Supporting Information

Diverse Secondary C(sp³)–H bond functionalization via Site-Selective Trifluoroacetoxylation of Aliphatic Amines

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Instrumentation and Chemical

NMR spectra were recorded on Bruker 400 and 600 M spectrometers, operating at 400 and 600 MHz for \(^1\)H NMR and 100 and 150 MHz for \(^{13}\)C NMR spectrophotometer using CDCl\(_3\) and TMS as the internal standard. Chemical shift values for \(^1\)H and \(^{13}\)C are referenced to residual solvent peaks (CHCl\(_3\) in CDCl\(_3\): 7.26 ppm for \(^1\)H, 77.00 ppm for \(^{13}\)C; Chemical shifts are reported in \(\delta\) ppm. All coupling constants (\(J\) values) were reported in Hertz (Hz). Data for \(^1\)H NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; \(s =\) singlet, \(d =\) doublet, \(t =\) triplet, \(q =\) quartet, \(dd =\) doublet of doublets, \(dt =\) doublet of triplets, \(m =\) multiplet), coupling constant (Hz) and integration. Column chromatography was performed on silica gel 200-300 mesh. High-resolution mass spectra (HRMS) were recorded on electron-spray ionization (ESI) technique.

All reactions were carried out under nitrogen atmosphere. Materials were obtained from commercial suppliers or prepared according to standard noteprocedures unless otherwise noted. CuI was purchased from Energy Chemical Reagent Co., Ltd., PhI(OTFA)\(_2\) was purchased from Beijing Innochem Science & Technology Co., Ltd. Tetrabuylammonium bromide (TBAB) was purchased from Tokyo Chemical Industry Co., Ltd. DCM was freshly distilled over CaH\(_2\) under N\(_2\).

General Procedure: Preparation of aliphatic amides

Procedure A

\[ \begin{array}{c}
\text{CN} \\
R^1 R^2 \\
1
\end{array} \]

1) \(n\)-BuLi (1.05 equiv) \(i\)-Pr\(_2\)NH (1.05 equiv) THF (40 mL), \(-78^\circ\text{C}\)
2) \(R^3 X\) (1.2 equiv) \(-78^\circ\text{C}\)

\[ \begin{array}{c}
\text{CN} \\
R^1 R^2 \\
2
\end{array} \]

\[ \begin{array}{c}
\text{R}^2 \text{R}^1 \\
\text{CN} \\
3
\end{array} \]

BzCl (0.95 equiv) \(Et_2N\) (2.0 equiv) DCM (1.0 M), 24 h

\[ \begin{array}{c}
\text{NHBz} \\
R^3 \\
\text{R}^2 \text{R}^1 \\
\text{a}
\end{array} \]

\(n\)-BuLi in hexane (2.5 M, 20 mmol, 1.05 equiv) was added dropwise to a solution of \(i\)-
Pr₂NH (3.5 mL, 21.0 mmol, 1.05 equiv) in THF (40 mL) at −78 ºC and stirred for 0.5 h. Then alkyl nitrile 1 (20 mmol, 1.0 equiv) was added dropwise to the resulting LDA solution at −78 ºC and stirred at this temperature for 1 h. Alkyl halide (30 mmol, 1.5 equiv) was then added dropwise to the solution at −78 ºC. After the addition, the mixture was warmed to room temperature and stirred overnight. After down, the mixture was quenched with saturated aqueous NH₄Cl, and extracted with EtOAc (20 mL × 3). Combined extracts were washed with water, brine solution and dried with anhydrous Na₂SO₄. Solvent was evaporated in Rota-evaporator. The residue was purified by silica gel chromatography (2%–10% EtOAc/petroleum ether) to provide corresponding nitrile 2.

LiAlH₄ (2.28 g, 60 mmol, 3.0 equiv) was slowly added to the solution of crude nitrile in THF (30 mL) at room temperature. Then the mixture was heated to 88 ºC for 24 hours. After that, the reaction was cooled down, the Na₂SO₄ · 10H₂O was added slowly until the mixture was clear to quench the reaction, filtered, solid was washed with Et₂O, the combined ether solution was concentrated in vacuo to give the desired amide 3.

