Supporting information for:

Metal-free, Visible-light Induced Enantioselective Three-component Dicarbofunctionalization and Oxytrifluoromethylation of Enamines via Chiral Phosphoric Acid Catalysis

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1. General Information

All glassware was thoroughly oven-dried. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Thin-layer chromatography (TLC) plates were visualized by exposure to ultraviolet light and/or staining with phosphomolybdic acid followed by heating on a hot plate. Flash chromatography was carried out using silica gel (200-300 mesh). $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AVANCE III 400 (400 MHz) and Bruker AVANCE NEO 600 (600 MHz). The spectra were recorded in CDCl$_3$, CD$_3$OD and $d_6$-DMSO as solvent at room temperature, $^1$H and $^{13}$C NMR chemical shifts are reported in ppm relative to the residual solvent peak. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale (CDCl$_3$: $\delta_H = 7.26$ ppm, $\delta_C = 77.00$ ppm; $d_6$-DMSO: $\delta_H = 2.50$ ppm, $\delta_C = 39.60$ ppm). Data for $^1$H NMR are reported as follows: chemical shift ($\delta$ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q=quartet, m = multiplet, dd = doublet), integration, coupling constant (Hz) and assignment. Data for $^{13}$C NMR are reported as chemical shift. HRMS were performed on a Bruker Apex II mass instrument (ESI). Enantiomeric excess values were determined by HPLC with Daicel Chirapak IA column on Agilent 1260 series with i-PrOH and n-hexane. Optical rotation was measured on the Perkin Elmer 341 polarimeter with $[\alpha]$D values reported in degrees. Concentration (c) is in 0.1g/100 mL.
2. Synthesis of Substrates

Synthesis of tert-butyl vinylcarbamate:

\[ \text{N-H} \quad \text{O} \quad + \quad \text{Boc}_2\text{O} \quad \xrightarrow{\text{DMAP, NaOH aq.}} \quad \text{NHBoc} \]

To a solution of N-vinylformamide (1.4 mL, 20 mmol) in THF (60 mL) were added Boc\(_2\)O (5.24 g, 24 mmol) and DMAP (0.24 g, 2 mmol). The reaction mixture was stirred for 22 h under N\(_2\) at room temperature, and the solvent was removed under reduced pressure. The residue was dissolved in THF (10 mL), and the mixture was added 2N NaOH (10 mL) at 0 ºC for 20 min. The reaction mixture was left at 0 ºC for 10 min and then stirred at room temperature for 5 h. The reaction mixture was diluted with water (20 mL) and extracted with MTBE (30 mL×3). The combined organic phase were washed with water and brine, and concentrated under reduced pressure. The crude mixture was purified by flash chromatography (silica gel, mixtures of petroleum/ethyl acetate) to afford the pure product.

Synthesis of tert-butyl methyl(vinyl)carbamate:

\[ \text{NHBoc} + \text{MeI} \quad \xrightarrow{\text{NaH}} \quad \text{N}^{\text{Boc}} \]

A flask was charged with NaH (2.4 mmol) under N\(_2\). Dry THF (15 mL) was added and cooled to 0 ºC. A solution of tert-butyl vinylcarbamate (286 mg, 2 mmol) dissolved in THF (5 mL) was added slowly and stirred for 20 min at 0 ºC. MeI (0.19 mL, 3 mmol) was added slowly dropwise. The reaction was warmed to room temperature and stirred for 16 h. Upon completion, the reaction was quenched with NH\(_4\)Cl aq. and extracted with EA. The combined organic layers were washed with brine and dried over Na\(_2\)SO\(_4\). The crude mixture was purified by flash chromatography (silica gel, mixtures of petroleum/ethyl acetate) to afford the pure product.
3. General Procedure

3.1 General procedure for the synthesis of product 4

A dried 10 mL reaction tube was charged with the catalyst $C_1$ (5 mol%, 3.8 mg), activated 3 Å molecular sieves (50 mg), $1$ (0.1 mmol, 1.0 equiv), Togni-II $2$ (0.15 mmol, 49.5 mg) and indole $3$ (0.2 mmol, 2.0 equiv). Then THF (1.0 mL) was added via a syringe. The reaction mixture was degassed by three cycles of freeze-pump-thaw. After the mixture was thoroughly degassed, the reaction was then irradiated at -20 °C under blue LEDs. After completion of the reaction, the crude mixture was purified by flash chromatography (silica gel, mixtures of petroleum/ethyl acetate) to afford the pure product $4$.

3.2 General procedure for the synthesis of product 6

A dried 10 mL reaction tube was charged with the catalyst $C_1$ (5 mol%, 3.8 mg), activated 3 Å molecular sieves (50 mg), $1a$ (0.1 mmol, 17.7 mg, 1.0 equiv), Togni-II $2$ (0.15 mmol, 49.5 mg) and alcohols $3$ (0.1 mmol, 1.0 equiv). Then THF (1.0 mL) was added via a syringe. The reaction mixture was degassed by three cycles of freeze-pump-thaw. After the mixture was thoroughly degassed, the reaction was then irradiated at 0 °C under blue LEDs. After completion of the reaction, the crude mixture was purified by flash chromatography (silica gel, mixtures of petroleum/ethyl acetate) to afford the pure product $6$.

3.3 General procedure for the synthesis of product 8
A dried 10 mL reaction tube was charged with the catalyst C1 (5 mol%, 3.8 mg), cat-CF₃Ph (1 mmol, 0.4 mg), activated 3 Å molecular sieves (100 mg), enamine 1c (0.2 mmol, 28.6 mg), 7 (0.1 mmol), indole 3 (0.15 mmol, 1.5 equiv) and K₃PO₄ (0.1 mmol, 21.2 mg, 1.0 equiv). Then THF (0.5 mL) was added via a syringe. The reaction mixture was degassed by three cycles of freeze-pump-thaw. After the mixture was thoroughly degassed, the reaction was then irradiated at room temperature under blue LEDs. After completion of the reaction, the crude mixture was purified by flash chromatography (silica gel, mixtures of petroleum/ethyl acetate) to afford the pure product 8.
4. Screening of Reaction Conditions

### Table S1. Screening of the solvent and catalyst

| Entry | (R)-CPA (5 mol%) | Solvent (0.1 M) | Yield (%) | ee (%) |
|-------|-----------------|-----------------|------------|--------|
| 1     | C1              | CH₂Cl₂          | 46         | 86     |
| 2     | --              | CH₂Cl₂          | 11         | --     |
| 3<sup>d</sup> | C1          | CH₂Cl₂          | 0          | --     |
| 4<sup>e</sup> | C1           | CH₂Cl₂          | 35         | 82     |
| 5     | C1              | THF             | 42         | 94     |
| 6     | C1              | DCE             | 35         | 87     |
| 7     | C1              | toluene         | trace      | --     |
| 8     | C1              | MeCN            | 31         | 73     |
| 9     | C1              | DMF             | 0          | --     |
| 10    | C1              | 1,4-dioxane     | 26         | 91     |
| 11    | C1              | acetone         | 36         | 89     |
| 12    | C1              | EA              | 32         | 91     |
| 13    | C1              | Et₂O            | 34         | 90     |
| 14    | C2              | THF             | 17         | 23     |
| 15    | C3              | THF             | 0          | --     |
| 16    | C4              | THF             | 18         | 38     |
| 17    | C5              | THF             | 28         | 88     |
| 18    | C6              | THF             | 15         | 29     |
| 19    | C7              | THF             | 17         | 91     |
| 20    | C8              | THF             | 18         | 88     |
| 21    | C9              | THF             | 16         | 94     |
Table S2. Screening of the reaction ratio

| Entry | Reaction ratio | Yield (%) | ee (%) |
|-------|----------------|-----------|--------|
| 1     | 1 : 1.2 : 1.5  | 42        | 94     |
| 2     | 1 : 1.2 : 2    | 41        | 94     |
| 3     | 1 : 1.5 : 1.5  | 42        | 94     |
| 4     | 1 : 1.5 : 2    | 44        | 94     |
| 5     | 1 : 2 : 1.5    | 42        | 94     |
| 6     | 1 : 2 : 2      | 44        | 94     |
| 7     | 2 : 1 : 2      | 39        | 94     |
| 8     | 1.5 : 1.5 : 1  | 37        | 94     |
| 9     | 2 : 2 : 1      | 39        | 94     |

Table S3. Screening of the concentration and the loading of the catalyst

| Entry | THF   | Yield (%) | ee (%) |
|-------|-------|-----------|--------|
| 1     | 0.5 ml| 44        | 94     |
| 2     | 2 ml  | 36        | 94     |
| 3     | 3 ml  | 32        | 95     |
| 4     | 4 ml  | 23        | 94     |

| Entry | CPA   | Yield (%) | ee (%) |
|-------|-------|-----------|--------|
| 5     | 7.5   | 44        | 94     |
| 6     | 10    | 43        | 94     |
| 7     | 15    | 43        | 94     |

aReaction conditions: 1a (x mmol), 2 (y mmol), 3a (z mmol), 4 Å MS (25 mg) and C1 (5 mol%) in THF (1.0 mL) at r.t. under irradiation of blue LEDs. bIsolated yield after chromatography. cDetermined by HPLC on a chiral stationary phase.
on a chiral stationary phase.

Table S4. Screening of the MS\textsuperscript{a}

| Entry | change     | Yield (%)\textsuperscript{b} | ee (%)\textsuperscript{c} |
|-------|------------|-------------------------------|---------------------------|
| 1     | 3Å MS      | 47                            | 94                        |
| 2     | 5Å MS      | 36                            | 94                        |
| 3     | Mg\textsubscript{2}SO\textsubscript{4} | 45                            | 94                        |
| 4     | 3Å MS (50 mg) | 50                            | 94                        |
| 5     | 3Å MS (100 mg) | 50                            | 94                        |

\textsuperscript{a}Reaction conditions: 1a (0.1 mmol), 2 (0.15 mmol), 3a (0.2 mmol), MS and C\textsubscript{1} (5 mol\%) in THF (1 mL) at r.t. under irradiation of blue LEDs for 3 h. \textsuperscript{b}Isolated yield after chromatography. \textsuperscript{c}Determined by HPLC on a chiral stationary phase.

Table S5. Screening of the additive and reaction temperature\textsuperscript{a}

| Entry | change               | Yield (%)\textsuperscript{b} | ee (%)\textsuperscript{c} |
|-------|----------------------|-------------------------------|---------------------------|
| 1     | NaHCO\textsubscript{3} (1 eq.) | 42                            | 94                        |
| 2     | K\textsubscript{3}PO\textsubscript{4} (1 eq.) | 0                             | --                       |
| 3     | K\textsubscript{2}CO\textsubscript{3} (1 eq.) | 0                             | --                       |
| 4     | PMPCO\textsubscript{2}H (1 eq.) | 48                            | 94                        |
| 5     | DIPEA (1 eq.)        | 0                             | --                       |
| 6     | 2,6-lutidine (1 eq.) | tarce                        | --                       |
| 7     | -20 ºC               | 54                            | 96                        |
| 8     | -30 ºC               | 48                            | 95                        |

\textsuperscript{a}Reaction conditions: 1a (0.1 mmol), 2 (0.15 mmol), 3a (0.2 mmol), 3Å MS (50 mg) and C\textsubscript{1} (5 mol\%) in THF (1 mL) under irradiation of blue LEDs for 3 h. \textsuperscript{b}Isolated yield after chromatography. \textsuperscript{c}Determined by HPLC on a chiral stationary phase.

Table S6. Further optimization\textsuperscript{a}

\begin{align*}
\text{Ar} = \text{4-MeOPh} & \quad \text{PMP} \\
\text{Ar} = \text{4-MeOPh} & \quad \text{PMP} \\
\text{Ar} = \text{4-MeOPh} & \quad \text{PMP}
\end{align*}

\begin{align*}
\text{C1 (5 mol\%)} & \quad \text{3 Å MS (50 mg)} \\
\text{THF (0.1 M), -20 ºC} & \quad \text{427 nm kessil LED}
\end{align*}

| Entry | Change/additives       | Yield (%)\textsuperscript{b} | ee (%)\textsuperscript{c} |
|-------|------------------------|-------------------------------|---------------------------|
| 1     | Ac\textsubscript{2}O (1 equiv.) | 51                            | 96                        |
| 2     | Boc\textsubscript{2}O (1 equiv.) | 51                            | 96                        |
| 3     | Acetyl chloride (1 equiv.) | 52                            | 95                        |
4  K$_2$PO$_4$ (1 equiv.)  0  --
5  K$_2$CO$_3$ (1 equiv.)  0  --
6  NaOAc (1 equiv.)  0  --
7  AcOH (1 equiv.)  48  95
8  propanoic acid (1 equiv.)  50  93
9  TFA (1 equiv.)  50  80
10  Cat-I (20 mol%)  49  84
11  Al$_2$O$_3$ instead of 3 Å MS  49  95
12  390 nm kessil LED  46  96

$^a$Reaction conditions: 1a (0.1 mmol), 2 (0.15 mmol), 3a (0.2 mmol), 3Å MS (50 mg) and C1 (5 mol%) in THF (1 mL) under irradiation of 427 nm kessil LEDs for 3 h. $^b$Isolated yield after chromatography.

Under the standard conditions, the side products were determined as BP1 in 6% yield, BP2 in 10% yield and BP3 in less than 5% yield. In addition, the enamine could decomposed under acidic conditions to generate the amide which could be detected by GCMS. In order to increase the yield, we carried out a series of reactions for condition optimization. We first added anhydrides and acyl chloride to the reaction mixture to remove the alcohol generated from Togni-II, but no change in yield was observed. (Entries 1-3) Then different bases were added and no products were obtained, probably because the hydrogen bond was destroyed. (Entries 4-6) Similarly, the addition of acids did not increase the yield, either, and the strong acids reduced the enantioselectivity of the product. (Entries 7-9) Furthermore, when thiourea was used as the co-catalyst, there was no promotion for the yield and lower enantioselectivity was observed (Entry 10). Finally, when we tested the 390 nm LED, no obvious change in yield was observed (Entry 12).

Table S7. Optimization of oxytrifluoromethylation reaction$^a$

| Entry | 5a (mmol) | T  | Yield (%)$^b$ | ee (%)$^c$ |
|-------|-----------|----|---------------|------------|
| 1     | 0.5       | r.t. | 69            | 83         |
| 2     | 0.2       | r.t. | 67            | 86         |
| 3     | 0.1       | r.t. | 69            | 89         |
| 4     | 1 ml (solvent) | r.t. | 72            | 0          |
| 5     | 0.1       | 0 ºC | 69            | 89         |
| 6     | 0.1       | -20 ºC | 0            | --         |

$^a$Reaction conditions: 1a (0.1 mmol), 2 (0.15 mmol), 5a (n mmol), 3Å MS (50 mg) and C1 (5 mol%) in THF (1 mL) under irradiation of blue LEDs for 3 h. $^b$Isolated yield after chromatography. $^c$Determined by HPLC on a chiral stationary phase.

Table S8. Optimization for the synthesis chiral γ-amino acid derivatives$^a$

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| Entry | PC   | I   | base    | Solvent     | Yield (%) | ee (%) |
|-------|------|-----|---------|-------------|-----------|--------|
| 1     | --   | 1a  | K$_3$PO$_4$ | THF (0.1 M)| 0         | 0      |
| 2     | 4CzIPN | 1a  | K$_3$PO$_4$ | THF         | 34        | 91     |
| 3     | 4CzIPN | 1b  | K$_3$PO$_4$ | THF         | 0         | --     |
| 4     | 4CzIPN | 1c  | K$_3$PO$_4$ | THF         | 37        | 96     |
| 5     | 4CzIPN | 1e  | K$_3$PO$_4$ | THF         | 0         | --     |
| 6     | 4CzIPN | 1c  | K$_2$CO$_3$ | THF         | 30        | 94     |
| 7     | 4CzIPN | 1c  | NaHCO$_3$   | THF         | 45        | 94     |
| 8     | Ir(ppy)$_2$(dabdpy)PF$_6$ | 1c  | K$_3$PO$_4$ | THF         | 24        | 96     |
| 9     | fac-Ir(ppy)$_3$ | 1c  | K$_3$PO$_4$ | THF         | 11        | 96     |
| 10    | Ru(bpy)$_3$(PF$_3$)$_2$ | 1c  | K$_3$PO$_4$ | THF         | 23        | 96     |
| 11    | Cat-CF$_3$Ph (PC1) | 1c  | K$_3$PO$_4$ | THF         | 49        | 96     |
| 12    | Cat-PMP (PC2) | 1c  | K$_3$PO$_4$ | THF         | 42        | 96     |
| 13    | Cat-Ph (PC3) | 1c  | K$_3$PO$_4$ | THF         | 38        | 95     |
| 14    | Cat-tBuPh (PC4) | 1c  | K$_3$PO$_4$ | THF         | 42        | 96     |
| 15    | Cat-Et (PC5) | 1c  | K$_3$PO$_4$ | THF         | 17        | 95     |
| 16    | Cat-CF$_3$Ph (PC1) | 1c  | K$_3$PO$_4$ | CH$_2$Cl$_2$| 0         | --     |
| 17    | Cat-CF$_3$Ph (PC1) | 1c  | K$_3$PO$_4$ | DCE         | 0         | --     |
| 18    | Cat-CF$_3$Ph (PC1) | 1c  | K$_3$PO$_4$ | toluene     | 0         | --     |
| 19    | Cat-CF$_3$Ph (PC1) | 1c  | K$_3$PO$_4$ | MeCN        | 0         | --     |
| 20    | Cat-CF$_3$Ph (PC1) | 1c  | K$_3$PO$_4$ | 1,4-dioxane | 35        | 96     |
| 21    | Cat-CF$_3$Ph (PC1) | 1c  | K$_3$PO$_4$ | DMF         | 0         | --     |
| 22    | Cat-CF$_3$Ph (PC1) | 1c  | K$_3$PO$_4$ | THF (0.05 M)| trace     | --     |
| 23    | Cat-CF$_3$Ph (PC1) | 1c  | K$_3$PO$_4$ | THF (0.2 M)| 60        | 96     |
| 24$^d$| Cat-CF$_3$Ph (PC1) | 1c  | K$_3$PO$_4$ | THF (0.2 M)| 29        | 87     |
| 25$^e$| Cat-CF$_3$Ph (PC1) | 1c  | K$_3$PO$_4$ | THF (0.2 M)| 41        | 96     |
| 26$^e$| Cat-CF$_3$Ph (PC1) | 1c  | K$_3$PO$_4$ | THF (0.2 M)| 34        | 93     |
| 27$^e$| Cat-CF$_3$Ph (PC1) | 1c  | K$_3$PO$_4$ | THF (0.2 M)| 65        | 96     |

$^a$Reaction conditions: 1 (0.2 mmol), 7a (0.1 mmol), 3a (0.15 mmol), 3Å MS (25 mg) and C1 (5 mol%) in solvent under irradiation of blue LEDs for 12 h. $^b$Isolated yield after chromatography. $^c$Determined by HPLC on a chiral stationary phase. $^d$under 0 °C. $^e$10 mol% C6 was used. $^f$C9 was used. $^g$100 mg 3Å MS was used.
5. Experimental and Characterization Data of Products

(R)-4-methoxy-N-(3,3,3-trifluoro-1-(1H-indol-3-yl)propyl)benzamide (4a)

Following the general procedure, compound 4a was obtained as a white solid (19.6 mg, yield: 54%); mp = 220-222°C; $^1$H NMR (400 MHz, DMSO-$d_6$): δ 11.04 (s, 1H), 8.68 (d, $J$ = 8.8 Hz, 1H), 7.86-7.84 (m, 2H), 7.66-7.64 (m, 1H), 7.40-7.36 (m, 2H), 7.11-7.07 (m, 1H), 7.00-6.97 (m, 3H), 5.85 (dt, $J$ = 2.8 Hz, 8.0 Hz, 1H), 3.79 (s, 3H), 3.20-2.95 (m, 2H); $^{19}$F NMR (376 MHz, DMSO-$d_6$): δ -62.7; $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 164.7, 161.7, 136.4, 129.2, 128.4, 126.83 (q, $J$ = 276 Hz), 126.76, 125.7, 122.9, 122.7, 121.4, 118.9, 118.7, 115.3, 113.5, 111.7, 55.4, 40.1 (d, $J$ = 3 Hz), 37.6 (q, $J$ = 26 Hz); HRMS (ESI) for C$_{19}$H$_{18}$F$_3$N$_2$O$_2$ [M+H]$^+$ calcd. 363.1242, found 363.1316; Enantiomeric excess established by HPLC analysis using a Chiralpak IA column, ee = 96% (HPLC: IA, 230 nm, hexane/isopropanol = 80:20, flow rate 1.0 mL/min, 25°C, $t_r$ (major) = 11.5 min, $t_r$ (minor) = 22.6 min.) [$\alpha$]$_D^{25}$ = -6.00 (c 1.0, MeOH).

