supplementary Figure 18.
Supplementary Figure 19.
Supplementary Figure 20.
Supplementary Figure 21.
Supplementary Figure 22.
Supplementary Figure 23.
Supplementary Figure 24.

| No. | Peak Name | Retention Time (min) | Area (mAU/min) | Height (mAU) | Relative Area (%) | Relative Height (%) | Amount (n.a.) |
|-----|-----------|----------------------|----------------|--------------|------------------|----------------------|---------------|
| 1   |           | 8.660                | 51147          | 196104       | 49.97            | 54.31                | n.a.          |
| 2   |           | 9.793                | 51295          | 164843       | 50.63            | 45.69                | n.a.          |
|     | Total:    |                      | 102351         | 351087       | 100.00           | 100.00               | n.a.          |

| No. | Peak Name | Retention Time (min) | Area (mAU/min) | Height (mAU) | Relative Area (%) | Relative Height (%) | Amount (n.a.) |
|-----|-----------|----------------------|----------------|--------------|------------------|----------------------|---------------|
| 1   |           | 8.647                | 45008          | 13285        | 7.23             | 8.41                 | n.a.          |
| 2   |           | 9.773                |                | 144030       | 92.80            | 91.59                | n.a.          |
|     | Total:    |                      | 40490          | 157915       | 100.00           | 100.00               | n.a.          |
Supplementary Figure 25.
Supplementary Figure 26.
Supplementary Figure 27.
Supplementary Figure 28.
Supplementary Figure 29.
Supplementary Figure 30.
Supplementary Figure 31.
Supplementary Figure 32.
Supplementary Figure 33.
Supplementary Figure 34.
Supplementary Figure 35.
Supplementary Figure 36.
Supplementary Figure 38

![Chemical structure of 1a](image)

**Chemical Shifts**
- 1H: 1.13, 4.93
- 13C: 10.84, 22.61, 39.61, 96.81

**NMR Spectrogram**

**f1 (ppm)**
- 90, 180, 170, 160, 150, 140, 130, 120, 110, 100, 90, 80, 70, 60, 50, 40, 30, 20, 10, 0, -10
Supplementary Figure 39
Supplementary Figure 42

![NMR spectrum of compound 1d]

S101
Supplementary Figure 43
Supplementary Figure 44
Supplementary Figure 45
Supplementary Figure 50
Supplementary Figure 51
Supplementary Figure 52

![Chemical Structure](image)

1j

S111
Supplementary Figure 55
Supplementary Figure 56
Supplementary Figure 58
Supplementary Figure 59
Supplementary Figure 60
Supplementary Figure 62
Supplementary Figure 65

![Supplementary Figure 65](image-url)
Supplementary Figure 66

[Chemical structure image]

S125
Supplementary Figure 67

S126
Supplementary Figure 69
Supplementary Figure 70

![Chemical structure diagram](image-url)
Supplementary Figure 71
Supplementary Figure 72
Supplementary Figure 73
Supplementary Figure 74

The image contains a nuclear magnetic resonance (NMR) spectrum of a compound labeled as 1u. The spectrum is plotted against ppm (parts per million) on the x-axis. The compound structure includes a benzene ring with substituents at specific positions indicated by chemical shifts. The spectrum shows multiple peaks corresponding to different chemical environments within the molecule.
Supplementary Figure 76
Supplementary Figure 79
Supplementary Figure 83
Supplementary Figure 85

The image contains a spectrum with peaks labeled at various ppm values, along with a chemical structure labeled as 2s.
Supplementary Figure 87
Supplementary Figure 88
Supplementary Figure 89
Supplementary Figure 93

2v
Supplementary Figure 94

\[ \text{Chemical Structure: } \begin{align*}
\text{2v} & \quad \text{O} \quad \text{CF}_3 \\
\text{Me} & \quad \text{O} \\
\end{align*} \]
Supplementary Figure 95

![Supplementary Figure 95](image_url)
Supplementary Figure 96

2w
Supplementary Figure 97
Supplementary Figure 99

L12
Supplementary Figure 101
Supplementary Figure 102

3aa
Supplementary Figure 104

3ba
Supplementary Figure 106

![Chemical structure of compound 3ca](image)

![NMR spectrum](image)
Supplementary Figure 107
Supplementary Figure 108
Supplementary Figure 111

3fa
Supplementary Figure 112

3fa
Supplementary Figure 113

3ga
Supplementary Figure 115
Supplementary Figure 117
Supplementary Figure 118
Supplementary Figure 119

[Chemical structure image]

3ja
Supplementary Figure 120

3ja

S179
Supplementary Figure 125
Supplementary Figure 126
Supplementary Figure 128

3ma

S187
Supplementary Figure 130

3na
Supplementary Figure 132

30a

S191
Supplementary Figure 134

3pa
Supplementary Figure 135

3ab
Supplementary Figure 135
Supplementary Figure 137

[Chemical structure image]

3ac
Supplementary Figure 138

3ad
Supplementary Figure 139

3ad
Supplementary Figure 140

![Supplementary Figure 140](image-url)
Supplementary Figure 141

![Supplementary Figure 141](image-url)
Supplementary Figure 143
Supplementary Figure 144

[Chemical structure diagram]

3af

S204
Supplementary Figure 146
Supplementary Figure 148
Supplementary Figure 149

3ai
Supplementary Figure 152
Supplementary Figure 154
Supplementary Figure 155

[Spectroscopic data and molecule structure image]
Supplementary Figure 157

3am

S217
Supplementary Figure 161

3ao
Supplementary Figure 163

3ap
Supplementary Figure 164
Supplementary Figure 167
Supplementary Figure 168
Supplementary Figure 169
Supplementary Figure 170
Supplementary Figure 172
Supplementary Figure 173

![Graphical representation of chemical structure](image-url)
Supplementary Figure 174
Supplementary Figure 177
Supplementary Figure 180

3aw
Supplementary Figure 187

3aaa
Supplementary Figure 192
Supplementary Figure 194

[Chemical structure image]

3aad
Supplementary Figure 195
Supplementary Figure 198

3aaf
Supplementary Figure 199
Supplementary Figure 201

[Chemical structure image]

3aah
Supplementary Figure 202
Supplementary Figure 203
Supplementary Figure 205
Supplementary Figure 208

![Chemical structure diagram with proton NMR spectrum](Image)

3sa
Supplementary Figure 209

3ta
Supplementary Figure 210

3ta
Supplementary Figure 212
Supplementary Figure 213

3bd
Supplementary Figure 214
Supplementary Figure 215
Supplementary Figure 218

3bi
Supplementary Figure 221

S281
Supplementary Figure 222
Supplementary Figure 223
Supplementary Figure 224

3bm

S284
Supplementary Figure 225
Supplementary Figure 226

3bo

$^{1}$ (ppm)

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Supplementary Figure 227

3br

S287
Supplementary Figure 228
Supplementary Figure 230
Supplementary Figure 231
Supplementary Figure 233

3bx
Supplementary Figure 235

3by

S295
Supplementary Figure 237

3bz
Supplementary Figure 240

3bac
Supplementary Figure 241

3bac

S301
Supplementary Figure 244
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