To a solution of amine 3 (10 mmol, 1.0 equiv) in dichloromethane (20 mL) was added triethylamine (2.78 mL, 20 mmol, 2.0 equiv) at 0 ºC. Benzoyl chloride (1.34 g, 9.5 mmol, 0.95 equiv) was added dropwise. Then the mixture was stirring overnight at room temperature. Then the mixture was quenched by water (20 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (20 mL × 2). The combined organic phase was washed with brine (30 mL), and then dried with anhydrous Na₂SO₄. Evaporation and column chromatography on silica gel (ethyl acetate/hexane = 1:100–1:5 as eluent) afforded corresponding amides a as white solid. Aliphatic amide substrates PG 2-PG 6, PG 8-PG 13, 2a-2f, 2k-2u, 2ag were prepared according to the procedure A.

PG 7 can be found in reference 1.

Procedure B
To a solution of 5-chloropentan-1-ol (20 mmol, 1.0 equiv) in acetone (20 mL) was added NaI (40 mmol, 2.0 equiv). Then the mixture was reflux for 5 hours until the 5-chloropentan-1-ol was consumed. Evaporation and column chromatography on silica gel (EA/PE/DCM = 1:20:0.5 as eluent) afforded corresponding 4 as colorless oil.

Follow procedure A to give the aliphatic amides 2g and 2h.

To a solution of amino alcohol 6 (10 mmol, 1.0 equiv) in dichloromethane (10 mL) was added triethylamine (4.17 mL, 30 mmol, 3.0 equiv) at room temperature. Benzoyl chloride (1.34 g, 9.5 mmol, 0.95 equiv) was added dropwise under the same temperature. Then the mixture was stirring for 30 min at room temperature (detected by TLC). After that, the mixture was quenched by water (20 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (20 mL × 2). The combined organic phase was washed with brine (30 mL), and then dried over Na$_2$SO$_4$. Evaporation and column chromatography on silica gel (EA/PE/DCM = 1:2:1 as eluent) afforded amino protected compound 7 as white solid. Compound 7 (10 mmol, 1.0 equiv) was dissolved in the DCM (10 mL), pyridine (2.41 mL, 30 mmol,
3.0 equiv) was added dropwise at 0 °C, then Tosyl Chloride (10 mmol, 1.0 equiv) was added portion wise. The mixture was stirring for 24 h. After that, the mixture was quenched by water (20 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (20 mL × 2). The combined organic phase was washed with brine (30 mL), and then dried over Na$_2$SO$_4$. Evaporation and column chromatography on silica gel (EA/PE/DCM = 1:10:0.5 as eluent) to give the desired product 2i and 2j.

**Procedure C:**

![Chemical reaction diagram]

The amino alcohol 8 (20 mmol, 1.0 equiv) was dissolved in DCM (20 mL), Et$_3$N (5.6 mL, 40 mmol, 2.0 equiv) was added dropwise, then BzCl was added at room temperature, the reaction mixture was stirring for 30 min. After that, the mixture was quenched by water (20 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (20 mL × 2). The combined organic phase was washed with brine (30 mL), and then dried over Na$_2$SO$_4$. Evaporation and column chromatography on silica gel (EA/PE/DCM = 1:20:0.5 as eluent) afforded amino protected compound 9 as white solid. Compound 9 was followed the same procedure as above to give 2v as a white solid.

2w-2y, 2z, 2aa were prepared as the above procedure C.

2ab$^2$, 2ac$^2$, 2ad$^2$, 2af$^3$ were synthesized according to previous reported procedure.

Preparation of 2ak:
Lithocholic acid (7.53 g, 20 mmol, 1.0 equiv) was dissolved in THF (100 mL), LiAlH₄ (1.9 g, 50 mmol, 2.5 equiv) was added portion wise under 0 ºC, then the mixture was refluxing for 12 h. After that, the reaction was cooled down, the Na₂SO₄ · 10H₂O was added slowly until the mixture was clear to quench the reaction, filtered, solid was washed with Et₂O, the combined ether solution was concentrated in vacuo to give the alcohol-10.

PPh₃ (9.83 g, 37.5 mmol, 2.5 equiv) and 1H-imidazole (4.6 g, 67.5 mmol, 4.5 equiv) were successively added to a soln. of alcohol-10 (5.43 g, 15 mmol, 1.0 equiv) in THF (150 mL). The mixture was cooled to −20 ºC and I₂ (7.61 g, 30 mmol, 2.0 equiv) was added in three portions each 5 min. After 15 min, the mixture was removed from the cooling bath and stirred for 30 min at rt. The reaction was quenched by slow addition of sat. NaHCO₃ soln. (15 mL) and sat. Na₂S₂O₃ soln. (15 mL). The aq. Layer was extracted with EtOAc (25 mL × 3), the combined organic layer dried over Na₂SO₄. Evaporation and column chromatography on silica gel (EA/PE/DCM = 1:8:0.5 as eluent) afforded I-11.
Then followed the procedure A afforded the product 2ag.