(R)-N-(3,3,3-trifluoro-1-(1H-indol-3-yl)propyl)benzamide (4b)

Following the general procedure, compound 4b was obtained as a white solid (17.1 mg, yield: 51%); mp = 168-170°C; $^1$H NMR (400 MHz, DMSO-$d_6$): δ 11.05 (s, 1H), 8.85 (d, $J$ = 8.4 Hz, 1H), 7.87-7.85 (m, 2H), 7.68-7.66 (m, 1H), 7.53-7.49 (m, 1H), 7.47-7.42 (m, 3H), 7.40-7.38 (m, 1H), 7.12-7.08 (m, 1H), 7.02-6.98 (m, 1H), 5.87 (dt, $J$ = 4.0 Hz, 9.2 Hz, 1H), 3.22-2.96 (m, 2H); $^{19}$F NMR (376 MHz, DMSO-$d_6$): δ -62.7; $^{13}$C NMR
(100 MHz, DMSO-d$_6$): $\delta$ 165.4, 136.4, 134.6, 128.3, 127.3, 126.8 (q, $J = 276$ Hz), 125.7, 122.9, 121.4, 118.9, 118.7, 115.2, 111.7, 37.6 (q, $J = 26$ Hz); HRMS (ESI) for C$_{18}$H$_{16}$F$_3$N$_2$O [M+H]$^+$ calcd. 333.1209, found 333.1209;
Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 98% (HPLC: IF-3, 280 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, $t_r$ (major) = 14.9 min, $t_r$ (minor) = 24.8 min.) $[\alpha]_{D}^{25}$ = 16.00 (c 1.0, MeOH).

\[
\text{(R)-4-chloro-N-(3,3,3-trifluoro-1-(1H-indol-3-yl)propyl)benzamide (4c)}
\]
Following the general procedure, compound 4c was obtained as a white solid (19.6 mg, yield: 53%); mp = 196-198°C; $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ 11.04 (s, 1H), 8.91 (d, $J = 8.8$ Hz, 1H), 7.88-7.84 (m, 2H), 7.63-7.62 (m, 1H), 7.55-7.51 (m, 2H), 7.42-7.41 (m, 1H), 7.38-7.36 (m, 1H), 7.11-7.10 (m, 1H), 7.01-6.97 (m, 1H), 5.82 (dt, $J = 4.0$ Hz, 9.2 Hz, 1H), 3.19-2.95 (m, 2H); $^{19}$F NMR (376 MHz, DMSO-d$_6$): $\delta$ -63.4; $^{13}$C NMR (100 MHz, DMSO-d$_6$): $\delta$ 164.4, 136.4, 136.1, 133.2, 129.3, 128.4, 126.7 (q, $J = 276$ Hz), 125.6, 123.0, 121.4, 118.9, 118.6, 114.9, 111.7, 40.3 (d, $J = 3$ Hz), 37.4 (q, $J = 26$ Hz); HRMS (ESI) for C$_{18}$H$_{15}$F$_3$ClN$_2$O [M+H]$^+$ calcd. 367.0820, found 367.0822;
Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 97% (HPLC: IF-3, 290 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, $t_r$ (major) = 12.9 min, $t_r$ (minor) = 1.93 min.) $[\alpha]_{D}^{25}$ = 2.00 (c 1.0, MeOH).

\[
\text{(R)-4-fluoro-N-(3,3,3-trifluoro-1-(1H-indol-3-yl)propyl)benzamide (4d)}
\]
Following the general procedure, compound 4d was obtained as a white solid (16.7 mg,
yield: 47%); mp = 201-203°C; \textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6): \delta 11.06 (s, 1H), 8.88 (d, \textit{J} = 8.8 Hz, 1H), 7.95-7.91 (m, 2H), 7.66-7.64 (m, 1H), 7.43 (d, \textit{J} = 2.0 Hz, 1H), 7.39-7.37 (m, 1H), 7.31-7.27 (m, 2H), 7.11-7.08 (m, 1H), 7.01-6.98 (m, 1H), 5.85 (dt, \textit{J} = 3.6 Hz, 9.2 Hz, 1H), 3.21-2.96 (m, 2H); \textsuperscript{19}F NMR (376 MHz, DMSO-\textit{d}_6): \delta -62.7, -109.4; \textsuperscript{13}C NMR (100 MHz, DMSO-\textit{d}_6): \delta 164.4, 164.0 (d, \textit{J} = 247 Hz), 136.4, 131.0 (d, \textit{J} = 3 Hz), 130.0 (d, \textit{J} = 9 Hz), 126.8 (q, \textit{J} = 276 Hz), 125.7, 123.0, 121.4, 118.9, 118.6, 115.3 (d, \textit{J} = 22 Hz), 115.0, 111.7, 40.3 (d, \textit{J} = 3 Hz), 37.5 (q, \textit{J} = 25 Hz); HRMS (ESI) for C\textsubscript{18}H\textsubscript{15}F\textsubscript{4}N\textsubscript{2}O [M+H]\textsuperscript{+} calcd. 351.1115, found 351.1116;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 97% (HPLC: IF-3, 290 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, \textit{t} \textsubscript{r} (major) = 11.8 min, \textit{t} \textsubscript{r} (minor) = 17.6 min.) [\alpha]\textsubscript{D}\textsuperscript{25} = 20.00 (c 1.0, CH\textsubscript{2}Cl\textsubscript{2}).

(R)-4-bromo-N-(3,3,3-trifluoro-1-(1H-indol-3-yl)propyl)benzamide (4e)

Following the general procedure, compound 4e was obtained as a white solid (16.8 mg, yield: 41%); mp = 166-168°C; \textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6): \delta 11.07 (s, 1H), 8.94 (d, \textit{J} = 8.8 Hz, 1H), 7.81-7.79 (m, 2H), 7.69-7.66 (m, 2H), 7.64-7.62 (m, 1H), 7.43-7.42 (m, 1H), 7.39-7.37 (m, 1H), 7.11-7.07 (m, 1H), 7.01-6.97 (m, 1H), 5.84 (dt, \textit{J} = 4.0 Hz, 9.2 Hz, 1H), 3.20-2.96 (m, 2H); \textsuperscript{19}F NMR (376 MHz, DMSO-\textit{d}_6): \delta -62.7; \textsuperscript{13}C NMR (100 MHz, DMSO-\textit{d}_6): \delta 164.5, 136.4, 133.6, 131.4, 129.5, 126.8 (q, \textit{J} = 276 Hz), 125.7, 125.1, 123.0, 121.4, 118.9, 118.6, 114.9, 111.7, 40.3 (d, \textit{J} = 3 Hz), 37.4 (q, \textit{J} = 26 Hz); HRMS (ESI) for C\textsubscript{18}H\textsubscript{13}F\textsubscript{3}BrN\textsubscript{2}O [M+H]\textsuperscript{+} calcd. 411.0314, found 411.0315;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 96% (HPLC: IF-3, 290 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, \textit{t} \textsubscript{r} (major) = 14.8 min, \textit{t} \textsubscript{r} (minor) = 22.8 min.) [\alpha]\textsubscript{D}\textsuperscript{25} = -3.00 (c 1.0, MeOH).
(R)-4-methyl-N-(3,3,3-trifluoro-1-(1H-indol-3-yl)propyl)benzamide (4f)

Following the general procedure, compound 4f was obtained as a white solid (14.9 mg, yield: 43%); mp = 222-224°C; $^1$H NMR (400 MHz, DMSO-$d_6$): δ 11.04 (s, 1H), 8.75 (d, J = 8.8 Hz, 1H), 7.77-7.75 (m, 2H), 7.66-7.64 (m, 1H), 7.41-7.36 (m, 2H), 7.26-7.24 (m, 2H), 7.11-7.07 (m, 1H), 7.01-6.97 (m, 1H), 5.85 (dt, J = 4.0 Hz, 9.2 Hz, 1H), 3.21-2.94 (m, 2H), 2.33 (s, 3H); $^{19}$F NMR (376 MHz, DMSO-$d_6$): δ -62.7; $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 165.5, 141.2, 136.4, 131.8, 128.9, 127.4, 126.8 (q, J = 276 Hz), 125.7, 122.9, 121.4, 118.9, 118.7, 115.3, 111.7, 40.2 (d, J = 3 Hz), 37.6 (q, J = 26 Hz), 21.0; HRMS (ESI) for C$_{19}$H$_{18}$F$_3$N$_2$O [M+H]$^+$ calcd. 347.1366, found 347.1367; Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 95% (HPLC: IF-3, 290 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, t$_r$ (major) = 18.7 min, t$_r$ (minor) = 37.0 min.) $[\alpha]_D^{25} = 6.00$ (c 1.0, MeOH).

(R)-N-(3,3,3-trifluoro-1-(1H-indol-3-yl)propyl)-[1,1'-biphenyl]-4-carboxamide (4g)

Following the general procedure, compound 4g was obtained as a white solid (14.8 mg, yield: 36%); mp = 196-198°C; $^1$H NMR (400 MHz, DMSO-$d_6$): δ 11.06 (s, 1H), 8.90 (d, J = 8.8 Hz, 1H), 7.98-7.95 (m, 2H), 7.77-7.75 (m, 2H), 7.72-7.67 (m, 3H), 7.50-7.46 (m, 2H), 7.44-7.43 (m, 1H), 7.41-7.38 (m, 2H), 7.12-7.08 (m, 1H), 7.02-6.99 (m, 1H), 5.89 (dt, J = 4.0 Hz, 9.2 Hz, 1H), 3.24-2.97 (m, 2H); $^{19}$F NMR (376 MHz, DMSO-$d_6$): δ -62.7; $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 165.5, 143.3, 139.7, 136.8, 133.7, 129.5, 128.5, 128.4, 127.3, 127.2 (q, J = 276 Hz), 127.0, 126.1, 123.3, 121.8, 119.3, 119.1, 115.6, 112.1, 37.9 (q, J = 26 Hz); HRMS (ESI) for C$_{24}$H$_{20}$F$_3$N$_2$O [M+H]$^+$ calcd.
Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 95% (HPLC: IF-3, 290 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, t_r (major) = 23.9 min, t_r (minor) = 49.3 min.) [α]_D^{25} = -27.00 (c 1.0, MeOH).

\((R)-3\text{-chloro-}\text{-}N(3,3,3\text{- trifluoro-}1\text{-}(1H\text{-indol-3-yl})\text{propyl})\text{benzamide (4h)}\)

Following the general procedure, compound 4h was obtained as a white solid (12.0 mg, yield: 33%); mp = 154-156 °C; \(^1\)H NMR (400 MHz, DMSO-d$_6$): δ 11.07 (s, 1H), 8.98 (d, J = 8.8 Hz, 1H), 7.89-7.88 (m, 1H), 7.83-7.81 (m, 1H), 7.64-7.62 (m, 1H), 7.60-7.58 (m, 1H), 7.51-7.48 (m, 1H), 7.44-7.43 (m, 1H), 7.39-7.37 (m, 1H), 7.11-7.07 (m, 1H), 7.01-6.98 (m, 1H), 5.83 (dt, J = 4.0 Hz, 9.2 Hz, 1H), 3.20-2.97 (m, 2H); \(^{19}\)F NMR (376 MHz, DMSO-d$_6$): δ -62.7; \(^{13}\)C NMR (100 MHz, DMSO-d$_6$): δ 163.9, 136.44, 136.38, 133.3, 131.2, 130.4, 127.0, 126.8 (q, J = 276 Hz), 126.2, 125.6, 123.0, 121.4, 118.9, 118.6, 114.8, 111.7, 40.4 (d, J = 3 Hz), 37.4 (q, J = 26 Hz); HRMS (ESI) for C$_{18}$H$_{15}$F$_3$ClN$_2$O [M+H]$^+$ calcd. 367.0820, found 367.0818; Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 96% (HPLC: IF-3, 290 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, t_r (major) = 10.8 min, t_r (minor) = 14.8 min.) [α]_D^{25} = 10.00 (c 1.0, MeOH).

\((R)-3\text{-methyl-}\text{-}N(3,3,3\text{- trifluoro-}1\text{-}(1H\text{-indol-3-yl})\text{propyl})\text{benzamide (4i)}\)

Following the general procedure, compound 4i was obtained as a white solid (18.0 mg,
yield: 52%; mp = 137-139°C; \(^1\)H NMR (400 MHz, DMSO-d\(_6\)): \(\delta\) 11.06 (s, 1H), 8.80 (d, \(J = 8.8\) Hz, 1H), 7.68-7.65 (m, 3H), 7.43-7.42 (m, 1H), 7.40-7.38 (m, 1H), 7.34-7.31 (m, 2H), 7.12-7.08 (m, 1H), 7.02-6.98 (m, 1H), 5.88 (dt, \(J = 4.0\) Hz, 9.2 Hz, 1H), 3.22-2.96 (m, 2H), 2.34 (s, 3H); \(^{19}\)F NMR (376 MHz, DMSO-d\(_6\)): \(\delta\) -62.7; \(^{13}\)C NMR (100 MHz, DMSO-d\(_6\)): \(\delta\) 165.5, 137.6, 136.4, 134.6, 131.8, 128.2, 127.8, 126.8 (q, \(J = 276\) Hz), 125.7, 124.6, 122.9, 121.4, 118.9, 118.7, 115.2, 116.7, 40.2 (d, \(J = 3\) Hz), 37.5 (q, \(J = 26\) Hz), 21.0; HRMS (ESI) for C\(_{19}\)H\(_{18}\)F\(_3\)N\(_2\)O \([M+H]^+\) calcd. 347.1366, found 347.1366;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 94% (HPLC: IF-3, 290 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, \(t_r\) (major) = 13.3 min, \(t_r\) (minor) = 20.6 min.) \([\alpha]_D^{25} = -17.00\) (c 1.0, MeOH).

(R)-2-methyl-N-(3,3,3-trifluoro-1-(1H-indol-3-yl)propyl)benzamide (4j)

Following the general procedure, compound 4j was obtained as a white solid (18.0 mg, yield: 52%); mp = 191-193°C; \(^1\)H NMR (400 MHz, DMSO-d\(_6\)): \(\delta\) 11.03 (s, 1H), 8.72 (d, \(J = 8.8\) Hz, 1H), 7.70-7.69 (m, 1H), 7.40-7.38 (m, 2H), 7.32-7.28 (m, 1H), 7.22-7.21 (m, 3H), 7.13-7.10 (m, 1H), 7.05-7.01 (m, 1H), 5.80 (dt, \(J = 4.4\) Hz, 8.8 Hz, 1H), 3.06-2.96 (m, 2H), 2.28 (s, 3H); \(^{19}\)F NMR (376 MHz, DMSO-d\(_6\)): \(\delta\) -62.6; \(^{13}\)C NMR (100 MHz, DMSO-d\(_6\)): \(\delta\) 168.1, 137.2, 136.4, 135.3, 130.4, 129.3, 127.8, 126.9, 126.8 (q, \(J = 276\) Hz), 125.6, 125.5, 122.7, 121.5, 118.8, 118.7, 115.2, 111.7, 37.6 (q, \(J = 26\) Hz), 19.2; HRMS (ESI) for C\(_{19}\)H\(_{18}\)F\(_3\)N\(_2\)O \([M+H]^+\) calcd. 347.1366, found 347.1367;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 97% (HPLC: IF-3, 290 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, \(t_r\) (major) = 22.1 min, \(t_r\) (minor) = 20.7 min.) \([\alpha]_D^{25} = 5.00\) (c 1.0, MeOH).
(R)-2-chloro-N-(3,3,3-trifluoro-1-(1H-indol-3-yl)propyl)benzamide (4k)

Following the general procedure, compound 4k was obtained as a white solid (10.4 mg, yield: 28%); mp = 190-192°C; $^1$H NMR (400 MHz, DMSO-$d_6$): δ 11.03 (s, 1H), 8.93 (d, $J = 8.4$ Hz, 1H), 7.70-7.68 (m, 1H), 7.48-7.44 (m, 1H), 7.43-7.35 (m, 4H), 7.32-7.29 (m, 1H), 7.14-7.10 (m, 1H), 7.05-7.01 (m, 1H), 5.76 (dt, $J = 5.6$ Hz, 8.4 Hz, 1H), 3.05-2.93 (m, 2H); $^{19}$F NMR (376 MHz, DMSO-$d_6$): δ -62.6; $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 165.3, 136.9, 136.4, 130.8, 130.0, 129.7, 128.7, 127.1, 126.7 (q, $J = 276$ Hz), 122.9, 121.5, 118.82, 118.76, 114.6, 111.6, 37.6 (q, $J = 26$ Hz); HRMS (ESI) for C$_{18}$H$_{15}$ClF$_3$N$_2$O $[M+H]^+$ caleld. 367.0820, found 367.0822;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 96% (HPLC: IF-3, 280 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, $t_r$ (major) = 19.3 min, $t_r$ (minor) = 22.3 min.) $[\alpha]_D^{25} = 4.00$ (c 1.0, MeOH).

(R)-3,5-dimethyl-N-(3,3,3-trifluoro-1-(1H-indol-3-yl)propyl)benzamide (4l)

Following the general procedure, compound 4l was obtained as a white solid (21.3 mg, yield: 59%); mp = 178-180°C; $^1$H NMR (400 MHz, DMSO-$d_6$): δ 11.05 (s, 1H), 8.73 (d, $J = 8.4$ Hz, 1H), 7.66-7.64 (m, 1H), 7.47 (s, 1H), 7.42-7.37 (m, 2H), 7.13-7.08 (m, 2H), 7.01-6.97 (m, 1H), 5.86 (dt, $J = 2.4$ Hz, 5.6 Hz, 1H), 3.21-2.96 (m, 2H), 2.30 (s, 6H); $^{19}$F NMR (376 MHz, DMSO-$d_6$): δ -62.7; $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 165.6, 137.4, 136.4, 134.6, 132.5, 126.8 (q, $J = 276$ Hz), 125.7, 125.1, 122.9, 121.4, 118.9, 118.7, 115.6, 111.6, 37.5 (q, $J = 26$ Hz), 20.9; HRMS (ESI) for C$_{20}$H$_{20}$F$_3$N$_2$O
[M+H]$^+$ calcd. 361.1522, found 361.1523;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 93% (HPLC: IF-3, 290 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, $t_r$ (major) = 9.9 min, $t_r$ (minor) = 14.6 min.) $[\alpha]_D^{25} = 10.00$ (c 1.0, MeOH).

\(\text{(R)}\)-N-(3,3,3-trifluoro-1-(1H-indol-3-yl)propyl)thiophene-2-carboxamide (4m)

Following the general procedure, compound **4m** was obtained as a colorless oil (15.0 mg, yield: 45%); mp = 132-134°C; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 11.07 (s, 1H), 8.83 (d, $J = 8.8$ Hz, 1H), 7.76-7.73 (m, 2H), 7.64-7.62 (m, 1H), 7.43-7.42 (m, 1H), 7.39-7.37 (m, 1H), 7.13-7.07 (m, 2H), 7.01-6.97 (m, 1H), 5.78 (dt, $J = 4.4$ Hz, 8.8 Hz, 1H), 3.18-2.97 (m, 2H); $^{19}$F NMR (376 MHz, DMSO-$d_6$): $\delta$ -62.7; $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 160.2, 139.3, 136.4, 131.1, 128.2, 127.9, 126.8 (q, $J = 276$ Hz), 125.7, 123.0, 121.5, 118.9, 118.7, 114.9, 111.7, 40.1 (d, $J = 3$ Hz), 37.4 (q, $J = 26$ Hz); HRMS (ESI) for C$_{16}$H$_{13}$F$_3$N$_2$OSNa [M+Na]$^+$ calcd. 361.0593, found 361.0593;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 93% (HPLC: IF-3, 290 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, $t_r$ (major) = 13.6 min, $t_r$ (minor) = 22.2 min.) $[\alpha]_D^{25} = 5.00$ (c 1.0, MeOH).

\(\text{(R)}\)-N-(3,3,3-trifluoro-1-(1H-indol-3-yl)propyl)furan-2-carboxamide (4n)

Following the general procedure, compound **4n** was obtained as a colorless oil (19.3 mg, yield: 66%); mp = 96-98 °C; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 11.04 (s, 1H), 8.73 (d, $J = 8.8$ Hz, 1H), 7.81-7.80 (m, 1H), 7.63-7.61 (m, 1H), 7.39-7.35 (m, 2H), 7.11-7.06
(m, 2H), 7.00-6.96 (m, 1H), 6.60 (dd, J = 1.6 Hz, 3.2Hz, H), 5.77 (dt, J = 3.6 Hz, 8.8 Hz, 1H), 3.23-3.09 (), 3.06-2.93 (m, 2H); \(^{19}\)F NMR (376 MHz, DMSO-\(d_6\)): δ -62.7; \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)): δ 156.8, 147.8, 145.0, 136.3, 126.7 (q, J = 276 Hz), 125.6, 123.0, 121.4, 118.9, 118.6, 114.9, 113.7, 111.9, 111.6, 37.3 (q, J = 26 Hz); HRMS (ESI) for C\(_{16}\)H\(_{13}\)F\(_3\)N\(_2\)O\(_2\)Na [M+Na]\(^+\) calcd. 345.0821, found 345.0824; Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 96% (HPLC: IF-3, 290 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, t\(_r\) (major) = 13.6 min, t\(_r\) (minor) = 22.9 min.) [\(\alpha\)]\(_D\)\(^{25}\) = 3.00 (c 1.0, MeOH).

(R)-N-(3,3,3-trifluoro-1-(1H-indol-3-yl)propyl)cinnamamide (4o)

Following the general procedure, compound 4o was obtained as a colorless oil (10.6 mg, yield: 30%); mp = 95-97°C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): δ 11.06 (s, 1H), 8.51 (d, J = 8.4 Hz, 1H), 7.60-7.58 (m, 1H), 7.55-7.54 (m, 2H), 7.48 (m, J = 15.6 Hz, 1H), 7.43-7.36 (m, 5H), 7.12-7.08 (m, 1H), 7.02-6.98 (m, 1H), 6.63 (d, J = 15.6 Hz, 1H), 5.70 (dt, J = 5.6 Hz, 8.8 Hz, 1H), 3.09-2.89 (m, 2H); \(^{19}\)F NMR (376 MHz, DMSO-\(d_6\)): δ -62.5; \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)): δ 164.0, 139.2, 136.4, 134.9, 129.5, 129.0, 127.6, 126.6 (q, J = 276 Hz), 125.6, 122.9, 122.1, 121.5, 118.9, 118.7, 114.7, 111.7, 37.7 (q, J = 26 Hz); HRMS (ESI) for C\(_{20}\)H\(_{17}\)F\(_3\)N\(_2\)O\(_2\)Na [M+Na]\(^+\) calcd. 381.1185, found 381.1183; Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 91% (HPLC: IF-3, 280 nm, hexane/isopropanol = 85:15, flow rate 1.0 mL/min, 25 °C, t\(_r\) (major) = 7.9 min, t\(_r\) (minor) = 12.9 min.) [\(\alpha\)]\(_D\)\(^{25}\) = 13.00 (c 1.0, MeOH).
(R)-4-methoxy-N-(3,3,3-trifluoro-1-(4-methyl-1H-indol-3-yl)propyl)benzamide
(4p)

Following the general procedure, compound 4p was obtained as a white solid (19.0 mg, yield: 51%); mp = 230-232°C; 1H NMR (400 MHz, DMSO-d6): δ 11.07 (d, J = 2.0 Hz, 1H), 8.68 (d, J = 8.4 Hz, 1H), 7.85-7.82 (m, 2H), 7.48-7.47 (m, 1H), 7.21-7.19 (m, 1H), 7.00-6.93 (m, 3H), 6.75-6.74 (m, 1H), 6.08 (dt, J = 5.6 Hz, 8.0 Hz, 1H), 3.80 (s, 3H), 3.04-2.85 (m, 2H), 2.66 (s, 3H); 19F NMR (376 MHz, DMSO-d6): δ -62.5; 13C NMR (100 MHz, DMSO-d6): δ 164.6, 161.7, 136.2, 129.2, 126.7, 126.4 (q, J = 276 Hz), 124.2, 123.6, 121.2, 120.7, 116.4, 113.5, 109.7, 55.4, 41.1 (d, J = 3 Hz), 20.1; HRMS (ESI) for C20H20F3N2O2 [M+H]⁺ calcd. 377.1471, found 377.1472;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 96% (HPLC: IF-3, 280 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, tₘ (major) = 9.0 min, tᵣ (minor) = 11.0 min.) [α]D²⁵ = -40.00 (c 1.0, MeOH).

(4q)

Following the general procedure, compound 4q was obtained as a white solid (16.6 mg, yield: 42%); mp = 210-212 °C; 1H NMR (400 MHz, DMSO-d6): δ 10.96 (d, J = 2.0 Hz, 1H), 8.56 (d, J = 8.8 Hz, 1H), 7.87-7.84 (m, 2H), 7.14-7.13 (m, 1H), 7.04-6.96 (m, 4H), 6.54-6.52 (m, 1H), 5.96 (q, J = 7.2 Hz, 1H), 3.91 (s, 3H), 3.81 (s, 3H), 2.90-2.80 (m, 2H); 19F NMR (376 MHz, DMSO-d6): δ -63.1; 13C NMR (100 MHz, DMSO-d6): δ 164.8, 161.7, 153.2, 138.2, 129.1, 126.9, 126.6 (q, J = 276 Hz), 122.4, 121.2, 115.9, 115.2, 113.7, 105.3, 99.3, 55.5, 55.1, 42.0 (d, J = 3 Hz); HRMS (ESI) for C20H20F3N2O3 [M+H]⁺ calcd. 393.1421, found 393.1422;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 97% (HPLC: IF-3, 280 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, tₘ (major) = 9.0 min, tᵣ (minor) = 11.0 min.) [α]D²⁵ = -40.00 (c 1.0, MeOH).
\( ^\circ \text{C}, t_r \text{ (major)} = 16.6 \text{ min}, t_r \text{ (minor)} = 29.7 \text{ min.} \) \([\alpha]_D^{25} = 78.00 \text{ (c 1.0, MeOH).}

(R)-N-(1-(4-chloro-1\text{H}-indol-3-yl)-3,3,3-trifluoropropyl)-4-methoxybenzamide (4r)

Following the general procedure, compound 4r was obtained as a white solid (12.4 mg, yield: 31\%); mp = 190-192\text{°C}; \(^1\text{H NMR (400 MHz, DMSO-\text{d}_6):} \delta 11.40 \text{ (d,} J = 2.0 \text{ Hz,}\ 1\text{H}), 8.74 \text{ (d,} J = 8.4 \text{ Hz,}\ 1\text{H}), 7.87-7.85 \text{ (m,}\ 2\text{H}), 7.50 \text{ (d,} J = 2.4 \text{ Hz,}\ 1\text{H}), 7.38-7.36 \text{ (m,}\ 1\text{H}), 7.10-7.00 \text{ (m,}\ 4\text{H}), 6.29-6.23 \text{ (m,}\ 1\text{H}), 3.81 \text{ (s,}\ 3\text{H}), 2.96-2.86 \text{ (m,}\ 2\text{H}); \(^{19}\text{F NMR (376 MHz, DMSO-\text{d}_6):} \delta -62.5; \(^{13}\text{C NMR (100 MHz, DMSO-\text{d}_6):} \delta 164.9, 161.7, 137.9, 129.2, 126.8, 126.3 \text{ (q,} J = 276 \text{ Hz,}\ 125.0, 124.1, 122.11, 119.8, 115.7, 113.6, 111.1, 55.4, 41.0; \text{HRMS (ESI) for} \text{C}_{19}\text{H}_{17}\text{ClF}_{3}\text{N}_{2}\text{O}_2 \text{ [M+H]}^+ \text{calcd. 397.0925, found 397.0927;}}

Enantiomeric excess established by HPLC analysis using a Chiralpak IA column, ee = >99\% (HPLC: IA, 290 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, t_r (major) = 8.7 min) \([\alpha]_D^{25} = -61.00 \text{ (c 1.0, MeOH).}

Methyl (R)-3-(3,3,3-trifluoro-1-(4-methoxybenzamido)propyl)-1H-indole-4-carboxylate (4s)

Following the general procedure, compound 4s was obtained as a white solid (20.0 mg, yield: 48\%); mp = 195-197 °C; \(^1\text{H NMR (400 MHz, DMSO-\text{d}_6):} \delta 11.50 \text{ (d,} J = 2.0 \text{ Hz,}\ 1\text{H}), 8.64 \text{ (d,} J = 8.4 \text{ Hz,}\ 1\text{H}), 7.85-7.83 \text{ (m,}\ 2\text{H}), 7.66-7.62 \text{ (m,}\ 2\text{H}), 7.56-7.54 \text{ (m,}\ 1\text{H}), 7.20-7.16 \text{ (m,}\ 1\text{H}), 7.02-7.00 \text{ (m,}\ 1\text{H}), 6.20 \text{ (dt,} J = 4.0 \text{ Hz,} 9.2 \text{ Hz,}\ 1\text{H}), 3.88 \text{ (s,}\ 3\text{H), 3.80 (s,}\ 3\text{H), 2.91-2.67 (m,}\ 2\text{H);} \(^{19}\text{F NMR (376 MHz, DMSO-\text{d}_6):} \delta -62.0; \(^{13}\text{C NMR}
(100 MHz, DMSO-$d_6$): $\delta$ 168.5, 164.9, 161.7, 138.2, 137.6, 129.2, 127.0, 126.5, 126.4 (q, $J = 277$ Hz), 122.9, 122.3, 122.2, 120.3, 116.46, 116.41, 113.6, 55.4, 52.1, 41.7 (d, $J = 3$ Hz); HRMS (ESI) for C$_{21}$H$_{20}$F$_3$N$_2$O$_4$ [M+H]$^+$ calcd. 421.1370, found 421.1373.

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 97% (HPLC: IF-3, 280 nm, hexane/isopropanol = 75:25, flow rate 1.0 mL/min, 25 °C, $t_r$ (major) = 6.1 min, $t_r$ (minor) = 25.2 min.) $[\alpha]_D^{25} = -83$ (c 1.0, MeOH).

**(R)-4-methoxy-N-(3,3,3-trifluoro-1-(5-methyl-1H-indol-3-yl)propyl)benzamide (4t)**

Following the general procedure, compound 4t was obtained as a white solid (18.5 mg, yield: 49%); mp = 195-197 °C; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 10.89 (s, 1H), 8.66 (d, $J = 8.8$ Hz, 1H), 7.86-7.82 (m, 2H), 7.43 (s, 2H), 7.34-7.33 (m, 1H), 7.26-7.24 (m, 1H), 7.01-6.97 (m, 1H), 6.92-6.90 (m, 1H), 5.79 (dt, $J = 4.0$ Hz, 9.2 Hz, 1H), 3.79 (s, 3H), 3.17-2.90 (m, 2H), 2.35 (s, 3H); $^{19}$F NMR (376 MHz, DMSO-$d_6$): $\delta$ -62.7; $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 164.9, 161.7, 134.7, 129.2, 127.2, 126.85, 126.80 (q, $J = 276$ Hz), 123.0, 118.3, 114.8, 113.5, 111.4, 55.4, 37.8 (q, $J = 26$ Hz), 21.5; HRMS (ESI) for C$_{20}$H$_{20}$F$_3$N$_2$O$_2$ [M+H]$^+$ calcd. 377.1471, found 377.1472.

Enantiomeric excess established by HPLC analysis using a Chiralpak IA column, ee = 92% (HPLC: IA, 290 nm, hexane/isopropanol = 80:20, flow rate 1.0 mL/min, 25 °C, $t_r$ (major) = 9.6 min, $t_r$ (minor) = 15.1 min.) $[\alpha]_D^{25} = -31.00$ (c 1.0, MeOH).

**(R)-4-methoxy-N-(3,3,3-trifluoro-1-(5-methoxy-1H-indol-3-yl)propyl)benzamide**
Following the general procedure, compound 4u was obtained as a white solid (12.5 mg, yield: 32%); mp = 173-175 °C; 1H NMR (400 MHz, DMSO-d6): δ 10.87 (d, J = 1.6 Hz, 1H), 8.67 (d, J = 8.4 Hz, 1H), 7.85-7.82 (m, 2H), 7.35-7.34 (m, 1H), 7.26-7.24 (m, 1H), 7.18-7.17 (m, 1H), 7.00-6.98 (m, 1H), 6.73 (dd, J = 2.4 Hz, 8.4 Hz, 1H), 5.79 (dt, J = 4.0 Hz, 9.2 Hz, 1H), 3.79 (s, 3H), 3.70 (s, 3H), 3.20-2.93 (m, 2H); 19F NMR (376 MHz, DMSO-d6): δ -62.6; 13C NMR (100 MHz, DMSO-d6): δ 165.0, 161.7, 153.2, 131.5, 129.2, 126.9 (q, J = 276 Hz), 126.8, 126.1, 123.4, 115.1, 113.6, 112.3, 111.4, 100.8, 55.4, 55.3, 37.3 (q, J = 26 Hz); HRMS (ESI) for C20H20F3N2O3 [M+H]+ calcd. 393.1421, found 393.1420;

Enantiomeric excess established by HPLC analysis using a Chiralpak IA column, ee = 90% (HPLC: IA, 290 nm, hexane/isopropanol = 80:20, flow rate 1.0 mL/min, 25 °C, t_r (major) = 13.0 min, t_r (minor) = 25.5 min.) [α]D 25 = -28.00 (c 1.0, MeOH).

(R)-N-(1-(5-chloro-1H-indol-3-yl)-3,3,3-trifluoropropyl)-4-methoxybenzamide (4v)

Following the general procedure, compound 4v was obtained as a white solid (13.4 mg, yield: 34%); mp = 140-142 °C; 1H NMR (400 MHz, DMSO-d6): δ 11.2 (s, 1H), 8.72 (d, J = 8.4 Hz, 1H), 7.84-7.80 (m, 2H), 7.71 (d, J = 2.0 Hz, 1H), 7.49 (d, J = 2.4 Hz, 1H), 7.39-7.37 (m, 1H), 7.09-7.07 (m, 1H), 7.01-6.97 (m, 2H), 5.76 (dt, J = 4.0 Hz, 9.2 Hz, 1H), 3.79 (s, 3H), 3.22-2.93 (m, 2H); 19F NMR (376 MHz, DMSO-d6): δ -62.6; 13C NMR (100 MHz, DMSO-d6): δ 165.0, 161.7, 134.8, 129.2, 126.8, 126.7 (q, J = 276 Hz), 126.6, 124.9, 123.6, 121.3, 118.1, 115.3, 113.6, 113.2, 55.4, 37.3 (q, J = 26 Hz); HRMS (ESI) for C19H17ClF3N2O2 [M+H]+ calcd. 397.0925, found 397.0928;

Enantiomeric excess established by HPLC analysis using a Chiralpak IA column, ee = 98% (HPLC: IA, 290 nm, hexane/isopropanol = 80:20, flow rate 1.0 mL/min, 25 °C, t_r
(major) = 9.0 min, tᵣ (minor) = 12.2 min.) [α]ᵣ<sup>25</sup> = -40.00 (c 1.0, MeOH).

(R)-N-(1-(5-bromo-1H-indol-3-yl)-3,3,3-trifluoropropyl)-4-methoxybenzamide (4w)

Following the general procedure, compound 4w was obtained as a white solid (16.1 mg, yield: 37%); mp = 171-173 °C; <sup>1</sup>H NMR (400 MHz, DMSO-<em>d</em><sub>6</sub>): δ 11.25 (s, 1H), 8.72 (d, <em>J</em> = 8.4 Hz, 1H), 7.86-7.81 (m, 3H), 7.48-7.47 (m, 1H), 7.35-7.33 (m, 1H), 7.20-7.18 (m, 1H), 7.00-6.98 (m, 1H), 5.75 (dt, <em>J</em> = 4.0 Hz, 9.2 Hz, 1H), 3.79 (s, 3H), 3.22-2.93 (m, 2H); <sup>19</sup>F NMR (376 MHz, DMSO-<em>d</em><sub>6</sub>): δ -62.6; <sup>13</sup>C NMR (100 MHz, DMSO-<em>d</em><sub>6</sub>): δ 165.0, 161.7, 135.0, 129.1, 127.5, 126.7 (q, <em>J</em> = 276 Hz), 126.6, 124.7, 123.8, 111.2, 115.2, 113.7, 113.6, 111.6, 55.4, 37.3 (q, <em>J</em> = 26 Hz); HRMS (ESI) for C<sub>19</sub>H<sub>17</sub>BrF<sub>3</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> calcd. 441.0420, 443.0400, found 441.0421, 443.0401; Enantiomeric excess established by HPLC analysis using a Chiralpak IA column, ee = 98% (HPLC: IA, 290 nm, hexane/isopropanol = 80:20, flow rate 1.0 mL/min, 25 °C, tᵣ (major) = 8.9 min, tᵣ (minor) = 12.3 min.) [α]ᵣ<sup>25</sup> = -49.00 (c 1.0, MeOH).

(R)-4-methoxy-N-(3,3,3-trifluoro-1-(6-methyl-1H-indol-3-yl)propyl)benzamide (4x)

Following the general procedure, compound 4x was obtained as a white solid (16.5 mg, yield: 44%); mp = 181-183 °C; <sup>1</sup>H NMR (400 MHz, DMSO-<em>d</em><sub>6</sub>): δ 10.85 (s, 1H), 8.63 (d, <em>J</em> = 8.8 Hz, 1H), 7.84-7.82 (m, 2H), 7.52-7.50 (m, 1H), 7.29 (d, <em>J</em> = 2.0 Hz, 1H), 7.15 (s, 1H), 6.99-6.97 (m, 2H), 6.82-6.80 (m, 1H), 5.80 (dt, <em>J</em> = 4.0 Hz, 9.2 Hz, 1H),
3.79 (s, 3H), 3.17-2.91 (m, 2H), 2.36 (s, 3H); $^{19}$F NMR (376 MHz, DMSO-$d_6$): δ -57.9; $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 164.8, 161.6, 136.8, 130.4, 129.2, 126.7, 126.82 (q, $J = 276$ Hz), 123.6, 122.1, 120.6, 118.4, 115.2, 113.5, 111.4, 55.4, 37.5 (q, $J = 26$ Hz), 21.4; HRMS (ESI) for C$_{20}$H$_{20}$F$_3$N$_2$O$_2$ [M+H]$^+$ calcd. 377.1471, found 377.1472; Enantiomeric excess established by HPLC analysis using a Chiralpak IA column, ee = 93% (HPLC: IA, 290 nm, hexane/isopropanol = 80:20, flow rate 1.0 mL/min, 25 °C, $t_r$ (major) = 11.5 min, $t_r$ (minor) = 19.4 min.) $[\alpha]_D^{25} = -9.00$ (c 1.0, MeOH).

(R)-N-(1-(6-chloro-1H-indol-3-yl)-3,3,3-trifluoropropyl)-4-methoxybenzamide (4y)

Following the general procedure, compound 4y was obtained as a white solid (15.7 mg, yield: 40%); mp = 178-180 °C; $^1$H NMR (400 MHz, DMSO-$d_6$): δ 11.18 (s, 1H), 8.70 (d, $J = 8.4$ Hz, 1H), 7.84-7.82 (m, 2H), 7.67-7.64 (m, 1H), 7.46-7.42 (m, 2H), 7.03-6.97 (m, 3H), 5.81 (dt, $J = 3.6$ Hz, 9.2 Hz, 1H), 3.79 (s, 3H), 3.20-2.94 (m, 2H); $^{19}$F NMR (376 MHz, DMSO-$d_6$): δ -62.6; $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 164.9, 161.7, 136.8, 129.2, 126.8 (q, $J = 276$ Hz), 126.6, 126.2, 124.5, 124.1, 120.1, 119.2, 115.7, 113.6, 111.3, 55.4, 37.4 (q, $J = 26$ Hz); HRMS (ESI) for C$_{19}$H$_{17}$ClF$_3$N$_2$O$_2$ [M+H]$^+$ calcd. 397.0925, found 397.0927; Enantiomeric excess established by HPLC analysis using a Chiralpak IA column, ee = 99% (HPLC: IA, 290 nm, hexane/isopropanol = 80:20, flow rate 1.0 mL/min, 25 °C, $t_r$ (major) = 10.8 min, $t_r$ (minor) = 14.4 min.) $[\alpha]_D^{25} = -18.00$ (c 1.0, MeOH).
(R)-4-methoxy-N-(3,3,3-trifluoro-1-(7-methyl-1H-indol-3-yl)propyl)benzamide (4z)

Following the general procedure, compound 4z was obtained as a white solid (18.6 mg, yield: 49%); mp = 191-193 °C; ^1H NMR (400 MHz, DMSO-d_6): δ 10.99 (s, 1H), 8.65 (d, J = 8.8 Hz, 1H), 7.85-7.83 (m, 2H), 7.49-7.47 (m, 1H), 7.39 (d, J = 2.0 Hz, 1H), 7.15 (s, 1H), 6.99-6.97 (m, 2H), 6.92-6.88 (m, 2H), 5.83 (dt, J = 4.0 Hz, 9.2 Hz, 1H), 3.79 (s, 3H), 3.20-2.93 (m, 2H), 2.45 (s, 3H); ^19F NMR (376 MHz, DMSO-d_6): δ -62.7; ^13C NMR (100 MHz, DMSO-d_6): δ 164.9, 161.7, 135.9, 129.2, 126.81 (q, J = 276 Hz), 126.78, 125.4, 122.6, 121.8, 120.8, 119.1, 116.3, 115.7, 113.5, 55.4, 37.7 (q, J = 26 Hz), 16.8; HRMS (ESI) for C_{20}H_{20}F_{3}N_{2}O_{2} [M+H]^+ calcd. 377.1471, found 377.1472;

Enantiomeric excess established by HPLC analysis using a Chiralpak IA column, ee = 91% (HPLC: IA, 280 nm, hexane/isopropanol = 80:20, flow rate 1.0 mL/min, 25 °C, t_r (major) = 12.5 min, t_r (minor) = 30.5 min.) [α]_D^{25} = 7.00 (c 1.0, MeOH).

(R)-4-methoxy-N-(3,3,3-trifluoro-1-(7-methoxy-1H-indol-3-yl)propyl)benzamide (4aa)

Following the general procedure, compound 4aa was obtained as a white solid (11.0 mg, yield: 28%); mp = 193-195 °C; ^1H NMR (400 MHz, DMSO-d_6): δ 11.11 (s, 1H), 8.63 (d, J = 8.8 Hz, 1H), 7.84-7.80 (m, 2H), 7.29-7.28 (m, 1H), 7.22-7.20 (m, 1H), 7.15 (s, 1H), 7.00-6.96 (m, 2H), 6.92-6.88 (m, 1H), 6.66-6.64 (m, 1H), 5.79 (dt, J = 4.0 Hz,
9.2 Hz, 1H), 3.89 (s, 3H), 3.79 (s, 3H), 3.16-2.91 (m, 2H); $^{19}$F NMR (376 MHz, DMSO-$d_6$): δ -62.7; $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 164.8, 161.6, 146.2, 129.2, 127.2, 126.8 (q, $J = 276$ Hz), 126.7, 126.4, 122.4, 119.5, 115.8, 113.5, 111.5, 101.9, 55.4, 55.2, 37.6 (q, $J = 26$ Hz); HRMS (ESI) for C$_{20}$H$_{20}$F$_3$N$_2$O$_3$ [M+H]$^+$ calcd. 393.1421, found 393.1421;

Enantiomeric excess established by HPLC analysis using a Chiralpak IA column, ee = 93% (HPLC: IA, 280 nm, hexane/isopropanol = 80:20, flow rate 1.0 mL/min, 25 ºC, $t_r$ (major) = 6.0 min, $t_r$ (minor) = 8.7 min.) [α]$_D^{25}$ = 2.00 (c 1.0, MeOH).