**Characterization Data for amides**

**N-(2,2-dimethylhexyl)benzamide (2a, PG 1)**

![Structure of 2a](image)

White solid. mp: 71.8–73.0 ºC; \(^1H\) NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.75 (d, \(J = 6.0\) Hz, 2H), 7.50 (t, \(J = 6.0\) Hz, 1H), 7.44 (dd, \(J = 6.0, 6.0\) Hz, 2H), 6.09 (br s, 1H), 3.30 (d, \(J = 6.0\) Hz, 2H), 1.24–1.30 (m, 6H), 0.95 (s, 6H), 0.91 (t, \(J = 6.0\) Hz, 3H). \(^13\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 167.59, 135.01, 131.09, 128.37, 126.74, 49.47, 39.72, 34.38, 26.00, 24.91, 23.42, 13.99. HRMS–ESI (m/z): [M+Na]\(^+\) calcd. for C\(_{15}\)H\(_{23}\)NNaO, 256.1672; found, 256.1675. IR (KBr, cm\(^{-1}\)): \(\nu\) 3414, 1637, 1400, 1118, 617.

**N-(2,2-dimethylhexyl)-4-methylbenzamide (PG 2)**

![Structure of PG 2](image)

White solid. mp: 68.2–68.6 ºC; \(^1H\) NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.66 (d, \(J = 7.9\) Hz, 2H), 7.23 (d, \(J = 7.8\) Hz, 2H), 6.13 (br s, 1H), 3.28 (d, \(J = 6.3\) Hz, 2H), 2.39 (s, 3H), 1.21–1.34 (m, 6H), 0.93 (s, 6H), 0.90 (t, \(J = 6.6\) Hz, 3H). \(^13\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 167.52, 141.61, 132.17, 129.17, 126.74, 49.44, 39.76, 34.39, 26.08, 25.00, 23.51, 21.39, 14.10. HRMS–ESI (m/z): [M+Na]\(^+\) calcd. for C\(_{16}\)H\(_{25}\)NNaO, 270.1828; found, 270.1821. IR (KBr, cm\(^{-1}\)): \(\nu\) 3474, 3415, 2957, 2925, 1639, 1397, 838.

**N-(2,2-dimethylhexyl)-4-chlorobenzamide (PG 3)**

![Structure of PG 3](image)

White solid. mp: 89.5–90.0 ºC; \(^1H\) NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.69 (d, \(J = 8.4\) Hz,
2H), 7.39 (d, \( J = 8.4 \) Hz, 2H), 6.25 (br s, 1H), 3.26 (d, \( J = 6.3 \) Hz, 2H), 1.21–1.34 (m, 6H), 0.93 (s, 6H), 0.90 (t, \( J = 6.6 \) Hz, 3H). \( \text{\textsuperscript{13}C NMR} \) (150 MHz, CDCl\(_3\)) \( \delta \) 166.60, 137.39, 133.36, 128.71, 128.23, 49.61, 39.75, 34.42, 26.05, 24.96, 23.48, 14.08.

HRMS–ESI (m/z): [M+Na]\(^{+}\) calcd. for C\(_{15}\)H\(_{22}\)ClNNaO, 290.1282; found, 290.1275.

IR (KBr, cm\(^{-1}\)): v 3476, 3415, 2961, 2926, 1789, 1637, 1597, 1484, 823.

**N-(2,2-dimethylhexyl)-4-methoxybenzamide (PG 4)**

![Image of PG 4]

White solid. mp: 86.0–87.3 ºC; \( \text{\textsuperscript{1}H NMR} \) (600 MHz, CDCl\(_3\)) \( \delta \) 7.73 (d, \( J = 8.4 \) Hz, 2H), 6.94 (d, \( J = 8.4 \) Hz, 2H), 6.01 (br s, 1H), 3.86 (s, 3H), 3.28 (d, \( J = 6.3 \) Hz, 2H), 1.23–1.33 (m, 6H), 0.94 (s, 6H), 0.91 (t, \( J = 6.3 \) Hz, 3H). \( \text{\textsuperscript{13}C NMR} \) (150 MHz, CDCl\(_3\)) \( \delta \) 167.07, 161.89, 128.51, 127.25, 113.60, 55.29, 49.42, 39.74, 34.38, 26.04, 24.95, 23.47, 14.06. HRMS–ESI (m/z): [M+H]\(^{+}\) calcd. for C\(_{16}\)H\(_{26}\)NO\(_2\), 264.1958; found, 264.1960. IR (KBr, cm\(^{-1}\)): v 3415, 1637, 1399, 1251, 1173, 614.