(R)-4-methoxy-$N$-(3,3,3-trifluoro-1-(2-hydroxy-4,6-dimethoxyphenyl)propyl)benz amide (4ab)

Following the general procedure, compound 4ab was obtained as a white solid (17.3 mg, yield: 43%); mp = 91-93 ºC; $^1$H NMR (400 MHz, CDCl$_3$): δ 9.11 (s, 1H), 7.72-7.69 (m, 2H), 7.54 (s, 1H), 6.86-6.84 (m, 2H), 6.24-6.20 (m, 1H), 6.08-6.02 (m, 2H), 3.79 (s, 3H), 3.78 (s, 3H), 3.67 (s, 3H), 3.12-2.99 (m, 1H), 2.72-2.58 (m, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$): δ -64.6; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 167.3, 162.5, 160.9, 158.6, 156.5, 128.9, 126.1 (q, $J = 276$ Hz), 126.0, 113.8, 107.4, 94.8, 91.6, 55.6, 55.3, 55.2, 40.4, 37.9 (q, $J = 26$ Hz); HRMS (ESI) for C$_{19}$H$_{21}$F$_3$NO$_5$ [M+H]$^+$ calcd. 400.1366, found 400.1366;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 81% (HPLC: IF-3, 230 nm, hexane/isopropanol = 85:15, flow rate 1.0 mL/min, 25 ºC, $t_r$ (major) = 23.1 min, $t_r$ (minor) = 10.3 min.) [α]$_D^{25}$ = 22.00 (c 1.0, CH$_2$Cl$_2$).
(S)-4-methoxy-N-(3,3,3-trifluoro-1-methoxypropyl)benzamide (6a)

Following the general procedure, compound 6a was obtained as a white solid (18.4 mg, yield: 66%); mp = 108-110 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.78 (d, $J$ = 8.8 Hz, 2H), 6.92 (d, $J$ = 8.8 Hz, 2H), 6.70 (d, $J$ = 9.2 Hz, 1H), 5.68 (dt, $J$ = 6.0 Hz, 9.6 Hz, 1H), 3.85 (s, 3H), 3.41 (s, 3H), 2.70-2.48 (m, 2H); $^{19}$F NMR (376 MHz, CDCl$_3$): δ -62.8; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 166.9, 162.7, 129.0, 125.5, 125.0 (q, $J$ = 275 Hz), 113.9, 76.5 (q, $J$ = 4 Hz), 56.0, 55.4, 39.5 (q, $J$ = 28 Hz); HRMS (ESI) for C$_{12}$H$_{14}$F$_3$NO$_3$Na [M+Na]$^+$ calcd. 300.0818, found 300.0821;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 89% (HPLC: IF-3, 250 nm, hexane/isopropanol = 95:5, flow rate 1.0 mL/min, 25 °C, $t_r$ (major) = 8.7 min, $t_r$ (minor) = 18.7 min.) $[\alpha]_D^{20}$ = 19.00 (c 1.0, CH$_2$Cl$_2$).

(5)-N-(1-ethoxy-3,3,3-trifluoropropyl)-4-methoxybenzamide (6b)

Following the general procedure, compound 6b was obtained as a white solid (19.4 mg, yield: 67%); mp = 102-104 °C; $^1$H NMR (600 MHz, CDCl$_3$): δ 7.77-7.75 (m, 2H), 6.94-6.92 (m, 2H), 6.51-6.49 (m, 1H), 5.78 (dt, $J$ = 6.0 Hz, 9.6 Hz, 1H), 3.85 (s, 3H), 3.74-3.69 (m, 1H), 3.62-3.57 (m, 1H), 2.67-2.50 (m, 2H), 1.20 (t, $J$ = 7.2 Hz, 3H); $^{19}$F NMR (376 MHz, CDCl$_3$): δ -62.9; $^{13}$C NMR (150 MHz, CDCl$_3$): δ 166.6, 162.7, 128.9, 125.6, 125.0 (q, $J$ = 275 Hz), 113.9, 75.0 (q, $J$ = 3 Hz), 64.2, 55.4, 39.8 (q, $J$ = 28 Hz), 14.9; HRMS (ESI) for C$_{13}$H$_{16}$F$_3$NO$_3$Na [M+Na]$^+$ calcd. 314.0974, found 314.0975;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 91% (HPLC: IF-3, 250 nm, hexane/isopropanol = 95:5, flow rate 1.0 mL/min, 25 °C, $t_r$ (major) = 13.1 min, $t_r$ (minor) = 21.3 min.) $[\alpha]_D^{25}$ = 27.00 (c 1.0, CH$_2$Cl$_2$).
(S)-4-methoxy-N-(3,3,3-trifluoro-1-isoproxypropyl)benzamide (6c)

Following the general procedure, compound 6c was obtained as a white solid (17.6 mg, yield: 58%); mp = 98-100 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.76-7.74 (m, 2H), 6.94-6.93 (m, 2H), 6.46-6.45 (m, 1H), 5.86 (dt, \(J = 6.6\) Hz, 9.2 Hz, 1H), 3.94-3.88 (m, 1H), 3.85 (s, 3H), 2.63-2.48 (m, 2H), 1.22 (d, \(J = 6.0\) Hz, 3H), 1.16 (d, \(J = 6.0\) Hz, 3H); \(^1^9\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -62.9; \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 166.3, 162.7, 128.9, 125.7, 125.0 (q, \(J = 275\) Hz), 113.9, 73.2 (q, \(J = 3\) Hz), 70.0, 40.3 (q, \(J = 28\) Hz), 23.3, 21.3; HRMS (ESI) for C\(_{14}\)H\(_{18}\)F\(_3\)NO\(_3\)Na [M+Na]\(^+\) calcd. 328.1131, found 328.1131;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 92% (HPLC: IF-3, 254 nm, hexane/isopropanol = 95:5, flow rate 1.0 mL/min, 25 °C, \(t\)\(_r\) (major) = 10.2 min, \(t\)\(_r\) (minor) = 12.8 min.) \([\alpha]_D^{25}\) = 50.00 (c 1.0, CH\(_2\)Cl\(_2\)).

(S)-N-(1-(tert-butoxy)-3,3,3-trifluoropropyl)-4-methoxybenzamide (6d)

Following the general procedure, compound 6d was obtained as a white solid (13.3 mg, yield: 42%); mp = 90-92 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.73-7.71 (m, 2H), 6.94-6.93 (m, 2H), 6.31-6.30 (m, 1H), 5.95 (dt, \(J = 6.0\) Hz, 8.4 Hz, 1H), 3.85 (s, 3H), 2.54-2.48 (m, 2H), 1.26 (s, 9H); \(^1^9\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -62.7; \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 165.1, 162.6, 128.7, 126.0, 125.0 (q, \(J = 275\) Hz), 113.9, 75.9, 70.5 (q, \(J = 3\) Hz), 55.4, 41.4 (q, \(J = 28\) Hz), 28.2; HRMS (ESI) for C\(_{15}\)H\(_{20}\)F\(_3\)NO\(_3\)Na [M+Na]\(^+\) calcd. 342.1287, found 342.1289;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 96% (HPLC: IF-3, 250 nm, hexane/isopropanol = 95:5, flow rate 1.0 mL/min, 25 °C, \(t\)\(_r\) (major) = 11.2 min, \(t\)\(_r\) (minor) = 14.6 min.) \([\alpha]_D^{25}\) = 21.00 (c 1.0, CH\(_2\)Cl\(_2\)).
(S)-4-methoxy-\textit{N}-(3,3,3-trifluoro-1-(methoxy-\textit{d}_3)propyl)benzamide (6e)

Following the general procedure, compound 6e was obtained as a white solid (13.5 mg, yield: 48%); mp = 107-109 °C; \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}): \(\delta\) 7.77-7.76 (m, 2H), 6.96-6.93 (m, 2H), 6.38 (d, \(J = 9.0\) Hz, 1H), 5.69 (dt, \(J = 6.0\) Hz, 9.6 Hz, 1H), 3.86 (s, 3H), 2.67-2.51 (m, 2H); \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}): \(\delta\) -62.8; \textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}): \(\delta\) 166.7, 162.8, 128.9, 125.5, 125.0 (q, \(J = 275\) Hz), 114.0, 76.5, 55.5, 39.7 (q, \(J = 28\) Hz); HRMS (ESI) for C\textsubscript{12}H\textsubscript{11}D\textsubscript{3}F\textsubscript{3}NO\textsubscript{3}Na [M+Na]\textsuperscript{+} calcd. 303.1006, found 303.1007; Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 93% (HPLC: IF-3, 254 nm, hexane/isopropanol = 95:5, flow rate 1.0 mL/min, 25 °C, \(t_r\) (major) = 8.6 min, \(t_r\) (minor) = 16.4 min.) \([\alpha]\)\textsubscript{D}\textsuperscript{25} = 19.00 (c 1.0, CH\textsubscript{2}Cl\textsubscript{2}).

(\textit{S})-4-methoxy-\textit{N}-(3,3,3-trifluoro-1-((4-methoxybenzyl)oxy)propyl)benzamide (6f)

Following the general procedure, compound 6f was obtained as a white solid (16.0 mg, yield: 42%); mp = 102-104 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.75-7.72 (m, 2H), 7.26-7.24 (m, 2H), 6.92-6.90 (m, 2H), 6.87-6.83 (m, 2H), 6.62-6.58 (m, 1H), 5.88 (dt, \(J = 6.0\) Hz, 9.6 Hz, 1H), 4.63-4.55 (m, 2H), 3.84 (s, 3H), 3.77 (s, 3H), 2.72-2.49 (m, 2H); \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}): \(\delta\) -62.7; \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 166.6, 162.7, 159.3, 129.44, 129.39, 129.0, 125.5, 125.0 (q, \(J = 275\) Hz), 113.9, 113.8, 74.8 (q, \(J = 4\) Hz), 70.4, 55.4, 55.2, 39.8 (q, \(J = 33\) Hz); HRMS (ESI) for C\textsubscript{10}H\textsubscript{20}F\textsubscript{3}NO\textsubscript{4}Na [M+Na]\textsuperscript{+} calcd. 406.1237, found 406.1240; Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee
= 90% (HPLC: IF-3, 250 nm, hexane/isopropanol = 95:5, flow rate 1.0 mL/min, 25 °C, t_r (major) = 27.8 min, t_r (minor) = 32.1 min.) [α]_D^{25} = 32.00 (c 1.0, CH₂Cl₂).

(S)-4-methoxy-N-(3,3,3-trifluoro-1-(thiophene-2-ylmethoxy)propyl)benzamide (6g)

Following the general procedure, compound 6g was obtained as a white solid (15.0 mg, yield: 45%); mp = 60-62 °C; ^1H NMR (600 MHz, CDCl₃): δ 7.75-7.73 (m, 2H), 7.28-7.26 (m, 1H), 7.04-7.03 (m, 1H), 6.95-6.93 (m, 3H), 6.54-6.52 (m, 1H), 5.92 (dt, J = 6.0 Hz, 9.6 Hz, 1H), 4.86-4.81 (m, 2H), 3.86 (s, 3H), 2.71-2.52 (m, 2H); ^19F NMR (376 MHz, CDCl₃): δ -62.8; ^13C NMR (150 MHz, CDCl₃): δ 166.7, 162.8, 139.8, 129.0, 127.0, 126.8, 126.1, 125.4, 124.9 (q, J = 275 Hz), 113.9, 74.9 (q, J = 3 Hz), 65.2, 55.4, 39.7 (q, J = 33 Hz); HRMS (ESI) for C₁₆H₁₆F₃NO₃Na [M+Na]^+ calcd. 382.0695, found 382.0697;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 91% (HPLC: IF-3, 290 nm, hexane/isopropanol = 95:5, flow rate 1.0 mL/min, 25 °C, t_r (major) = 7.9 min, t_r (minor) = 21.1 min.) [α]_D^{25} = 34.00 (c 1.0, CH₂Cl₂).

(S)-N-(1-(cyclobutylmethoxy)-3,3,3-trifluoropropyl)-4-methoxybenzamide (6h)

Following the general procedure, compound 6h was obtained as a white solid (16.9 mg, yield: 51%); mp = 88-90 °C; ^1H NMR (400 MHz, CDCl₃): δ 7.78-7.76 (m, 2H), 6.95-6.91 (m, 2H), 6.57-6.55 (m, 1H), 5.76 (dt, J = 6.0 Hz, 9.6 Hz, 1H), 3.86 (s, 3H), 3.65-
3.61 (m, 1H), 3.53-3.49 (m, 1H), 2.69-2.48 (m, 2H), 2.09-1.97 (m, 2H), 1.92-1.80 (m, 2H), 1.79-1.66 (m, 2H); $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -63.0; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 166.6, 162.7, 128.9, 125.6, 125.0 (q, $J = 275$ Hz), 113.9, 75.4 (q, $J = 4$ Hz), 73.1, 55.4, 39.7 (q, $J = 33$ Hz), 34.7, 24.8, 24.7, 18.4; HRMS (ESI) for C$_{16}$H$_{20}$F$_3$NO$_3$Na $[M+Na]^+$ calcd. 354.1287, found 354.1290;

Enantiomeric excess established by HPLC analysis using a Chiralpak IA column, ee = 84% (HPLC: IA, 250 nm, hexane/isopropanol = 95:5, flow rate 1.0 mL/min, 25 °C, $t_r$ (major) = 13.1 min, $t_r$ (minor) = 17.3 min.) $[\alpha]_D^{25} = 35.00$ (c 1.0, CH$_2$Cl$_2$).

(S)-4-methoxy-N-(3,3,3-trifluoro-1-hydroxypropyl)benzamide (6i)

Following the general procedure, compound 6i was obtained as a white solid (15.4 mg, yield: 59%); mp = 100-102 °C; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 8.85 (d, $J = 8.4$ Hz, 1H), 7.87-7.84 (m, 2H), 7.02-6.99 (m, 2H), 6.26 (d, $J = 4.8$ Hz, 1H), 5.78-5.72 (m, 1H), 3.81 (s, 3H), 2.76-2.57 (m, 2H); $^{19}$F NMR (376 MHz, DMSO-$d_6$): $\delta$ -62.3; $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 165.1, 161.9, 129.4, 126.2, 125.9 (q, $J = 275$ Hz), 113.6, 78.9 (q, $J = 33$ Hz), 68.2 (q, $J = 4$ Hz), 55.4; HRMS (ESI) for C$_{16}$H$_{12}$F$_3$NO$_3$Na $[M+Na]^+$ calcd. 286.0661, found 286.0664;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 80% (HPLC: IF-3, 280 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, $t_r$ (major) = 6.8 min, $t_r$ (minor) = 10.1 min.) $[\alpha]_D^{25} = -14.00$ (c 1.0, CH$_2$Cl$_2$).

$\text{tert-butyl (R)-(1-(1H-indol-3-yl)-4-oxo-4-phenylbutyl)carbamate (8a)}$

Following the general procedure, compound 8a was obtained as a white solid (26.5 mg, yield: 65%); mp = 112-114 °C; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 10.86 (s, 1H), 7.93-
7.91 (m, 2H), 7.69-7.67 (m, 1H), 7.63-7.59 (m, 1H), 7.51-7.48 (m, 2H), 7.37-7.35 (m, 1H), 7.23 (d, J = 2.0 Hz, 1H), 7.17-7.15 (m, 1H), 7.10-7.06 (m, 1H), 7.01-6.97 (m, 1H), 4.97-4.92 (m, 1H), 3.17-2.98 (m, 2H), 2.32-2.23 (m, 1H), 2.14-2.06 (m, 1H), 1.36 (s, 9H); 13C NMR (100 MHz, DMSO-d6): δ 199.7, 155.4, 136.8, 136.4, 133.1, 128.7, 127.8, 126.0, 122.1, 121.1, 118.9, 118.4, 117.2, 111.5, 77.5, 46.5, 35.1, 29.8, 28.3; HRMS (ESI) for C23H26N2O3Na [M+Na]+ calcd. 401.1836, found 401.1835;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 96% (HPLC: IF-3, 280 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, t_r (major) = 15.5 min, t_r (minor) = 14.1 min.) [α]D25 = 21.00 (c 1.0, CH2Cl2).

tert-butyl (R)-(1-(1H-indol-3-yl)-4-oxo-4-(p-tolyl)butyl)carbamate (8b)
Following the general procedure, compound 8b was obtained as a white solid (18.8 mg, yield: 48 %); mp = 116-118 °C; 1H NMR (600 MHz, CDCl3): δ 8.48 (s, 1H), 7.82-7.80 (m, 2H), 7.69 (d, J = 5.2 Hz, 1H), 7.35-7.33 (m, 1H), 7.21-7.17 (m, 3H), 7.12-7.10 (m, 1H), 7.04 (s, 1H), 5.09-5.08 (m, 1H), 4.89-4.88 (m, 1H), 3.13-3.00 (m, 2H), 2.40-2.38 (m, 5H), 1.41 (s, 9H); 13C NMR (150 MHz, CDCl3): δ 199.8, 155.6, 143.7, 136.6, 134.4, 129.2, 128.1, 125.9, 122.3, 121.4, 119.6, 119.3, 117.1, 111.4, 79.2, 47.5, 35.6, 29.7, 28.3, 21.5; HRMS (ESI) for C24H28N2O3Na [M+Na]+ calcd. 415.1992, found 415.1987;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 95% (HPLC: IF-3, 280 nm, hexane/isopropanol = 85:15, flow rate 1.0 mL/min, 25 °C, t_r (major) = 18.8 min, t_r (minor) = 16.2 min.) [α]D25 = 37.00 (c 1.0, CH2Cl2).

tert-butyl (R)-(1-(1H-indol-3-yl)-4-(4-methoxyphenyl)-4-oxobutyl)carbamate (8c)
Following the general procedure, compound 8c was obtained as a white solid (19.2 mg,
yield: 47 %); mp = 152-154 °C; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.48 (s, 1H), 7.90-7.88 (m, 2H), 7.70-7.69 (m, 1H), 7.36-7.34 (m, 1H), 7.20-7.17 (m, 1H), 7.13-7.10 (m, 1H), 7.06 (s, 1H), 6.88-6.87 (m, 1H), 5.10-5.08 (m, 1H), 4.90 (s, 1H), 3.84 (s, 3H), 3.11-2.98 (m, 2H), 2.40-2.39 (m, 2H), 1.41 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 198.7, 163.4, 155.6, 136.6, 130.3, 130.0, 125.9, 122.3, 121.5, 119.6, 119.3, 117.1, 113.6, 111.4, 79.2, 55.4, 47.5, 35.4, 29.8, 28.3; HRMS (ESI) for C$_{24}$H$_{28}$N$_2$O$_4$Na [M+Na]$^+$ calcd. 431.1941, found 431.1938;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 95% (HPLC: IF-3, 280 nm, hexane/isopropanol = 75:25, flow rate 1.0 mL/min, 25 °C, $t_r$ (major) = 13.1 min, $t_r$ (minor) = 11.4 min.) $[\alpha]_{D}^{25}$ = 37.00 (c 1.0, CH$_2$Cl$_2$).

**tert-butyl (R)-(4-(4-ethylphenyl)-1-(1H-indol-3-yl)-4-oxobutyl)carbamate (8d)**

Following the general procedure, compound 8d was obtained as a white solid (18.1 mg, yield: 45 %); mp = 112-114 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.40 (s, 1H), 7.85-7.83 (m, 2H), 7.71-7.69 (m, 1H), 7.36-7.34 (m, 1H), 7.24-7.22 (m, 2H), 7.21-7.17 (m, 1H), 7.14-7.10 (m, 1H), 7.14-7.10 (m, 1H), 7.08-7.07 (m, 1H), 5.10-5.08 (m, 1H), 4.88-4.86 (m, 1H), 3.15-3.00 (m, 2H), 2.68 (q, $J$ = 7.6 Hz, 2H), 2.42-2.40 (m, 2H), 1.41 (s, 9H), 1.24 (t, $J$ = 7.6 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 199.8, 155.6, 149.9, 136.6, 134.6, 128.3, 128.0, 125.9, 122.3, 121.4, 119.7, 119.3, 117.2, 111.3, 79.2, 47.5, 35.6, 29.8, 28.9, 28.3, 15.2; HRMS (ESI) for C$_{25}$H$_{30}$N$_2$O$_3$Na [M+Na]$^+$ calcd. 429.2149, found 429.2149;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 96% (HPLC: IF-3, 280 nm, hexane/isopropanol = 85:15, flow rate 1.0 mL/min, 25 °C, $t_r$ (major) = 18.8 min, $t_r$ (minor) = 16.7 min.) $[\alpha]_{D}^{25}$ = 38.00 (c 1.0, CH$_2$Cl$_2$).
**tert-butyl (R)-(4-([1,1'-biphenyl]-4-yl)-1-(1H-indol-3-yl)-4-oxobutyl)carbamate (8e)**

Following the general procedure, compound 8e was obtained as a white solid (19.2 mg, yield: 39%); mp = 88-90 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.43 (s, 1H), 7.98-7.96 (m, 2H), 7.72-7.70 (m, 1H), 7.63-7.58 (m, 5H), 7.47-7.43 (m, 2H), 7.40-7.38 (m, 1H), 7.36-7.34 (m, 1H), 7.21-7.17 (m, 1H), 7.14-7.10 (m, 1H), 7.07 (s, 1H), 5.12-5.10 (m, 1H), 4.90 (s, 1H), 3.19-3.04 (m, 2H), 2.44-2.42 (m, 2H), 1.41 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 199.8, 155.6, 139.8, 136.6, 135.6, 128.9, 128.6, 128.1, 127.2, 127.1, 125.9, 122.3, 121.5, 119.7, 119.3, 117.1, 111.4, 79.3, 47.5, 35.8, 29.8, 28.3; HRMS (ESI) for C₂₉H₃₀N₂O₃Na [M+Na]⁺ calcd. 477.2149, found 477.2149;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 93% (HPLC: IF-3, 280 nm, hexane/isopropanol = 85:15, flow rate 1.0 mL/min, 25 °C, tᵣ (major) = 24.8 min, tᵣ (minor) = 22.5 min.) [α]₀²⁵ = 34.00 (c 1.0, CH₂Cl₂).

![tert-butyl (R)-(4-([1,1'-biphenyl]-4-yl)-1-(1H-indol-3-yl)-4-oxobutyl)carbamate (8e)](image)

**tert-butyl (R)-(4-(4-chlorophenyl)-1-(1H-indol-3-yl)-4-oxobutyl)carbamate (8f)**

Following the general procedure, compound 8f was obtained as a white solid (16.6 mg, yield: 40%); mp = 118-120 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.31 (s, 1H), 7.84-7.82 (m, 2H), 7.70-7.68 (m, 1H), 7.39-7.35 (m, 3H), 7.22-7.18 (m, 1H), 7.14-7.09 (m, 2H), 5.09-5.07 (m, 1H), 4.86-4.84 (m, 1H), 3.14-2.98 (m, 2H), 2.44-2.38 (m, 2H), 1.41 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 198.8, 155.6, 139.4, 136.6, 135.2, 129.4, 128.9, 125.9, 122.4, 121.4, 119.8, 119.3, 117.1, 111.4, 79.4, 47.5, 35.7, 29.7, 28.4; HRMS (ESI) for C₂₉H₂₃ClN₂O₃Na [M+Na]⁺ calcd. 435.1446, found 435.1444;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 95% (HPLC: IF-3, 290 nm, hexane/isopropanol = 85:15, flow rate 1.0 mL/min, 25 °C, tᵣ (major) = 15.0 min, tᵣ (minor) = 14.2 min.) [α]₀²⁵ = 47.00 (c 1.0, CH₂Cl₂).
tert-butyl (R)-(4-(4-bromophenyl)-1-(1H-indol-3-yl)-4-oxobutyl)carbamate (8g)

Following the general procedure, compound 8g was obtained as a white solid (17.3 mg, yield: 37 %); mp = 116-118 °C; 1H NMR (600 MHz, CDCl₃): δ 8.39 (s, 1H), 7.75-7.74 (m, 2H), 7.69-7.67 (m, 1H), 7.54-7.53 (m, 2H), 7.36-7.35 (m, 1H), 7.21-7.18 (m, 1H), 7.13-7.11 (m, 1H), 7.07 (s, 1H), 5.08-5.07 (m, 1H), 4.87-4.86 (m, 1H), 3.09-2.98 (m, 2H), 2.42-2.39 (m, 2H), 1.41 (s, 9H); 13C NMR (150 MHz, CDCl₃): δ 199.0, 155.6, 136.5, 135.6, 131.8, 129.5, 128.1, 125.8, 122.4, 121.4, 119.7, 117.9, 117.0, 111.4, 79.3, 47.4, 35.7, 29.6, 28.3; HRMS (ESI) for C₂₃H₂₅BrN₂O₃Na [M+Na]⁺ calcd. 479.0941, found 479.0942;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 95% (HPLC: IF-3, 280 nm, hexane/isopropanol = 85:15, flow rate 1.0 mL/min, 25 °C, tᵣ (major) = 16.2 min, tᵣ (minor) = 15.4 min.) [α]D²⁵ = 33.00 (c 1.0, CH₂Cl₂).

tert-butyl (R)-(1-(1H-indol-3-yl)-4-oxo-4-(m-tolyl)butyl)carbamate (8h)

Following the general procedure, compound 8h was obtained as a white solid (19.4 mg, yield: 49 %); mp = 124-126 °C; 1H NMR (600 MHz, CDCl₃): δ 8.43 (s, 1H), 7.72-7.69 (m, 3H), 7.36-7.33 (m, 2H), 7.31-7.28 (m, 1H), 7.20-7.18 (m, 1H), 7.13-7.11 (m, 1H), 7.06 (s, 1H), 5.10-5.09 (m, 1H), 4.89-4.87 (m, 1H), 3.14-3.02 (m, 2H), 2.42-2.37 (m, 5H), 1.41 (s, 9H); 13C NMR (150 MHz, CDCl₃): δ 200.4, 155.6, 138.2, 136.9, 136.6, 133.7, 128.6, 128.4, 125.9, 125.2, 122.3, 121.4, 119.7, 119.3, 117.1, 111.4, 79.2, 47.5, 35.8, 29.7, 28.3, 21.3; HRMS (ESI) for C₂₃H₂₈N₂O₃Na [M+Na]⁺ calcd. 415.1992, found 415.1992;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 95% (HPLC: IF-3, 230 nm, hexane/isopropanol = 85:15, flow rate 1.0 mL/min, 25
37°C, t_r (major) = 19.0 min, t_r (minor) = 18.0 min.) [α]_D^{25} = 47.00 (c 1.0, CH_2Cl_2).

**tert-butyl (R)-(1-(1H-indol-3-yl)-4-(3-methoxyphenyl)-4-oxobutyl)carbamate (8i)**

Following the general procedure, compound 8i was obtained as a white solid (19.1 mg, yield: 47 %); mp = 60-62 °C; ¹H NMR (600 MHz, CDCl₃): δ 8.38 (s, 1H), 7.70-7.69 (m, 1H), 7.48-7.47 (m, 1H), 7.45 (s, 1H), 7.36-7.34 (m, 1H), 7.32-7.30 (m, 1H), 7.20-7.18 (m, 1H), 7.13-7.11 (m, 1H), 7.08-7.06 (m, 2H), 5.10-5.09 (m, 1H), 4.88 (s, 1H), 3.81 (s, 3H), 3.14-3.02 (m, 2H), 2.43-2.41 (m, 2H), 1.41 (s, 9H); ¹³C NMR (150 MHz, CDCl₃): δ 199.9, 159.7, 155.6, 138.3, 136.6, 129.5, 125.9, 122.3, 121.4, 120.7, 119.7, 119.5, 119.3, 117.1, 112.2, 111.4, 79.2, 55.3, 47.5, 35.9, 29.7, 28.3; HRMS (ESI) for C_{24}H_{28}N_{2}O_{4}Na [M+Na]^+ calcd. 431.1941, found 431.1942; Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 93% (HPLC: IF-3, 280 nm, hexane/isopropanol = 75:25, flow rate 1.0 mL/min, 25 °C, t_r (major) = 14.7 min, t_r (minor) = 22.2 min.) [α]_D^{25} = 37.00 (c 1.0, CH₂Cl₂).

**tert-butyl (R)-(4-(3-chlorophenyl)-1-(1H-indol-3-yl)-4-oxobutyl)carbamate (8j)**

Following the general procedure, compound 8j was obtained as a white solid (18.2 mg, yield: 44 %); mp = 50-62 °C; ¹H NMR (600 MHz, CDCl₃): δ 8.33 (s, 1H), 7.87 (s, 1H), 7.77-7.75 (m, 1H), 7.69-7.68 (m, 1H), 7.50-7.48 (m, 1H), 7.38-7.33 (m, 2H), 7.21-7.19 (m, 1H), 7.14-7.11 (m, 1H), 7.08 (s, 1H), 5.09-5.08 (m, 1H), 4.86 (s, 1H), 3.11-3.01 (m, 2H), 2.44-2.40 (m, 2H), 1.41 (s, 9H); ¹³C NMR (150 MHz, CDCl₃): δ 198.7, 155.6, 138.4, 136.6, 134.8, 132.9, 129.8, 128.1, 126.1, 125.8, 122.4, 121.4, 119.8, 119.3, 117.0, 111.4, 79.3, 47.4, 35.8, 29.5, 28.3; HRMS (ESI) for C_{23}H_{25}ClN_{2}O_{3}Na [M+Na]^+ calcd. 435.1446, found 435.1447; Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee
= 95% (HPLC: IF-3, 280 nm, hexane/isopropanol = 75:25, flow rate 1.0 mL/min, 25 °C, t_r (major) = 10.1 min, t_r (minor) = 15.8 min.) [α]_D^{25} = 35.00 (c 1.0, CH2Cl2).

tert-butyl (R)-(1-(1H-indol-3-yl)-4-oxo-4-(thiophen-2-yl)butyl)carbamate (8k)
Following the general procedure, compound 8k was obtained as a white solid (12.5 mg, yield: 33 %); mp = 132-134 °C; ^1H NMR (600 MHz, CDCl3): δ 8.39 (s, 1H), 7.70-7.68 (m, 1H), 7.64-7.63 (m, 1H), 7.60-7.59 (m, 1H), 7.37-7.35 (m, 1H), 7.21-7.18 (m, 1H), 7.13-7.11 (m, 1H), 7.08-7.06 (m, 2H), 5.09-5.08 (m, 1H), 4.86-4.85 (m, 1H), 3.11-2.97 (m, 2H), 2.42-2.41 (m, 2H), 1.41 (s, 9H); ^13C NMR (150 MHz, CDCl3): δ 193.0, 155.6, 144.2, 136.6, 133.5, 131.9, 128.0, 125.9, 122.4, 121.4, 119.7, 119.3, 117.1, 111.4, 79.2, 47.5, 36.4, 29.9, 28.3; HRMS (ESI) for C_{21}H_{24}N_{2}O_{3}SNa [M+Na]^+ calcd. 407.1400, found 407.1400;
Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 90% (HPLC: IF-3, 260 nm, hexane/isopropanol = 85:15, flow rate 1.0 mL/min, 25 °C, t_r (major) = 16.1 min, t_r (minor) = 14.7 min.) [α]_D^{25} = 41.00 (c 1.0, CH2Cl2).

tert-butyl (R)-(4-(3,4-dimethoxyphenyl)-1-(1H-indol-3-yl)-4-oxobutyl)carbamate (8l)
Following the general procedure, compound 8l was obtained as a white solid (18.5 mg, yield: 42 %); mp = 132-134 °C; ^1H NMR (600 MHz, CDCl3): δ 8.60 (s, 1H), 7.51-7.69 (m, 1H), 7.52-7.50 (m, 2H), 7.36-7.34 (m, 1H), 7.19-7.17 (m, 1H), 7.13-7.10 (m, 1H), 7.05 (s, 1H), 6.82-6.80 (m, 1H), 5.10-5.09 (m, 1H), 4.92-4.91 (m, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 3.12-3.00 (m, 2H), 2.41-2.40 (m, 2H), 1.42 (s, 9H); ^13C NMR (150 MHz, CDCl3): δ 198.8, 155.6, 153.1, 148.8, 136.6, 130.0, 125.9, 122.7, 122.2, 121.5, 119.6, 119.2, 117.0, 114.0, 110.0, 109.9, 79.2, 56.0, 55.8, 47.5, 35.2, 30.0, 28.3; HRMS (ESI)
for C$_{25}$H$_{30}$N$_2$O$_5$Na [M+Na]$^+$ calcd. 461.2047, found 461.2046;

Enantiomeric excess established by HPLC analysis using a Chiralpak IA column, ee = 96% (HPLC: IA, 280 nm, hexane/isopropanol = 80:20, flow rate 1.0 mL/min, 25°C, $t_r$ (major) = 15.7 min, $t_r$ (minor) = 19.4 min.) [$\alpha$]$_D^{25}$ = 39.00 (c 1.0, CH$_2$Cl$_2$).

**tert-butyl (R)-(4-cyclopropyl-1-(1H-indol-3-yl)-4-oxobutyl)carbamate (8m)**

Following the general procedure, compound 8m was obtained as a colorless oil (17.5 mg, yield: 51%); ¹H NMR (600 MHz, CDCl$_3$): δ 8.62 (s, 1H), 7.67-7.65 (m, 1H), 7.34-7.33 (m, 1H), 7.19-7.16 (m, 1H), 7.11-7.09 (m, 1H), 6.98 (s, 1H), 4.99-4.97 (m, 1H), 4.89 (s, 1H), 2.73-2.61 (m, 2H), 2.25-2.24 (m, 2H), 1.89-1.85 (m, 1H), 1.42 (s, 9H), 1.00-0.99 (m, 2H), 0.84-0.82 (m, 2H); ¹³C NMR (150 MHz, CDCl$_3$): δ 211.0, 155.6, 136.6, 125.8, 122.2, 121.5, 119.5, 119.2, 116.9, 111.4, 79.2, 47.5, 40.4, 29.2, 28.4, 20.5, 10.8, 10.7; HRMS (ESI) for C$_{20}$H$_{26}$N$_2$O$_3$Na [M+Na]$^+$ calcd. 365.1836, found 365.1833;

Enantiomeric excess established by HPLC analysis using a Chiralpak IC-3 column, ee = 94% (HPLC: IC-3, 280 nm, hexane/isopropanol = 75:25, flow rate 1.0 mL/min, 25°C, $t_r$ (major) = 10.6 min, $t_r$ (minor) = 13.5 min.) [$\alpha$]$_D^{25}$ = 37.00 (c 1.0, CH$_2$Cl$_2$).

**methyl (R)-4-((tert-butoxycarbonyl)amino)-4-(1H-indol-3-yl)butanoate (8n)**

Following the general procedure, compound 8n was obtained as a colorless oil (15.9 mg, yield: 48%); ¹H NMR (600 MHz, CDCl$_3$): δ 8.47 (s, 1H), 7.67-7.65 (m, 1H), 7.35-7.34 (m, 1H), 7.20-7.18 (m, 1H), 7.12-7.10 (m, 1H), 7.02 (s, 1H), 5.01-5.00 (m, 1H), 4.87-4.86 (m, 1H), 3.64 (s, 3H), 2.48-2.38 (m, 2H), 2.33-2.27 (m, 2H), 1.44 (s, 9H); ¹³C NMR (150 MHz, CDCl$_3$): δ 174.0, 155.5, 136.6, 125.7, 122.3, 121.5, 119.6, 119.2, 116.7, 111.4, 79.3, 51.6, 47.4, 31.2, 30.5, 28.4; HRMS (ESI) for C$_{18}$H$_{24}$N$_2$O$_4$Na
$\text{[M+Na]}^+$ calcd. 355.1628, found 355.1628;

Enantiomeric excess established by HPLC analysis using a Chiralpak IC-3 column, ee = 92\% (HPLC: IC-3, 280 nm, hexane/isopropanol = 75:25, flow rate 1.0 mL/min, 25 °C, $t_r$ (major) = 10.2 min, $t_r$ (minor) = 12.1 min.) $[\alpha]_D^{25} = 38.00 \ (c \ 1.0, \text{CH}_2\text{Cl}_2)$.

![Chemical structure](attachment:image.png)

**benzyl (R)-4-((tert-butoxycarbonyl)amino)-4-(1H-indol-3-yl)butanoate (8o)**

Following the general procedure, compound 8o was obtained as a white solid (26.0 mg, yield: 64 \%); mp = 120-122 °C; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.48-8.45 (m, 1H), 7.64-7.63 (m, 1H), 7.35-7.30 (m, 6H), 7.18-7.16 (m, 1H), 7.10-7.08 (m, 1H), 6.95 (s, 1H), 5.11-5.05 (m, 2H), 5.01-5.00 (m, 1H), 4.88 (s, 1H), 2.51-2.41 (m, 2H), 2.33-2.27 (m, 2H), 1.44 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 173.3, 155.5, 136.5, 135.8, 128.5, 128.1, 125.7, 122.2, 121.5, 119.6, 119.2, 116.5, 111.4, 79.3, 66.2, 47.4, 31.4, 30.4, 28.4; HRMS (ESI) for C$_{24}$H$_{28}$N$_2$O$_4$Na [M+Na]$^+$ calcd. 431.1941, found 431.1938;

Enantiomeric excess established by HPLC analysis using a Chiralpak IC-3 column, ee = 87\% (HPLC: IC-3, 280 nm, hexane/isopropanol = 75:25, flow rate 1.0 mL/min, 25 °C, $t_r$ (major) = 9.3 min, $t_r$ (minor) = 11.5 min.) $[\alpha]_D^{25} = 35.00 \ (c \ 1.0, \text{CH}_2\text{Cl}_2)$.

![Chemical structure](attachment:image.png)

**diethyl (R)-2-((tert-butoxycarbonyl)amino)-2-(1H-indol-3-yl)ethyl)malonate (8p)**

Following the general procedure, compound 8p was obtained as a white solid (29.2 mg, yield: 70 \%); mp = 98-100 °C; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.60 (s, 1H), 7.68-7.66 (m, 1H), 7.35-7.33 (m, 1H), 7.18-7.16 (m, 1H), 7.11-7.09 (m, 1H), 7.00 (s, 1H), 5.12-5.11 (m, 2H), 4.87-4.85 (m, 1H), 4.24-4.16 (m, 2H), 4.15-4.11 (m, 2H), 3.54 (t, $J$ = 7.2 Hz, 1H), 2.63-2.58 (m, 1H), 2.54-2.52 (m, 1H), 1.43 (s, 9H), 1.26 (t, $J$ = 7.2 Hz, 3H), 1.21 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 169.7, 169.2, 155.4, 136.5,
125.6, 122.2, 121.5, 119.6, 119.2, 116.3, 111.4, 79.3, 61.53, 61.45, 49.6, 46.3, 34.2, 28.4, 28.3, 14.0, 13.9; HRMS (ESI) for C_{22}H_{30}N_{2}O_{6}Na [M+Na]^+ calcd. 441.1996, found 441.1997;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 92% (HPLC: IF-3, 280 nm, hexane/isopropanol = 85:15, flow rate 1.0 mL/min, 25 °C, t_r (major) = 9.4 min, t_r (minor) = 10.8 min.) [α]_D^{25} = 34.00 (c 1.0, CH₂Cl₂).

**tert-butyl (R)-(1-(4-methyl-1H-indol-3-yl)-4-oxo-4-phenylbutyl)carbamate (8q)**

Following the general procedure, compound 8q was obtained as a white solid (23.2 mg, yield: 59 %); mp = 106-108 °C; ^1H NMR (600 MHz, CDCl₃): δ 8.50 (s, 1H), 7.93-7.92 (m, 2H), 7.53-7.51 (m, 1H), 7.42-7.40 (m, 2H), 7.20-7.19 (m, 1H), 7.10-7.05 (m, 2H), 6.87-6.86 (m, 1H), 5.31-5.30 (m, 1H), 4.81-4.80 (m, 1H), 3.22-3.09 (m, 2H), 2.69 (s, 3H), 2.39-2.36 (m, 2H), 1.41 (s, 9H); ^13C NMR (150 MHz, CDCl₃): δ 200.1, 155.0, 136.9, 133.0, 130.9, 128.5, 128.0, 124.9, 122.4, 121.6, 117.4, 109.2, 79.2, 47.4, 36.1, 30.6, 28.3, 20.1; HRMS (ESI) for C_{24}H_{28}N_{2}O_{6}Na [M+Na]^+ calcd. 415.1992, found 415.1990;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 94% (HPLC: IF-3, 280 nm, hexane/isopropanol = 85:15, flow rate 1.0 mL/min, 25 °C, t_r (major) = 15.3 min, t_r (minor) = 13.1 min.) [α]_D^{25} = 42.00 (c 1.0, CH₂Cl₂).

**tert-butyl (R)-(1-(4-methoxy-1H-indol-3-yl)-4-oxo-4-phenylbutyl)carbamate (8r)**

Following the general procedure, compound 8r was obtained as a white solid (20.1 mg,
yield: 49 %); mp = 92-94 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 8.45 (s, 1H), 7.87-7.85 (m, 2H), 7.51-7.49 (m, 1H), 7.40-7.37 (m, 2H), 7.12-7.09 (m, 1H), 7.00-6.99 (m, 1H), 6.95 (s, 1H), 6.54-6.53 (m, 1H), 5.84-5.83 (m, 1H), 5.05-5.01 (m, 1H), 3.98 (s, 3H), 3.06-2.88 (m, 2H), 2.42-2.36 (m, 1H), 2.26-2.20 (m, 1H), 1.40 (s, 9H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 200.3, 155.6, 153.0, 138.7, 137.0, 132.7, 128.4, 128.0, 122.9, 122.4, 121.2, 116.8, 115.6, 105.0, 99.7, 78.8, 55.2, 48.6, 36.3, 32.0, 28.4; HRMS (ESI) for \(\text{C}_{24}\text{H}_{28}\text{N}_{2}\text{O}_{4}\text{Na}[\text{M+Na}]^+\) calcd. 431.1941, found 431.1941;

Enantiomeric excess established by HPLC analysis using a Chiralpak IC-3 column, ee = 94% (HPLC: IC-3, 280 nm, hexane/isopropanol = 75:25, flow rate 1.0 mL/min, 25 °C, \(t_r\) (major) = 18.0 min, \(t_r\) (minor) = 11.7 min.) \([\alpha]_D^{25}\) = 43.00 (c 1.0, CH\(_2\)Cl\(_2\)).

**tert-butyl \(R\)-(1-(4-chloro-1H-indol-3-yl)-4-oxo-4-phenylbutyl)carbamate (8s)**

Following the general procedure, compound 8s was obtained as a white solid (14.5 mg, yield: 35 %); mp = 96-98 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 8.59 (s, 1H), 7.93-7.92 (m, 2H), 7.54-7.52 (m, 1H), 7.44-7.41 (m, 2H), 7.26-7.24 (m, 1H), 7.12-7.05 (m, 3H), 5.44-5.43 (m, 1H), 5.18 (s, 1H), 3.20-3.06 (m, 2H), 2.41-2.39 (m, 2H), 1.41 (s, 9H);

\(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 200.4, 155.4, 153.2, 138.2, 136.9, 133.0, 128.5, 128.1, 125.7, 123.2, 123.1, 122.7, 120.9, 117.5, 110.2, 79.2, 47.9, 36.1, 31.4, 28.4; HRMS (ESI) for \(\text{C}_{23}\text{H}_{25}\text{ClN}_{2}\text{O}_{3}\text{Na}[\text{M+Na}]^+\) calcd. 435.1446, found 435.1443;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 96% (HPLC: IF-3, 280 nm, hexane/isopropanol = 85:15, flow rate 1.0 mL/min, 25 °C, \(t_r\) (major) = 10.6 min, \(t_r\) (minor) = 8.9 min.) \([\alpha]_D^{25}\) = 25.00 (c 1.0, CH\(_2\)Cl\(_2\)).
**tert-butyl (R)-(1-(5-methyl-1H-indol-3-yl)-4-oxo-4-phenylbutyl)carbamate (8t)**

Following the general procedure, compound 8t was obtained as a white solid (26.5 mg, yield: 68 %); mp = 128-130 °C; \[^1^H\text{NMR (600 MHz, CDCl}_3\): δ 8.20 (s, 1H), 7.92-7.91 (m, 2H), 7.54-7.51 (m, 1H), 7.47 (s, 1H), 7.43-7.40 (m, 2H), 7.26-7.24 (m, 1H), 7.06-7.02 (m, 2H), 5.07-5.06 (m, 1H), 4.84 (s, 1H), 3.16-3.03 (m, 2H), 2.44-2.41 (m, 5H), 1.42 (s, 9H); \[^{13}\text{C NMR (150 MHz, CDCl}_3\): δ 200.1, 155.6, 136.9, 134.9, 132.9, 129.0, 128.5, 128.0, 126.1, 124.0, 121.5, 119.0, 116.7, 111.0, 79.2, 47.5, 35.8, 29.6, 28.4, 21.5; HRMS (ESI) for C\text{24}H\text{28}N\text{2}O\text{3}Na [M+Na]^{+} \text{calcd. 431.1992, found 431.1992; Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 95\% (HPLC: IF-3, 280 nm, hexane/isopropanol = 85:15, flow rate 1.0 mL/min, 25 °C, t\_r (major) = 11.9 min, t\_r (minor) = 22.1 min.) [\[\alpha\]D\text{25} = 25.00 (c 1.0, CH}_2\text{Cl}_2].