**N-(2,2-dimethylhexyl)-4-nitrobenzamide (PG 5)**

![Image of PG 5]

White solid. mp: 73.1–74.2 ºC; \( \text{\textsuperscript{1}H NMR} \) (600 MHz, CDCl\(_3\)) \( \delta \) 8.31 (d, \( J = 8.4 \) Hz, 2H), 7.92 (d, \( J = 8.4 \) Hz, 2H), 6.12 (br s, 1H), 3.32 (d, \( J = 6.1 \) Hz, 2H), 1.26–1.34 (m, 6H), 0.96 (s, 6H), 0.92 (t, \( J = 6.6 \) Hz, 3H). \( \text{\textsuperscript{13}C NMR} \) (150 MHz, CDCl\(_3\)) \( \delta \) 165.72, 149.33, 140.64, 128.00, 123.73, 49.88, 39.74, 34.48, 26.04, 24.95, 23.45, 14.06. HRMS–ESI (m/z): [M+Na]\(^{+}\) calcd. for C\(_{15}\)H\(_{22}\)N\(_2\)NaO\(_3\), 301.1523; found, 301.1515. IR (KBr, cm\(^{-1}\)): v 3475, 3415, 2927, 1640, 1399, 1108, 866.
\[ \text{N-(2,2-dimethylhexyl)-2-nitrobenzamide (PG 6)} \]

\[
\text{\begin{center}
\includegraphics[width=0.2\textwidth]{pg6.png}
\end{center}}
\]

White solid. mp: 72.3–73.4 °C; \textbf{\textsuperscript{1}H NMR} (600 MHz, CDCl\textsubscript{3}) \( \delta \) 8.07 (d, \( J = 8.1 \) Hz, 1H), 7.68 (t, \( J = 7.5 \) Hz, 1H), 7.59 (t, \( J = 7.8 \) Hz, 1H), 7.53 (d, \( J = 7.5 \) Hz, 1H), 5.78 (br s, 1H), 3.32 (d, \( J = 6.3 \) Hz, 2H), 1.22–1.35 (m, 6H), 0.97 (s, 6H), 0.92 (t, \( J = 6.6 \) Hz, 3H). \textbf{\textsuperscript{13}C NMR} (150 MHz, CDCl\textsubscript{3}) \( \delta \) 166.65, 146.31, 133.58, 133.13, 130.27, 128.67, 124.39, 49.79, 39.67, 34.31, 26.01, 24.89, 23.44, 14.07. \textbf{HRMS–ESI} (\( m/z \)): [M+Na]\textsuperscript{+} calcd. for C\textsubscript{15}H\textsubscript{22}N\textsubscript{2}NaO\textsubscript{3}, 301.1523; found, 301.1515. \textbf{IR} (KBr, cm\textsuperscript{-1}): \( \nu \) 3416, 1638, 1399, 1119, 616.

\[ \text{N-(2,2-dimethylhexyl)-4-methylbenzenesulfonamide (PG 7)} \]

\[
\text{\begin{center}
\includegraphics[width=0.2\textwidth]{pg7.png}
\end{center}}
\]

White solid. \textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.74 (d, \( J = 8.1 \) Hz, 2H), 7.31 (d, \( J = 8.1 \) Hz, 2H), 4.30 (t, \( J = 6.9 \) Hz, 1H), 2.68 (d, \( J = 6.9 \) Hz, 2H), 2.43 (s, 3H), 1.19–1.25 (m, 2H), 1.09–1.17 (m, 4H), 0.84 (t, \( J = 7.2 \) Hz, 3H), 0.82 (s, 6H).

\[ \text{N-(2,2-dimethylhexyl)-2,3,4,5,6-pentafluorobenzamide (PG 8)} \]

\[
\text{\begin{center}
\includegraphics[width=0.2\textwidth]{pg8.png}
\end{center}}
\]

Yellow solid. mp: 31.9–33.4 °C; \textbf{\textsuperscript{1}H NMR} (600 MHz, CDCl\textsubscript{3}) \( \delta \) 5.86 (br s, 1H), 3.30 (d, \( J = 6.3 \) Hz, 2H), 1.22–1.33 (m, 6H), 0.94 (s, 6H), 0.91 (t, \( J = 6.9 \) Hz, 3H). \textbf{\textsuperscript{13}C NMR} (150 MHz, CDCl\textsubscript{3}) \( \delta \) 157.43, 49.87, 39.55, 34.30, 26.01, 24.85, 23.44, 14.01. \textbf{HRMS–ESI} (\( m/z \)): [M+Na]\textsuperscript{+} calcd. for C\textsubscript{15}H\textsubscript{18}F\textsubscript{5}NNaO, 346.1201; found, 346.1192.
IR (KBr, cm$^{-1}$): $\nu$ 3474, 3415, 1620, 1399, 1115, 618.