**tert-butyl (R)-(1-(5-methoxy-1H-indol-3-yl)-4-oxo-4-phenylbutyl)carbamate (8u)**

Following the general procedure, compound 8u was obtained as a white solid (24.0 mg, yield: 59 %); mp = 118-120 °C; \[^1^H\text{NMR (600 MHz, CDCl}_3\): δ 8.26 (s, 1H), 7.93-7.92 (m, 2H), 7.55-7.52 (m, 1H), 7.44-7.41 (m, 2H), 7.25-7.24 (m, 1H), 7.15 (s, 1H), 7.06 (s, 1H), 6.87-6.85 (m, 1H), 5.10-5.08 (m, 1H), 4.82-4.81 (m, 1H), 3.83 (s, 3H), 3.18-3.06 (m, 2H), 2.42-2.41 (m, 2H), 1.41 (s, 9H); \[^{13}\text{C NMR (150 MHz, CDCl}_3\): δ 200.1, 155.7, 154.1, 136.9, 133.0, 131.6, 128.5, 128.0, 126.5, 121.9, 117.0, 112.9, 112.1, 100.8, 79.2, 55.7, 47.2, 35.7, 29.3, 28.3; HRMS (ESI) for C\text{24}H\text{28}N\text{2}O\text{4}Na [M+Na]^{+} \text{calcd. 431.1941, found 431.1943; Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 95\% (HPLC: IF-3, 280 nm, hexane/isopropanol = 85:15, flow rate 1.0 mL/min, 25 °C, t\_r (major) = 11.9 min, t\_r (minor) = 22.1 min.) [\[\alpha\]D\text{25} = 25.00 (c 1.0, CH}_2\text{Cl}_2].
 tert-butyl (R)-(1-(5-(benzyloxy)-1H-indol-3-yl)-4-oxo-4-phenylbutyl)carbamate (8v)

Following the general procedure, compound 8v was obtained as a white solid (26.5 mg, yield: 55 %); mp = 116-118 °C; ¹H NMR (600 MHz, CDCl₃): δ 8.33-8.31 (m, 1H), 7.92-7.91 (m, 2H), 7.53-7.51 (m, 1H), 7.46-7.45 (m, 2H), 7.42-7.40 (m, 2H), 7.38-7.35 (m, 2H), 7.31-7.28 (m, 1H), 7.25-7.22 (m, 2H), 7.02 (s, 1H), 6.93-6.91 (m, 1H), 5.08-5.04 (m, 3H), 4.84 (s, 1H), 3.15-3.13 (m, 2H), 2.39-2.38 (m, 2H), 1.41 (s, 9H); ¹³C NMR (150 MHz, CDCl₃): δ 200.1, 155.7, 137.5, 136.9, 133.0, 131.8, 128.5, 128.4, 128.0, 127.75, 127.66, 126.4, 122.0, 116.9, 113.4, 112.1, 102.5, 79.2, 70.7, 47.3, 35.7, 29.4, 28.3; HRMS (ESI) for C₁₃H₁₂N₂O₄Na [M+Na]⁺ calcd. 507.2254, found 507.2258;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 96% (HPLC: IF-3, 280 nm, hexane/isopropanol = 75:25, flow rate 1.0 mL/min, 25 °C, tᵣ (major) = 20.0 min, tᵣ (minor) = 33.5 min.) [α]D²⁵ = 24.00 (c 1.0, CH₂Cl₂).

 tert-butyl (R)-(1-(5-bromo-1H-indol-3-yl)-4-oxo-4-phenylbutyl)carbamate (8w)

Following the general procedure, compound 8w was obtained as a white solid (14.4 mg, yield: 32 %); mp = 72-74 °C; ¹H NMR (600 MHz, CDCl₃): δ 8.37 (s, 1H), 7.93-7.92 (m, 2H), 7.82-7.81 (m, 1H), 7.56-7.53 (m, 1H), 7.45-7.42 (m, 2H), 7.28-7.26 (m, 1H),
7.23-7.21 (m, 1H), 7.09 (s, 1H), 5.04-5.03 (m, 1H), 4.83 (s, 1H), 3.17-3.05 (m, 2H), 2.41-2.39 (m, 2H), 1.42 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$): δ 200.3, 155.6, 136.8, 135.2, 133.1, 128.6, 128.0, 127.7, 125.3, 122.6, 122.0, 117.2, 113.1, 112.8, 79.6, 47.4, 35.6, 29.4, 28.4; HRMS (ESI) for C$_{23}$H$_{25}$BrN$_2$O$_3$Na $[M+Na]^+$ calcd. 479.0941, found 479.0944;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 96% (HPLC: IF-3, 280 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, $t_r$ (major) = 11.3 min, $t_r$ (minor) = 10.2 min.) $[\alpha]_D^{25} = 26.00$ (c 1.0, CH$_2$Cl$_2$).

**tert-butyl (R)-(1-(6-methyl-1H-indol-3-yl)-4-oxo-4-phenylbutyl)carbamate (8x)**

Following the general procedure, compound 8x was obtained as a white solid (27.0 mg, yield: 69 %); mp = 102-104 °C; $^1$H NMR (400 MHz, DMSO-$d_6$): δ 10.68 (s, 1H), 7.92-7.90 (m, 2H), 7.63-7.59 (m, 1H), 7.55-7.48 (m, 3H), 7.14-7.12 (m, 3H), 6.83-6.81 (m, 1H), 4.93-4.87 (m, 1H), 3.15-2.96 (m, 2H), 2.38 (s, 3H), 2.30-2.21 (m, 1H), 2.12-2.03 (m, 1H), 1.36 (s, 9H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 199.8, 155.4, 136.9, 133.0, 130.0, 128.7, 127.8, 123.9, 121.3, 120.2, 118.7, 117.0, 111.3, 77.5, 46.6, 35.1, 29.8, 28.3, 21.4; HRMS (ESI) for C$_{24}$H$_{28}$N$_2$O$_3$Na $[M+Na]^+$ calcd. 415.1992, found 415.1992;

Enantiomeric excess established by HPLC analysis using a Chiralpak IA column, ee = 96% (HPLC: IA, 280 nm, hexane/isopropanol = 85:15, flow rate 1.0 mL/min, 25 °C, $t_r$ (major) = 21.7 min, $t_r$ (minor) = 25.4 min.) $[\alpha]_D^{25} = 12.00$ (c 1.0, CH$_2$Cl$_2$).

**tert-butyl (R)-(1-(6-methoxy-1H-indol-3-yl)-4-oxo-4-phenylbutyl)carbamate (8y)**
Following the general procedure, compound 8y was obtained as a white solid (20.7 mg, yield: 51 %); mp = 100-102 °C; ^1^H NMR (600 MHz, CDCl\textsubscript{3}): δ 8.30 (s, 1H), 7.91-7.90 (m, 2H), 7.57-7.55 (m, 1H), 7.53-7.51 (m, 1H), 6.95 (s, 1H), 6.83 (s, 1H), 6.80-6.78 (m, 1H), 5.05-5.04 (m, 1H), 4.87-4.86 (m, 1H), 3.80 (s, 3H), 3.14-3.02 (m, 2H), 2.39-2.38 (m, 2H), 1.41 (s, 9H); ^1^C NMR (150 MHz, CDCl\textsubscript{3}): δ 200.2, 156.6, 155.6, 137.4, 136.9, 132.9, 128.5, 128.0, 120.3, 119.7, 117.1, 109.7, 94.8, 79.2, 55.6, 47.5, 35.7, 29.6, 28.3; HRMS (ESI) for C\textsubscript{24}H\textsubscript{28}N\textsubscript{2}O\textsubscript{4}Na [M+Na\textsuperscript+]+ calcd. 431.1941, found 431.1941;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 96% (HPLC: IF-3, 280 nm, hexane/isopropanol = 85:15, flow rate 1.0 mL/min, 25 °C, t\textsubscript{r} (major) = 19.4 min, t\textsubscript{r} (minor) = 33.8 min.) [α]D\textsuperscript{20} = 40.00 (c 1.0, CH\textsubscript{2}Cl\textsubscript{2}).

\[ \text{t}_{\text{er}-\text{butyl (R)-(1-(6-chloro-1H-indol-3-yl)-4-oxo-4-phenylbutyl)carbamate (8z)}} \]

Following the general procedure, compound 8z was obtained as a white solid (19.8 mg, yield: 48 %); mp = 174-176 °C; ^1^H NMR (600 MHz, CDCl\textsubscript{3}): δ 8.44 (s, 1H), 7.92-7.91 (m, 2H), 7.60-7.59 (m, 1H), 7.55-7.53 (m, 1H), 7.44-7.42 (m, 2H), 7.33 (s, 1H), 7.09-7.06 (m, 2H), 5.07-5.06 (m, 1H), 4.85-4.84 (m, 1H), 3.16-3.06 (m, 2H), 2.41-2.37 (m, 2H), 1.40 (s, 9H); ^1^C NMR (150 MHz, CDCl\textsubscript{3}): δ 200.1, 155.6, 136.9, 136.8, 133.1, 128.5, 128.3, 124.5, 121.9, 120.4, 120.2, 117.6, 111.2, 79.4, 47.3, 35.6, 29.5, 28.3; HRMS (ESI) for C\textsubscript{23}H\textsubscript{25}ClN\textsubscript{2}O\textsubscript{3}Na [M+Na\textsuperscript+] calcd. 435.1446, found 435.1448;

Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 98% (HPLC: IF-3, 280 nm, hexane/isopropanol = 85:15, flow rate 1.0 mL/min, 25 °C, t\textsubscript{r} (major) = 11.6 min, t\textsubscript{r} (minor) = 10.6 min.) [α]D\textsuperscript{25} = 28.00 (c 1.0, CH\textsubscript{2}Cl\textsubscript{2}).
**tert-butyl (R)-(1-(7-methyl-1H-indol-3-yl)-4-oxo-4-phenylbutyl)carbamate (8aa)**

Following the general procedure, compound **8aa** was obtained as a white solid (27.4 mg, yield: 70 %); mp = 102-104 °C; ^1^H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) 10.82 (s, 1H), 7.92-7.90 (m, 2H), 7.63-7.59 (m, 1H), 7.51-7.48 (m, 3H), 7.21-7.20 (m, 1H), 7.15-7.13 (m, 1H), 6.91-6.86 (m, 2H), 4.95-4.89 (m, 1H), 3.15-2.97 (m, 2H), 2.44 (s, 3H), 2.30-2.22 (m, 1H), 2.13-2.04 (m, 1H), 1.36 (s, 9H); ^1^C NMR (100 MHz, DMSO-\(d_6\)): \(\delta\) 199.6, 155.3, 136.8, 135.9, 133.1, 128.7, 127.8, 125.6, 121.8, 121.6, 120.5, 118.7, 117.6, 116.6, 77.5, 46.6, 35.1, 29.9, 28.3, 16.8; HRMS (ESI) for C\(_{24}\)H\(_{28}\)N\(_2\)O\(_3\)Na [M+Na]^+ calcld. 415.1992, found 415.1992.

Enantiomeric excess established by HPLC analysis using a Chiralpak IA column, ee = 97% (HPLC: IA, 280 nm, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, \(t_r\) (major) = 23.2 min, \(t_r\) (minor) = 29.3 min.) [\(\alpha\)]\(_D\)\(^{25}\) = 15.00 (c 1.0, CH\(_2\)Cl\(_2\)).

**tert-butyl (R)-(1-(7-methoxy-1H-indol-3-yl)-4-oxo-4-phenylbutyl)carbamate (8ab)**

Following the general procedure, compound **8ab** was obtained as a white solid (16.9 mg, yield: 41 %); mp = 105-107 °C; ^1^H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 8.36 (s, 1H), 7.92-7.91 (m, 2H), 7.54-7.51 (m, 1H), 7.43-7.40 (m, 2H), 7.06-7.04 (m, 1H), 6.66-6.65 (m, 1H), 5.08-5.07 (m, 1H), 4.86-4.85 (m, 1H), 3.94 (s, 3H), 2.43-2.42 (m, 2H), 1.40 (s, 9H); ^1^C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 200.0, 155.5, 146.2, 136.9, 132.9, 128.5, 128.0,
127.2, 127.1, 121.0, 120.2, 117.7, 112.1, 102.2, 79.2, 55.3, 47.6, 35.8, 29.7, 28.3;
HRMS (ESI) for C_{24}H_{28}N_{2}O_{4}Na [M+Na]^+ calcd. 431.1941, found 431.1941;
Enantiomeric excess established by HPLC analysis using a Chiralpak IA column, ee = 95% (HPLC: IA, 280 nm, hexane/isopropanol = 85:15, flow rate 1.0 mL/min, 25°C, t_r (major) = 29.7 min, t_r (minor) = 25.6 min.) [α]_D^{25} = 35.00 (c 1.0, CH₂Cl₂).

**tert-butyl (R)-(4-(hydroxyimino)-1-(1H-indol-3-yl)-4-phenylbutyl)carbamate (9)**

Following the general procedure, compound 9 was obtained as a white solid (36.4 mg, yield: 92 %); mp = 182-184 °C; ^1H NMR (600 MHz, DMSO-d_6): δ 11.18 (s, 1H), 10.85 (s, 1H), 7.59-7.58 (m, 3H), 7.35-7.33 (m, 4H), 7.23-7.21 (m, 2H), 7.08-7.06 (m, 1H), 6.97-6.95 (m, 1H), 4.92-4.88 (m, 1H), 2.78-2.70 (m, 2H), 2.08-2.02 (m, 1H), 1.98-1.92 (m, 1H), 1.39 (s, 9H); ^13C NMR (150 MHz, DMSO-d_6): δ 156.5, 155.3, 136.4, 136.2, 128.6, 128.5, 126.0, 125.8, 122.2, 121.1, 118.9, 118.4, 116.9, 111.5, 77.5, 47.5, 31.8, 28.4, 22.9; HRMS (ESI) for C_{23}H_{27}N_{3}O_{4}Na [M+Na]^+ calcd. 416.1945, found 416.1946;
Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 99% (HPLC: IF-3, 280 nm, hexane/isopropanol = 85:15, flow rate 1.0 mL/min, 25 °C, t_r (major) = 8.3 min, t_r (minor) = 10.5 min.) [α]_D^{25} = 21.00 (c 1.0, CH₂Cl₂).

**tert-butyl (R)-(1-(1H-indol-3-yl)-4-phenylpent-4-en-1-yl)carbamate (10)**

Following the general procedure, compound 10 was obtained as a colorless oil (37.1 mg, yield: 99 %); ^1H NMR (600 MHz, CDCl₃): δ 8.19 (s, 1H), 7.60-7.59 (m, 1H), 7.35-7.31 (m, 3H), 7.29-7.22 (m, 3H), 7.19-7.16 (m, 1H), 7.10-7.07 (m, 1H), 6.959-6.956 (m, 1H), 5.28 (s, 1H), 5.09 (s, 1H), 5.03 (s, 1H), 4.80 (s, 1H), 2.65-2.52 (m, 2H), 2.15-2.04 (m, 2H), 1.45 (s, 9H); ^13C NMR (150 MHz, CDCl₃): δ 155.5, 147.8, 141.0, 136.6, 128.2, 127.3, 126.1, 125.8, 122.2, 121.3, 119.6, 117.5, 112.5, 111.3, 79.2, 47.8, 34.3, 32.3, 28.4; HRMS (ESI) for C_{24}H_{28}N_{2}O_{4}Na [M+Na]^+ calcd. 399.2043, found 399.2045;
Enantiomeric excess established by HPLC analysis using a Chiralpak IF-3 column, ee = 99% (HPLC: IF-3, 280 nm, hexane/isopropanol = 85:15, flow rate 1.0 mL/min, 25 °C, t_r (major) = 8.3 min, t_r (minor) = 10.5 min.) \([\alpha]_D^{25} = 41.00 (c 1.0, \text{CH}_2\text{Cl}_2)\).
6. Mechanistic Studies

6.1 Trapping Experiments with TEMPO

As shown in eqs 1-2, the radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added into the reaction mixture. After 12 h, no desired products were observed by TLC, indicating that the reaction might involve a radical process.

6.2 Control Experiments

The pre-prepared trifluoromethylated enamine 11 generated from the reaction of 1a and Togni-II was employ as the substrate to react with indole under the action of chiral phosphoric acid. After 12 h, only trace amount of the product was detected by TLC, indicating that the reaction proceed via the imine intermediate instead of enamine.
When N-Me protected enamine or/and indole were used as the substrates to engage the reaction under the standard conditions, the reaction was completely inhibited, indicating that the generated imine and indole might both interact with chiral phosphoric acid through the hydrogen-bonding to provide the product.

As shown in eq 5, when Togni-II 2 react with 1a under the standard conditions for 3 h, full conversion of 2 was observed, accompanied by the generation of trifluoromethylated enamine 8 and oxytrifluoromethylated product 9.

As shown in eq 6, when Togni-II 2 react with 3a under the standard conditions for 3 h, full conversion of 2 was observed, accompanied by the detection of trifluoromethylated indole.
As shown in eq 7, when only Togni-II was treated with the standard conditions for 3 h, the full conversion of 2 was also observed, accompanied by the formation of alcohol 10 and acetal 11 which might be obtained by a HAT and radical-radical coupling process.

In addition, without the addition of chiral phosphoric acid, Togni-II need more time to be completely transformed.

In summary, under the irradiation of visible-light, the Togni-II could decompose to form the trifluoromethyl radical. And chiral phosphoric acid could accelerate this process.

6.3 UV-Vis absorption spectra
UV/vis absorption spectra based on Togni-II 2 (0.1 M in THF), C1 (0.01 M in THF) and the mixture of 2 and C1 (2:C1 = 1:1) were recorded respectively in 1 cm path quartz cuvettes using a U-3900H spectrometer
Figure S1. UV/vis absorption spectra

UV/vis absorption spectrometry showed a bathochromic shift by mixing Togni-II with 10 mol% C1 in THF.

6.4 ¹H NMR of Togni-II with C1 in CD₃Cl

With the increase of the loading of C1, the change of the chemical shift of the CH₃ in Togni-II indicates that there is an interaction between the Togni-II and C1.

6.5 Linear Effect Experiments
The relationship between the ee of CPA and the ee of product 4c was evaluated and the linear correlation result strongly suggests that only a single molecule of the chiral phosphate is included in the second C–C bond-forming step.
| Entry | C1     | ee (%) |
|-------|--------|--------|
| 1     | 0% ee  | 0      |
| 2     | 20% ee | 20     |
| 3     | 40% ee | 45     |
| 4     | 60% ee | 58     |
| 5     | 80% ee | 76     |
| 6     | >99% ee| 96     |

The relationship between the ee of CPA and the ee of product 8a was evaluated and the linear correlation result strongly suggests that only a single molecule of the chiral phosphate is included in the second C–C bond-forming step.
7. Synthetic applications

7a (0.1 mmol, 37.8 mg, 1.0 eq), Hydroxylamine hydrochloride (0.16 mmol, 11.2 mg, 1.6 eq) and sodium acetate (0.2 mmol, 16.4 mg, 2.0 eq) were added to a dry reaction tube equipped with a magnetic stir bar. Then 80% aq. EtOH (1 ml) was added and the mixture was stirred at 80 °C for 1.5 h. The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography to give oxime (36.4 mg, 92% yield, 99% ee).

To a solution of Methyltriphenylphosphonium bromide (0.2 mmol, 71.4 mg, 2.0 eq) in THF (0.5 mL) was added potassium t-butoxide (0.2 mmol, 22.4 mg, 2.0 eq) under N2. After stirred at room temperature for 30 min, the solution of 7a (0.1 mmol, 37.8 mg, 1.0 eq) in THF (0.5 mL) was added slowly to the reaction mixture. The reaction mixture was heated to reflux overnight and then was cooled to room temperature. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography to give alkene (37.1 mg, 99% yield, 99% ee).

8. References:

(1) A. J. Boyington, C. P. Seath; A. M. Zearfoss, Z.Xu, N. T. C. Jui, J. Am. Chem. Soc. 2019, 141, 4147.
9. X-Ray Crystallographic Data

9.1 X-Ray Crystallographic Data of Product 8a (CCDC: 2108166):

| Bond precision: | C-C = 0.0036 Å | Wavelength=1.54184 |
|-----------------|-----------------|---------------------|
| Cell:           | a=9.4239(1)     | b=10.0699(1)        |
|                 | c=11.2350(1)    |                     |
|                 | alpha=90        | beta=103.712(1)     |
|                 | gamma=90        |                     |
| Temperature:    | 298 K           |                     |
| Volume          | 1035.789(18)    | 1035.789(18)        |
| Space group     | P 21            | P 1 21 1            |
| Hall group      | P 2yb           | P 2yb               |
| Moiety formula  | C23 H26 N2 O3   | C23 H26 N2 O3       |
| Sum formula     | C23 H26 N2 O3   | C23 H26 N2 O3       |
| Mr              | 378.46          | 378.46              |
| Dx,g cm-3       | 1.214           | 1.213               |
| Z               | 2               | 2                   |
| Mu (mm-1)       | 0.645           | 0.645               |
| F000            | 404.0           | 404.0               |
| F000’           | 405.19          |                     |
| h,k,lmax        | 11,12,14        | 11,12,14            |
| Nref            | 4402[2330]      | 4103                |
| Tmin,Tmax       | 0.918,0.950     | 0.709,1.000         |
| Tmin’           | 0.914           |                     |
| Correction method= # Reported T Limits: Tmin=0.709 Tmax=1.000 |
| AbsCorr = MULTI-SCAN |
| Data completeness= 1.76/0.93 | Theta(max)= 77.509 |
| R(reflections)= 0.0331(3994) | wR2(reflections)= 0.0884(4103) |
| S = 1.094 | Npar= 270 |
10. Enantioselectivities as Determined by Chiral HPLC

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area %  |
|--------|---------------|--------------|--------------|-------------|-----------------|--------|
| 1      | 11.829        | 3209.1       | 76.5         | 0.6116      | 0.399           | 50.351 |
| 2      | 23.067        | 3164.4       | 43.4         | 0.9967      | 0.504           | 49.649 |

**Figure S1.** HPLC traces of rac-4a (reference) and (R)-4a.
**Figure S2.** HPLC traces of rac-$4b$ (reference) and ($R$)-$4b$. 

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|-------|---------------|--------------|--------------|-------------|----------------|--------|
| 1     | 13.884        | 8007.6       | 196.5        | 0.6124      | 0.49           | 50.237 |
| 2     | 22.316        | 7932.1       | 151.3        | 0.8036      | 0.474          | 49.763 |

$\text{Rac-}4b$ 

$\text{(R)-}4b$, 98% ee
Table 1. HPLC data for rac-4c (reference) and (R)-4c.

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|--------|---------------|--------------|--------------|-------------|----------------|--------|
| 1      | 13.056        | 5769.5       | 156          | 0.5775      | 0.63           | 49.555 |
| 2      | 19.126        | 5873.1       | 129.8        | 0.6877      | 0.575          | 50.445 |

Figure S3. HPLC traces of rac-4c (reference) and (R)-4c.
**Figure S4.** HPLC traces of rac-4d (reference) and (R)-4d.

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|--------|---------------|--------------|--------------|-------------|----------------|--------|
| 1      | 11.998        | 3045.9       | 64.5         | 0.6429      | 0.95           | 50.531 |
| 2      | 17.513        | 2981.8       | 57           | 0.8266      | 0.833          | 49.469 |

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|--------|---------------|--------------|--------------|-------------|----------------|--------|
| 1      | 11.785        | 9952.8       | 247.1        | 0.6379      | 0.76           | 98.267 |
| 2      | 17.632        | 175.5        | 3.8          | 0.5834      | 0.957          | 1.733  |
| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|--------|---------------|--------------|--------------|-------------|----------------|-------|
| 1      | 14.973        | 6406.5       | 142.7        | 0.6999      | 0.691          | 49.895|
| 2      | 22.499        | 6433.5       | 119.7        | 0.8231      | 0.615          | 50.105|

**Figure S5.** HPLC traces of rac-4e (reference) and (R)-4e.
| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|-------|--------------|--------------|--------------|-------------|----------------|--------|
| 1     | 19.564       | 2982.8       | 61           | 0.7446      | 0.554          | 50.027 |
| 2     | 37.556       | 2979.7       | 40.9         | 1.0881      | 0.577          | 49.973 |

Figure S6. HPLC traces of rac-4f (reference) and (R)-4f.
| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area %  |
|-------|---------------|--------------|--------------|-------------|----------------|--------|
| 1     | 22.326        | 8690.5       | 155.6        | 0.9307      | 0              | 48.594 |
| 2     | 45.653        | 9193.5       | 94.4         | 1.3936      | 0.512          | 51.406 |

Figure S7. HPLC traces of rac-4g (reference) and (R)-4g.
Table 1. HPLC Peak Parameters

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|--------|---------------|--------------|--------------|-------------|----------------|--------|
| 1      | 10.721        | 3867.5       | 97.2         | 0.624       | 0.93           | 49.693 |
| 2      | 14.337        | 3915.3       | 88.8         | 0.6944      | 0.803          | 50.307 |

Figure S8. HPLC traces of rac-4h (reference) and (R)-4h.
**Figure S9.** HPLC traces of rac-4i (reference) and (R)-4i.

- **Rac-4i**

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|--------|---------------|--------------|--------------|-------------|-----------------|-------|
| 1      | 13.466        | 3823.7       | 94.2         | 0.6194      | 0.55            | 50.239|
| 2      | 20.316        | 3787.3       | 77.6         | 0.7456      | 0.496           | 49.761|

- **(R)-4i, 94% ee**

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|--------|---------------|--------------|--------------|-------------|-----------------|-------|
| 1      | 13.26         | 10510.9      | 271          | 0.5926      | 0.472           | 96.837|
| 2      | 20.633        | 343.3        | 6.8          | 0.7155      | 0.696           | 3.163 |
| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|-------|--------------|--------------|--------------|------------|----------------|--------|
| 1     | 20.593       | 1849         | 36.4         | 0.7579     | 0.748          | 48.823 |
| 2     | 22.375       | 1938.1       | 34.6         | 0.8363     | 0.641          | 51.177 |

**Figure S10.** HPLC traces of rac-4j (reference) and (R)-4j.
| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|-------|---------------|---------------|--------------|-------------|----------------|--------|
| 1     | 19.503        | 3468.6        | 66.5         | 0.7747      | 0.433          | 48.993 |
| 2     | 21.759        | 3611.1        | 62.4         | 0.8554      | 0.468          | 51.007 |

Figure S11. HPLC traces of rac-4k (reference) and (R)-4k.
| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|-------|--------------|--------------|--------------|-------------|----------------|--------|
| 1     | 10.061       | 12364.6      | 385.5        | 0.4882      | 0.522          | 49.923 |
| 2     | 14.29        | 12402.9      | 303.2        | 0.6072      | 0.354          | 50.077 |

**Figure S12.** HPLC traces of rac-4l (reference) and (R)-4l.
### Table 1: HPLC Data for rac-4m and (R)-4m

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|--------|---------------|--------------|--------------|-------------|-----------------|--------|
| 1      | 13.249        | 6807.2       | 144.1        | 0.703       | 0.447           | 49.132 |
| 2      | 20.193        | 7047.6       | 124.1        | 0.8406      | 0.466           | 50.868 |

### Figure S13. HPLC traces of rac-4m (reference) and (R)-4m.
**Figure S14.** HPLC traces of rac-4n (reference) and (R)-4n.
| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|-------|---------------|--------------|--------------|-------------|----------------|--------|
| 1     | 8.182         | 6739.7       | 221.5        | 0.4769      | 1.118          | 50.861 |
| 2     | 13.251        | 6511.5       | 180.1        | 0.5577      | 0.67           | 49.139 |

**Figure S15.** HPLC traces of rac-4o (reference) and (R)-4o.
**Figure S16.** HPLC traces of rac-4p (reference) and (R)-4p.  

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area %  |
|--------|---------------|--------------|--------------|-------------|----------------|--------|
| 1      | 9.011         | 15365.8      | 520.1        | 0.4367      | 0.469          | 97.664 |
| 2      | 11.029        | 368          | 12.9         | 0.474       | 0.748          | 2.339  |
Figure S17. HPLC traces of rac-4q (reference) and (R)-4q.

| Peak # | RetTime [min] | Area [Mau*s] | Height [mA] | Width [min] | Symmetry factor | Area % |
|--------|---------------|--------------|-------------|-------------|----------------|--------|
| 1      | 5.552         | 5819.5       | 331.1       | 0.2929      | 0.497          | 48.490 |
| 2      | 57.674        | 6181.9       | 33.1        | 3.1092      | 0.548          | 51.510 |

\(Rac-4q\)

\((R)-4q, 92\% \text{ ee}\)
| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|-------|---------------|--------------|--------------|-------------|----------------|--------|
| 1     | 8.707         | 4346.4       | 159.1        | 0.4048      | 0.475          | 51.095 |
| 2     | 30.068        | 4160.1       | 45.5         | 1.2507      | 0.551          | 48.905 |

**Figure S18.** HPLC traces of *rac-4r* (reference) and *(R)-4r*. 
| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|-------|---------------|--------------|--------------|-------------|-----------------|--------|
| 1     | 6.088         | 5083.4       | 380.3        | 0.1999      | 0.646           | 48.940 |
| 2     | 25.126        | 5303.5       | 120.3        | 0.6705      | 0.633           | 51.060 |

**Figure S19.** HPLC traces of rac-4s (reference) and (R)-4s.
### Table 1: Peak Analysis

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|--------|---------------|--------------|--------------|-------------|----------------|--------|
| 1      | 9.68          | 4231.8       | 122.8        | 0.5102      | 0.453          | 50.160 |
| 2      | 14.818        | 4204.7       | 90.7         | 0.6706      | 0.416          | 49.840 |

![Figure S20. HPLC traces of rac-4t (reference) and (R)-4t.](image-url)
### Table 1: HPLC Analysis of rac-4u and (R)-4u

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area [%] |
|--------|---------------|--------------|--------------|-------------|----------------|----------|
| 1      | 13.238        | 2571.1       | 54           | 0.6871      | 0.381          | 49.938   |
| 2      | 25.216        | 2577.5       | 32.5         | 1.0086      | 0.49           | 50.062   |

### Table 2: HPLC Analysis of rac-4u and (R)-4u

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area [%] |
|--------|---------------|--------------|--------------|-------------|----------------|----------|
| 1      | 13.021        | 9230.1       | 185.7        | 0.7137      | 0.341          | 94.972   |
| 2      | 25.518        | 488.6        | 5.9          | 1.0294      | 0.48           | 5.028    |

*Figure S21. HPLC traces of rac-4u (reference) and (R)-4u.*
### Peak # 1:
- RetTime: 9.171 min
- Area: 1661.9 Mau*s
- Height: 48 mAU
- Width: 0.512 min
- Symmetry factor: 0.489
- Area %: 49.858

### Peak # 2:
- RetTime: 12.007 min
- Area: 1671.4 Mau*s
- Height: 41.7 mAU
- Width: 0.5777 min
- Symmetry factor: 0.536
- Area %: 50.142

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**Figure S22.** HPLC traces of rac-4v (reference) and (R)-4v.
Figure S23. HPLC traces of rac-4w (reference) and (R)-4w.
### HPLC traces of rac-4x (reference) and (R)-4x.

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|--------|---------------|--------------|--------------|-------------|-----------------|--------|
| 1      | 11.64         | 1578.2       | 34.4         | 0.6671      | 0.477           | 51.175 |
| 2      | 19.356        | 1505.7       | 23.9         | 0.9223      | 0.5             | 48.825 |

**Figure S24.** HPLC traces of rac-4x (reference) and (R)-4x.
| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|-------|---------------|--------------|--------------|-------------|----------------|-------|
| 1     | 10.743        | 4179.6       | 108.5        | 0.5693      | 0.483          | 51.399|
| 2     | 14.249        | 3952.1       | 83.8         | 0.69        | 0.526          | 48.601|

**Figure S25.** HPLC traces of rac-4y (reference) and (R)-4y.
### Figure S26. HPLC traces of *rac-4z* (reference) and *(R)-4z*.

| Peak # | RetTime [min] | Area [Mau*s] | Height [mA] | Width [min] | Symmetry factor | Area % |
|--------|---------------|--------------|-------------|-------------|-----------------|-------|
| 1      | 12.806        | 9145.4       | 196.1       | 0.6842      | 0.41            | 50.366|
| 2      | 30.819        | 9012.7       | 94.6        | 1.3617      | 0.496           | 49.634|

**Rac-4z**

**Me**

\[
\text{HN} \quad \text{CF}_3
\]

**MeO**

\[
\text{NH} \quad \text{CF}_3
\]

**HNMe**

\[
\text{HNMe} \quad \text{CF}_3
\]

**MeO**

\[
\text{MeO} \quad \text{CF}_3
\]

**HNMe**

\[
\text{HNMe} \quad \text{CF}_3
\]

**Figure S26.** HPLC traces of *rac-4z* (reference) and *(R)-4z*. 
Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area %
--- | --- | --- | --- | --- | --- | ---
1 | 6.087 | 12487.8 | 814.6 | 0.2269 | 0.554 | 50.004
2 | 9.188 | 12485.6 | 514.4 | 0.3552 | 0.529 | 49.996

**Figure S27.** HPLC traces of *rac-4aa* (reference) and *(R)-4aa*.
Rac-4ab

\[ (R)-4\text{ab}, \text{81\% ee} \]

**Figure S28.** HPLC traces of *rac-4ab* (reference) and *(R)-4ab*. 
**Rac-6a**

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|--------|---------------|--------------|--------------|-------------|----------------|-------|
| 1      | 8.617         | 15588.2      | 791.4        | 0.3038      | 0.872          | 50.321 |
| 2      | 17.554        | 15389.1      | 401.3        | 0.5794      | 0.453          | 49.679 |

**Figure S29.** HPLC traces of rac-6a (reference) and (S)-6a.
### Table

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|--------|---------------|--------------|--------------|-------------|----------------|--------|
| 1      | 13.001        | 20987.8      | 681.3        | 0.4854      | 0.969          | 49.911 |
| 2      | 20.495        | 21063        | 424          | 0.7455      | 0.374          | 50.089 |

### Figure S30

HPLC traces of rac-6b (reference) and (S)-6b. The (S)-6b has a 91% ee.
| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|-------|---------------|--------------|--------------|-------------|----------------|-------|
| 1     | 10.006        | 300696       | 853.4        | 0.471       | 1.922          | 51.198|
| 2     | 12.126        | 28659.2      | 1122.8       | 0.3958      | 1.131          | 48.802|

Figure S31. HPLC traces of rac-6c (reference) and (S)-6c.
Figure S32. HPLC traces of rac-6d (reference) and (S)-6d.
### Peak Data

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|--------|---------------|--------------|--------------|-------------|-----------------|-------|
| 1      | 8.158         | 31231.2      | 1698.4       | 0.2865      | 0.774           | 49.809|
| 2      | 16.258        | 31470.6      | 802.9        | 0.5933      | 0.378           | 50.191|

**Figure S33.** HPLC traces of rac-6e (reference) and (S)-6e.
| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|-------|--------------|--------------|--------------|-------------|----------------|-------|
| 1     | 27.198       | 31039.1      | 543.8        | 0.88        | 0.633          | 50.112|
| 2     | 30.318       | 30900        | 405          | 1.1221      | 0.424          | 49.888|

Figure S34. HPLC traces of rac-6f (reference) and (S)-6f.
**Figure S35.** HPLC traces of rac-6g (reference) and (S)-6g.
| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|-------|--------------|--------------|--------------|-------------|-----------------|-------|
| 1     | 13.302       | 28361.1      | 699.7        | 0.6289      | 1.421           | 48.690|
| 2     | 17.081       | 29887.3      | 579.9        | 0.7793      | 0.607           | 51.310|

**Figure S36.** HPLC traces of rac-6h (reference) and (S)-6h.
Figure S37. HPLC traces of rac-6i (reference) and (S)-6i.
The table shows the retention time (RT), area, height, width, symmetry factor, and area percentage for two peaks. The first peak has a retention time of 13.595 minutes, an area of 5101.6 Mau*s, a height of 178.6 mAU, a width of 0.4293 min, a symmetry factor of 0.567, and an area percentage of 49.523%. The second peak has a retention time of 14.951 minutes, an area of 5199.8 Mau*s, a height of 160.3 mAU, a width of 0.4864 min, a symmetry factor of 0.496, and an area percentage of 50.477%.

The figure shows HPLC traces of rac-8a (reference) and (R)-8a. The peak at 14.085 minutes with an area of 214.2 Mau*s, height of 7.5 mAU, width of 0.4393 min, symmetry factor of 0.68, and area percentage of 1.978% is (R)-8a. The peak at 15.494 minutes with an area of 10619.6 Mau*s, height of 329.8 mAU, width of 0.4917 min, symmetry factor of 0.498, and area percentage of 98.022% is (R)-8a.

**Figure S38.** HPLC traces of rac-8a (reference) and (R)-8a.
Figure S39. HPLC traces of *rac-8b* (reference) and *(R)-8b*. 

### HPLC traces of *rac-8b* (reference) and *(R)-8b*.

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|--------|---------------|--------------|--------------|-------------|----------------|--------|
| 1      | 15.593        | 37707        | 1083.2       | 0.5802      | 0.585          | 49.936 |
| 2      | 18.148        | 37803.3      | 867.4        | 0.6705      | 0.465          | 50.064 |

### HPLC traces of *rac-8b* (reference) and *(R)-8b*.

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|--------|---------------|--------------|--------------|-------------|----------------|--------|
| 1      | 16.226        | 157.3        | 4.6          | 0.4909      | 0.676          | 2.667  |
| 2      | 18.791        | 5740.1       | 134          | 0.6596      | 0.501          | 97.333 |
### Figure S40.

HPLC traces of rac-8c (reference) and (R)-8c.

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|--------|---------------|--------------|--------------|-------------|----------------|--------|
| 1      | 11.259        | 19474.2      | 756.8        | 0.3882      | 0.562          | 49.725 |
| 2      | 12.957        | 319689.8     | 617.5        | 0.474       | 0.507          | 50.275 |

**Rac-8c**

![HPLC trace of rac-8c](image)

**(R)-8c, 95% ee**

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|--------|---------------|--------------|--------------|-------------|----------------|--------|
| 1      | 11.448        | 633.9        | 23.8         | 0.387       | 0.517          | 2.667  |
| 2      | 13.086        | 23132.9      | 697.1        | 0.5051      | 0.515          | 97.333 |
| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|--------|---------------|--------------|--------------|-------------|----------------|--------|
| 1      | 16.538        | 7418.4       | 211.9        | 0.5405      | 0.579          | 49.539 |
| 2      | 18.995        | 7556.4       | 178.4        | 0.6341      | 0.4823         | 50.461 |

**Figure S41.** HPLC traces of rac-8d (reference) and (R)-8d.
Figure S42. HPLC traces of rac-8e (reference) and (R)-8e.
### Table 1: Retention Time and Peak Characteristics

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area [%] |
|--------|---------------|--------------|--------------|-------------|----------------|---------|
| 1      | 14.067        | 10199.7      | 327.3        | 0.4835      | 0.523          | 47.199  |
| 2      | 15.176        | 11410.4      | 324.9        | 0.5337      | 0.43           | 52.801  |

**Figure S43.** HPLC traces of rac-8f (reference) and (R)-8f.
### Table 1

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|-------|---------------|--------------|--------------|-------------|----------------|--------|
| 1     | 15.342        | 9835.5       | 306.4        | 0.4925      | 0.555          | 47.310 |
| 2     | 16.465        | 10954        | 290.4        | 0.5781      | 0.446          | 52.690 |

**Figure S44.** HPLC traces of *rac-8g* (reference) and *(R)-8g*. 

![HPLC trace of *rac-8g*](image1.png)

![HPLC trace of *(R)-8g*](image2.png)

**Figure S44.** HPLC traces of *rac-8g* (reference) and *(R)-8g*. 

![HPLC trace of *rac-8g*](image1.png)

![HPLC trace of *(R)-8g*](image2.png)
### Table 1: MS Data of Racemates

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|--------|--------------|--------------|--------------|-------------|----------------|--------|
| 1      | 17.94        | 7305.2       | 208.3        | 0.5391      | 0.571          | 47.069 |
| 2      | 19.163       | 8214.9       | 199.7        | 0.6159      | 0.521          | 52.931 |

**Figure S45.** HPLC traces of rac-8h (reference) and (R)-8h.
**Figure S46.** HPLC traces of rac-8i (reference) and (R)-8i.
### Table 1

| Peak | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|------|---------------|--------------|--------------|-------------|----------------|--------|
| 1    | 10.175        | 18905.8      | 546.5        | 0.5036      | 0.49           | 51.051 |
| 2    | 15.793        | 18127.7      | 303.2        | 0.8815      | 0.556          | 48.949 |

### Diagram 1

**Figure S47.** HPLC traces of rac-8j (reference) and (R)-8j.
| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|-------|--------------|--------------|--------------|-------------|----------------|--------|
| 1     | 14.591       | 3711         | 122.7        | 0.4628      | 0.573          | 48.824 |
| 2     | 16.187       | 3889.9       | 107.1        | 0.5417      | 0.493          | 51.176 |

*Figure S48.* HPLC traces of *rac-8k* (reference) and *(R)-8k.*
| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|-------|---------------|--------------|--------------|-------------|----------------|--------|
| 1     | 15.766        | 16003.2      | 327.1        | 0.7508      | 0.438          | 49.782 |
| 2     | 18.368        | 16143.5      | 177.2        | 1.2332      | 0.33           | 50.218 |

**Figure S49.** HPLC traces of rac-8l (reference) and (R)-8l.
| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|-------|---------------|--------------|--------------|-------------|----------------|-------|
| 1     | 10.565        | 5949.4       | 185.5        | 0.4662      | 0.565          | 51.756 |
| 2     | 13.516        | 5545.4       | 118.7        | 0.6809      | 0.6            | 48.244 |

Figure S50. HPLC traces of *rac-8m* (reference) and *(R)-8m*. 