$N$-(2,2-dimethylhexyl)picolinamide ($\text{PG} \ 9$)

[Chemical structure image]

Yellow oil; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.56 (d, $J = 4.2$ Hz, 1H), 8.21 (d, $J = 7.8$ Hz, 1H), 8.17 (br s, 1H), 7.85 (t, $J = 7.8$ Hz, 1H), 7.43 (t, $J = 6.3$ Hz, 1H), 3.30 (d, $J = 6.6$ Hz, 2H), 1.23–1.37 (m, 6H), 0.96 (s, 6H), 0.91 (t, $J = 6.3$ Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 164.09, 149.79, 147.82, 137.12, 125.83, 122.01, 49.02, 39.55, 34.31, 25.94, 24.81, 23.33, 13.94. HRMS–ESI ($m/z$): [M+Na]$^+$ calcd. for C$_{14}$H$_{22}$N$_2$NaO, 257.1624; found, 257.1624. IR (KBr, cm$^{-1}$): $\nu$ 3397, 3060, 2929, 2866, 1680, 1529, 1388, 1293, 624.

$tert$-butyl (2,2-dimethylhexyl)carbamate ($\text{PG} \ 10$)

[Chemical structure image]

White solid. mp: 72.3–73.4 ºC; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 5.63 (br s, 1H), 3.07 (d, $J = 6.0$ Hz, 2H), 1.26–1.32 (m, 4H), 1.21 (s, 9H), 1.17–1.18 (m, 2H), 0.90 (t, $J = 7.2$ Hz, 3H), 0.86 (s, 6H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 178.20, 48.74, 39.69, 38.83, 34.20, 27.63, 27.05, 26.01, 24.96, 23.48, 14.05. HRMS–ESI ($m/z$): [M+Na]$^+$ calcd. for C$_{13}$H$_{27}$NNaO, 236.1985; found, 236.1985. IR (KBr, cm$^{-1}$): $\nu$ 3416, 2961, 1638, 1220, 1184, 702.

$N$-(2,2-dimethylhexyl)acetamide ($\text{PG} \ 11$)

[Chemical structure image]
Yellow oil. $^1\text{H NMR}$ (600 MHz, CDCl$_3$) $\delta$ 5.62 (br s, 1H), 3.07 (d, $J = 6.3$ Hz, 2H), 2.01 (s, 3H), 1.17–1.30 (m, 6H), 0.90 (t, $J = 7.2$ Hz, 3H), 0.86 (s, 6H). $^{13}\text{C NMR}$ (150 MHz, CDCl$_3$) $\delta$ 170.11, 49.22, 39.62, 33.95, 26.01, 24.85, 23.48, 23.40, 14.06. 

HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{10}$H$_{21}$NNaO, 194.1515; found, 194.1513. IR (KBr, cm$^{-1}$): v 3414, 2960, 2630, 1655, 1556, 1466, 605.

methyl (2,2-dimethylhexyl)carbamate (PG 12)

Yellow oil. $^1\text{H NMR}$ (600 MHz, CDCl$_3$) $\delta$ 4.65 (s, 1H), 3.67 (s, 3H), 3.00 (d, $J = 6.4$ Hz, 2H), 1.24–1.29 (m, 2H), 1.16–1.24 (m, 4H), 0.90 (t, $J = 7.2$ Hz, 3H), 0.85 (s, 6H). $^{13}\text{C NMR}$ (150 MHz, CDCl$_3$) $\delta$ 157.33, 52.02, 51.01, 39.43, 34.16, 26.02, 24.74, 23.51, 14.08. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{10}$H$_{21}$NNaO$_2$, 210.1465; found, 210.1462. IR (KBr, cm$^{-1}$): v 3416, 2956, 1638, 1399, 1122, 615.