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| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|-------|--------------|--------------|--------------|-------------|----------------|--------|
| 1     | 10.137       | 9708.4       | 314.2        | 0.4565      | 0.519          | 49.186 |
| 2     | 11.847       | 10029.6      | 241.6        | 0.6023      | 0.485          | 50.814 |

**Figure S51.** HPLC traces of *rac-8n* (reference) and *(R)-8n*. 

\[ \text{MeO} \quad \begin{array}{c} \text{O} \\ \text{NH} \text{Boc} \end{array} \quad \begin{array}{c} \text{MeO} \\ \text{NH} \end{array} \]

\( (R)-8n, \text{ 92\% ee} \)
Figure S52. HPLC traces of \textit{rac-8o} (reference) and \textit{(R)-8o}.
### Table 1

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area [%] |
|--------|---------------|--------------|--------------|-------------|----------------|----------|
| 1      | 9.712         | 2892         | 149.9        | 0.2931      | 0.626          | 50.225   |
| 2      | 11.076        | 2866.1       | 128.3        | 0.3387      | 0.658          | 49.775   |

**Rac-8p**

Figure S53. HPLC traces of *rac-8p* (reference) and *(R)-8p*. 

**Figure S53.** HPLC traces of *rac-8p* (reference) and *(R)-8p*.
| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|-------|---------------|--------------|--------------|-------------|----------------|-------|
| 1     | 13.114        | 2410.3       | 78.8         | 0.4667      | 0.622          | 48.898|
| 2     | 15.902        | 2519         | 48.1         | 0.7855      | 0.549          | 51.102|

Figure S54. HPLC traces of rac-8q (reference) and (R)-8q.
### Table 1: HPLC Data for Rac-8r

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area %  |
|--------|---------------|--------------|--------------|-------------|-----------------|--------|
| 1      | 11.735        | 2679.6       | 64.6         | 0.6058      | 0.562           | 51.340 |
| 2      | 18.019        | 2539.8       | 42.7         | 0.8654      | 0.542           | 48.660 |

### Table 2: HPLC Data for (R)-8r

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area %  |
|--------|---------------|--------------|--------------|-------------|-----------------|--------|
| 1      | 11.75         | 303.6        | 8.7          | 0.5265      | 0.724           | 2.434  |
| 2      | 18.006        | 12171.5      | 205.8        | 0.8661      | 0.539           | 97.566 |

**Figure S55.** HPLC traces of *rac-8r* (reference) and *(R)-8r*. 

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(R)-8r, 95% ee
### Table 1: Peak Parameters

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area %  |
|--------|---------------|--------------|--------------|-------------|----------------|---------|
| 1      | 9.033         | 3054.9       | 144.3        | 0.319       | 0.609          | 48.608  |
| 2      | 10.858        | 3229.8       | 124.3        | 0.3911      | 0.603          | 51.392  |

### Figure S56

HPLC traces of rac-8s (reference) and (R)-8s.

(R)-8s, 96% ee
### Table 1: HPLC Data of Rac-

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|--------|---------------|--------------|--------------|-------------|----------------|--------|
| 1      | 11.894        | 5230.4       | 133.1        | 0.5705      | 0.527          | 51.091 |
| 2      | 21.942        | 5007         | 58.1         | 1.2558      | 0.523          | 48.909 |

### Figure S57: HPLC traces of rac-8t (reference) and (R)-8t.

![HPLC traces](image_url)

Rac-8t

(R)-8t, 95% ee

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|--------|---------------|--------------|--------------|-------------|----------------|--------|
| 1      | 11.937        | 8926         | 231.3        | 0.5642      | 0.494          | 97.404 |
| 2      | 22.13         | 237.9        | 2.8          | 1.4296      | 0.776          | 2.596  |
### Table

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|--------|---------------|--------------|--------------|-------------|-----------------|--------|
| 1      | 9.615         | 8703         | 342          | 0.3989      | 1.288           | 50.035 |
| 2      | 11.665        | 8690.8       | 388.4        | 0.3451      | 0.766           | 49.965 |

### Figure S58

**Rac-8u**

**Figure S58.** HPLC traces of *rac-8u* (reference) and *(R)-8u*. 

***(R)-8u, 91% ee***
### Table 1: HPLC Data

| Peak # | RetTime [min] | Area [Mau*s] | Height [mA] | Width [min9] | Symmetry factor | Area % |
|--------|---------------|--------------|-------------|--------------|-----------------|-------|
| 1      | 20.172        | 8932.8       | 113.2       | 1.1587       | 0.479           | 51.665|
| 2      | 33.838        | 8356.9       | 61.7        | 1.6997       | 0.513           | 48.335|

**Figure S59.** HPLC traces of *rac-8v* (reference) and *(R)-8v*. 

![HPLC traces](image-url)
**Figure S60.** HPLC traces of *rac-8w* (reference) and *(R)-8w.*
**Rac-8x**

![HPLC trace of Rac-8x](image)

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|-------|---------------|--------------|--------------|-------------|-----------------|--------|
| 1     | 22.225        | 5330.1       | 66.1         | 1.1609      | 0.376           | 47.800 |
| 2     | 24.657        | 5820.8       | 67.2         | 1.2125      | 0.403           | 52.200 |

**Figure S61.** HPLC traces of rac-8x (reference) and (R)-8x.

![HPLC trace of (R)-8x](image)

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|-------|---------------|--------------|--------------|-------------|-----------------|--------|
| 1     | 21.671        | 13340.3      | 132.4        | 1.6791      | 0.317           | 97.964 |
| 2     | 25.413        | 277.3        | 3.8          | 1.2266      | 0.517           | 2.036  |
**Rac-8y**

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area [%] |
|---|---|---|---|---|---|---|
| 1 | 19.874 | 3556.9 | 50.4 | 1.0212 | 0.484 | 50.441 |
| 2 | 34.273 | 3494.7 | 26.8 | 1.5719 | 0.579 | 49.559 |

**Figure S62.** HPLC traces of rac-8y (reference) and (R)-8y.
### Peak #1

- **Retention Time (RetTime):** 10.345 min
- **Area:** 3093.2 Mau*s
- **Height:** 140.4 mAU
- **Width:** 0.333 min
- **Symmetry Factor:** 0.671
- **Area %:** 52.057

### Peak #2

- **Retention Time (RetTime):** 11.529 min
- **Area:** 2848.7 Mau*s
- **Height:** 114 mAU
- **Width:** 0.3775 min
- **Symmetry Factor:** 0.572
- **Area %:** 47.943

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**Figure S63.** HPLC traces of rac-8z (reference) and (R)-8z.
| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|-------|---------------|--------------|--------------|-------------|-----------------|-------|
| 1     | 23.569        | 5282.6       | 71.8         | 1.0408      | 0.441           | 52.078|
| 2     | 29.3          | 4861         | 54.8         | 1.264       | 0.554           | 47.922|

**Figure S64.** HPLC traces of rac-8aa (reference) and (R)-8aa.
### Table 1: Chromatographic Parameters for Rac-8ab and (R)-8ab

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|--------|--------------|--------------|--------------|------------|-----------------|-------|
| 1      | 25.478       | 6226.7       | 112.5        | 0.8299     | 0.493           | 49.964 |
| 2      | 30.082       | 6235.6       | 97.2         | 0.9748     | 0.47            | 50.036 |

**Figure S65.** HPLC traces of rac-8ab (reference) and (R)-8ab.
**Figure S66.** HPLC traces of rac-9 (reference) and (R)-9.

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|--------|---------------|--------------|--------------|-------------|----------------|--------|
| 1      | 8.187         | 7307         | 346.3        | 0.3222      | 0.855          | 50.126 |
| 2      | 10.302        | 7270.4       | 295.1        | 0.3795      | 0.752          | 49.874 |

**Figure S66.** HPLC traces of rac-9 (reference) and (R)-9.

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|--------|---------------|--------------|--------------|-------------|----------------|--------|
| 1      | 8.331         | 4851.2       | 217.5        | 0.3442      | 0.871          | 99.641 |
| 2      | 10.533        | 17.5         | 0.73         | 0.4019      | 0.654          | 0.359  |
**Figure S67.** HPLC traces of *rac-10* (reference) and *(R)-10*. 

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|--------|---------------|--------------|--------------|-------------|----------------|--------|
| 1      | 5.638         | 2341.4       | 172.2        | 0.2086      | 0.933          | 49.619 |
| 2      | 6.611         | 2377.1       | 155.6        | 0.2303      | 0.805          | 50.381 |

| Peak # | RetTime [min] | Area [Mau*s] | Height [mAU] | Width [min] | Symmetry factor | Area % |
|--------|---------------|--------------|--------------|-------------|----------------|--------|
| 1      | 5.448         | 17874.2      | 1231.6       | 0.2293      | 0.919          | 99.414 |
| 2      | 6.371         | 105.4        | 6.4          | 0.2762      | 0.96           | 0.586  |
11. NMR Spectra of New Compounds

$^1$H NMR of 4a in DMSO-$d_6$ (400 M)

$^{13}$C NMR of 4a in DMSO-$d_6$ (100 M)
\( ^{19}\text{F NMR of } 4a \text{ in DMSO-}d_6 (376 \text{ M}) \)

\( ^{1}\text{H NMR of } 4b \text{ in DMSO-}d_6 (400 \text{ M}) \)
$^{13}$C NMR of 4b in DMSO-$d_6$ (100 M)

$^{19}$F NMR of 4b in DMSO-$d_6$ (376 M)
$^1$H NMR of 4c in DMSO-$d_6$ (400 M)

$^{13}$C NMR of 4c in DMSO-$d_6$ (100 M)
$^{19}$F NMR of 4c in DMSO-$d_6$ (376 M)

$^1$H NMR of 4d in DMSO-$d_6$ (400 M)
$^{13}$C NMR of 4d in DMSO-$d_6$ (100 M)

$^{19}$F NMR of 4d in DMSO-$d_6$ (376 M)
$^1$H NMR of 4e in DMSO-$d_6$ (400 M)

$^{13}$C NMR of 4e in DMSO-$d_6$ (100 M)
$^{19}$F NMR of 4e in DMSO-$d_6$ (376 M)

$^1$H NMR of 4f in DMSO-$d_6$ (400 M)
$^{13}$C NMR of **4f** in DMSO-$d_6$ (100 M)

![$^{13}$C NMR spectrum of 4f in DMSO-$d_6$](image)

$^{19}$F NMR of **4f** in DMSO-$d_6$ (376 M)

![$^{19}$F NMR spectrum of 4f in DMSO-$d_6$](image)
$^1$H NMR of 4g in DMSO-$d_6$ (400 M)

$^{13}$C NMR of 4g in DMSO-$d_6$ (100 M)
19F NMR of 4g in DMSO-d6 (376 M)

1H NMR of 4h in DMSO-d6 (400 M)
$^{13}$C NMR of 4h in DMSO-$d_6$ (100 M)

$^{19}$F NMR of 4h in DMSO-$d_6$ (376 M)
$^1$H NMR of 4i in DMSO-$d_6$ (400 M)

$^{13}$C NMR of 4i in DMSO-$d_6$ (100 M)
$^{19}$F NMR of 4i in DMSO-$d_6$ (376 M)

$^1$H NMR of 4j in DMSO-$d_6$ (400 M)
$^{13}$C NMR of 4j in DMSO-$d_6$ (100 M)

$^{19}$F NMR of 4j in DMSO-$d_6$ (376 M)
$^1$H NMR of 4k in DMSO-$d_6$ (400 M)

$^{13}$C NMR of 4k in DMSO-$d_6$ (100 M)
$^{19}$F NMR of 4k in DMSO-$d_6$ (376 M)

$^1$H NMR of 4l in DMSO-$d_6$ (400 M)
$^{13}$C NMR of 41 in DMSO-$d_6$ (100 M)

$^{19}$F NMR of 41 in DMSO-$d_6$ (376 M)
$^1$H NMR of 4m in DMSO-$d_6$ (400 M)

$^{13}$C NMR of 4m in DMSO-$d_6$ (100 M)
$^{19}$F NMR of $4m$ in DMSO-$d_6$ (376 M)

$^1$H NMR of $4n$ in DMSO-$d_6$ (400 M)
$^{13}$C NMR of 4n in DMSO-$d_6$ (100 M)

$^{19}$F NMR of 4n in DMSO-$d_6$ (376 M)
$^1$H NMR of 4o in CDCl$_3$ (400 M)

$^{13}$C NMR of 4o in CDCl$_3$ (100 M)
$^{19}$F NMR of $4o$ in CDCl$_3$ (376 M)

$^1$H NMR of $4p$ in DMSO-$d_6$ (400 M)
$^{13}$C NMR of 4p in DMSO-$d_6$ (100 M)

$^{19}$F NMR of 4p in DMSO-$d_6$ (376 M)
$^1$H NMR of 4q in DMSO-$d_6$ (400 M)

$^{13}$C NMR of 4q in DMSO-$d_6$ (100 M)
$^{19}$F NMR of 4q in DMSO-$d_6$ (376 M)

$^1$H NMR of 4r in DMSO-$d_6$ (400 M)
$^{13}$C NMR of 4r in DMSO-$d_6$ (100 M)

$^{19}$F NMR of 4r in DMSO-$d_6$ (376 M)
$^1$H NMR of 4s in DMSO-$d_6$ (400 M)

$^{13}$C NMR of 4s in DMSO-$d_6$ (100 M)
$^{19}$F NMR of 4s in DMSO-$d_6$ (376 M)

$^1$H NMR of 4t in DMSO-$d_6$ (400 M)
$^{13}$C NMR of $4t$ in DMSO-$d_6$ (100 M)

$^{19}$F NMR of $4t$ in DMSO-$d_6$ (376 M)
$^1$H NMR of 4u in DMSO-$d_6$ (400 M)

$^{13}$C NMR of 4u in DMSO-$d_6$ (100 M)
$^{19}$F NMR of 4u in DMSO-$d_6$ (376 M)

$^1$H NMR of 4v in DMSO-$d_6$ (400 M)
^{13}\text{C} \text{NMR of 4v in DMSO-}d_6 (100 \text{ M})

^{19}\text{F} \text{NMR of 4v in DMSO-}d_6 (376 \text{ M})
$^1$H NMR of 4w in DMSO-$d_6$ (400 M)

$^{13}$C NMR of 4w in DMSO-$d_6$ (100 M)
$^{19}$F NMR of 4w in DMSO-$d_6$ (376 M)

$^1$H NMR of 4x in DMSO-$d_6$ (400 M)
$^{13}$C NMR of 4x in DMSO-$d_6$ (100 M)

$^{19}$F NMR of 4x in DMSO-$d_6$ (376 M)
$^1$H NMR of 4y in DMSO-$d_6$ (400 M)

$^{13}$C NMR of 4y in DMSO-$d_6$ (100 M)
$^{19}$F NMR of 4y in DMSO-$d_6$ (376 M)

$^1$H NMR of 4z in DMSO-$d_6$ (400 M)
$^{13}$C NMR of $4z$ in DMSO-$d_6$ (100 M)

$^{19}$F NMR of $4z$ in DMSO-$d_6$ (376 M)
$^1$H NMR of 4aa in DMSO-$d_6$ (400 M)

$^{13}$C NMR of 4aa in DMSO-$d_6$ (100 M)
$^{19}$F NMR of 4aa in DMSO-$d_6$ (376 M)

$^1$H NMR of 4ab in DMSO-$d_6$ (400 M)
$^{13}$C NMR of 4ab in DMSO-$d_6$ (100 M)

$^{19}$F NMR of 4ab in DMSO-$d_6$ (376 M)
$^1$H NMR of 6a in CDCl$_3$ (400 M)

$^{13}$C NMR of 6a in CDCl$_3$ (100 M)
$^{19}$F NMR of 6a in CDCl$_3$ (376 M)

$^1$H NMR of 6b in CDCl$_3$ (600 M)
$^{13}$C NMR of $6b$ in CDCl$_3$ (150 M)

$^{19}$F NMR of $6b$ in CDCl$_3$ (376 M)
$^1\text{H NMR of} \ 6c \ \text{in CDCl}_3 (600 \text{ M})$

$^{13}\text{C NMR of} \ 6c \ \text{in CDCl}_3 (150 \text{ M})$
$^{19}$F NMR of 6c in CDCl$_3$ (376 M)

$^1$H NMR of 6d in CDCl$_3$ (600 M)
$^{13}$C NMR of 6d in CDCl$_3$ (150 M)

$^{19}$F NMR of 6d in CDCl$_3$ (376 M)
$^1$H NMR of 6e in CDCl$_3$ (600 M)

$^{13}$C NMR of 6e in CDCl$_3$ (150 M)
$^{19}$F NMR of **6e** in CDCl$_3$ (376 M)

$^1$H NMR of **6f** in CDCl$_3$ (400 M)
$^{13}$C NMR of $6f$ in CDCl$_3$ (100 M)

$^{19}$F NMR of $6f$ in CDCl$_3$ (376 M)
$^1$H NMR of 6g in CDCl$_3$ (600 M)

$^{13}$C NMR of 6g in CDCl$_3$ (150 M)
$^{19}$F NMR of 6g in CDCl$_3$ (376 M)

$^1$H NMR of 6h in CDCl$_3$ (400 M)
$^{13}$C NMR of 6h in CDCl$_3$ (100 M)

$^{19}$F NMR of 6h in CDCl$_3$ (376 M)
$^1$H NMR of 6i in DMSO-$d_6$ (400 M)

$^{13}$C NMR of 6i in DMSO-$d_6$ (100 M)
$^{19}$F NMR of 6i in DMSO-$d_6$ (376 M)

$^1$H NMR of 8a in DMSO-$d_6$ (400 M)
$^{13}$C NMR of 8a in CDCl$_3$ (100 M)

$^1$H NMR of 8b in CDCl$_3$ (600 M)
$^{13}$C NMR of $8b$ in CDCl$_3$ (150 M)

$^1$H NMR of $8c$ in CDCl$_3$ (600 M)
$^{13}$C NMR of 8c in CDCl$_3$ (150 M)

$^1$H NMR of 8d in CDCl$_3$ (400 M)
$^1$H NMR of 8c in CDCl$_3$ (400 M)
$^{13}$C NMR of 8e in CDCl$_3$ (100 M)

$^1$H NMR of 8f in CDCl$_3$ (400 M)
$^{13}$C NMR of 8f in CDCl$_3$ (100 M)

$^1$H NMR of 8g in CDCl$_3$ (600 M)
$^{13}$C NMR of 8g in CDCl$_3$ (150 M)

![Carbon NMR spectrum of 8g in CDCl$_3$](image)

$^1$H NMR of 8h in CDCl$_3$ (600 M)

![Hydrogen NMR spectrum of 8h in CDCl$_3$](image)
\(^{13}\)C NMR of 8h in CDCl\(_3\) (150 M)

\(^1\)H NMR of 8i in CDCl\(_3\) (600 M)
$^{13}$C NMR of 8i in CDCl$_3$ (150 M)

\[ \text{[Chemical Structure Image]} \]

$^1$H NMR of 8j in CDCl$_3$ (600 M)

\[ \text{[Chemical Structure Image]} \]
$^{13}$C NMR of $8j$ in CDCl$_3$ (150 M)

$^1$H NMR of $8k$ in CDCl$_3$ (600 M)
$^{13}$C NMR of 8k in CDCl$_3$ (150 M)

$^1$H NMR of 8l in CDCl$_3$ (600 M)
$^1$H NMR of 8m in CDCl$_3$ (600 M)

$^{13}$C NMR of 8l in CDCl$_3$ (150 M)
$^{13}$C NMR of $8m$ in CDCl$_3$ (150 M)

$^1$H NMR of $8n$ in CDCl$_3$ (600 M)
$^{13}$C NMR of 8n in CDCl$_3$ (150 M)

$^1$H NMR of 8o in CDCl$_3$ (600 M)
$^{13}$C NMR of $8o$ in CDCl$_3$ (150 M)

$^1$H NMR of $8p$ in CDCl$_3$ (600 M)
$^{13}$C NMR of 8p in CDCl$_3$ (150 M)

$^1$H NMR of 8q in CDCl$_3$ (600 M)
$^{13}$C NMR of 8q in CDCl$_3$ (150 M)

$^1$H NMR of 8r in CDCl$_3$ (600 M)
$^{13}$C NMR of 8r in CDCl$_3$ (150 M)

$^1$H NMR of 8s in CDCl$_3$ (600 M)
$^{13}$C NMR of 8s in CDCl$_3$ (150 M)

$^1$H NMR of 8t in CDCl$_3$ (600 M)
$^{13}$C NMR of 8t in CDCl$_3$ (150 M)

$^1$H NMR of 8u in CDCl$_3$ (600 M)
$^{13}$C NMR of $8u$ in CDCl$_3$ (150 M)

$^1$H NMR of $8v$ in CDCl$_3$ (600 M)
$^{13}$C NMR of $8v$ in CDCl$_3$ (150 M)

$^1$H NMR of $8w$ in CDCl$_3$ (600 M)
$^{13}$C NMR of 8w in CDCl$_3$ (150 M)

$^1$H NMR of 8x in DMSO-$d_6$ (400 M)
$^{13}$C NMR of 8x in DMSO-$d_6$ (100 M)

$^1$H NMR of 8y in CDCl$_3$ (600 M)
$^{13}$C NMR of $8\text{y}$ in CDCl$_3$ (150 M)

$^1$H NMR of $8\text{z}$ in CDCl$_3$ (600 M)
$^{13}$C NMR of 8z in CDCl$_3$ (150 M)

$^1$H NMR of 8aa in DMSO-$d_6$ (400 M)
$^{13}$C NMR of 8aa in DMSO-$d_6$ (100 M)

$^1$H NMR of 8ab in CDCl$_3$ (600 M)
$^{13}$C NMR of $8ab$ in CDCl$_3$ (150 M)

1H NMR of $9$ in CDCl$_3$ (600 M)
$^{13}$C NMR of 9 in CDCl$_3$ (150 M)

$^1$H NMR of 10 in CDCl$_3$ (600 M)
$^{13}$C NMR of 10 in CDCl$_3$ (150 M)