N-(2,2-dimethylhexyl)-2,2,2-trifluoroacetamide (PG 13)

Yellow oil. $^1\text{H NMR}$ (600 MHz, CDCl$_3$) $\delta$ 6.40 (br s, 1H), 3.19 (d, $J = 6.3$ Hz, 2H), 1.20–1.36 (m, 6H), 0.90 (t, $J = 7.2$ Hz, 3H), 0.90 (s, 6H). $^{13}\text{C NMR}$ (150 MHz, CDCl$_3$) $\delta$ 157.42 (q, $J = 42.0$ Hz), 115.99 (q, $J = 285.0$ Hz), 49.50, 39.49, 34.29, 25.95, 24.67, 23.37, 13.96. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{10}$H$_{18}$F$_3$NNaO, 248.1233; found, 248.1230. IR (KBr, cm$^{-1}$): v 3414, 2963, 2934, 1706, 1621, 1592, 1121, 1167, 723.

N-(2,2-dimethylpentyl)benzamide (2b)
White solid. mp: 70.1–70.4 ºC; \( ^1H \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 7.76 (d, J = 8.0 \text{ Hz}, 2H), 7.50 (t, J = 8.0 \text{ Hz}, 1H), 7.44 (t, J = 8.0, 8.0 \text{ Hz}, 2H), 6.11 (s, 1H), 3.30 (d, J = 8.0 \text{ Hz}, 2H), 1.30–1.37 (m, 2H), 1.21–1.28 (m, 2H), 0.95 (s, 6H), 0.91 (t, J = 8.0 \text{ Hz}, 3H). \( ^{13}C \text{NMR} (150 \text{ MHz, CDCl}_3) \delta 167.62, 135.05, 131.24, 128.52, 126.76, 49.55, 42.50, 34.52, 25.00, 17.10, 14.94. \text{HRMS–ESI} (m/z): [M+H]^+ \text{calcd. for C}_{14}H_{22}NO, 220.1696; \text{found, 220.1699. IR} (\text{KBr, cm}^{-1}): \nu 3475, 3414, 1638, 1399, 1119, 618.

\( N-(2,2\text{-dimethyldecyl})\text{benzamide (2c)} \)

White solid. mp: 55.8–56.1 ºC; \( ^1H \text{NMR} (600 \text{ MHz, CDCl}_3) \delta 7.76 (d, J = 6.0 \text{ Hz}, 2H), 7.50 (t, J = 6.0 \text{ Hz}, 1H), 7.45 (dd, J = 6.0, 6.0 \text{ Hz}, 2H), 6.09 (br s, 1H), 3.30 (d, J = 6.0 \text{ Hz}, 2H), 1.22–1.35 (m, 14H), 0.94 (s, 6H), 0.88 (t, J = 6.9 \text{ Hz}, 3H). \( ^{13}C \text{NMR} (150 \text{ MHz, CDCl}_3) \delta 167.62, 135.07, 131.25, 128.53, 126.76, 49.53, 40.08, 34.43, 31.85, 30.48, 29.57, 29.28, 25.01, 23.86, 22.63, 14.09. \text{HRMS–ESI} (m/z): [M+Na]^+ \text{calcd. for C}_{19}H_{31}NNaO, 312.2298; \text{found, 312.2296. IR} (\text{KBr, cm}^{-1}): \nu 3475, 3414, 1638, 1399, 1119, 617.

\( N-(2,2\text{-dimethyltetradecyl})\text{benzamide (2d)} \)

White solid. mp: 58.2–59.0 ºC; \( ^1H \text{NMR} (600 \text{ MHz, CDCl}_3) \delta 7.75 (d, J = 6.0 \text{ Hz}, 2H), 7.50 (t, J = 6.0 \text{ Hz}, 1H), 7.44 (dd, J = 6.0, 6.0 \text{ Hz}, 2H), 6.09 (br s, 1H), 3.30 (d, J = 6.0 \text{ Hz}, 2H), 1.22–1.30 (m, 22H), 0.94 (s, 6H), 0.88 (t, J = 6.0 \text{ Hz}, 3H). \( ^{13}C \text{NMR} \)
(150 MHz, CDCl$_3$) $\delta$ 167.63, 135.09, 131.22, 128.51, 126.77, 49.55, 40.11, 34.44, 31.87, 30.49, 29.63, 29.62, 29.61, 29.30, 25.01, 23.87, 22.64, 14.07. **HRMS–ESI** ($m/z$): [M+Na]$^+$ calcd. for C$_{23}$H$_{39}$NNaO, 368.2924; found, 368.2927. **IR** (KBr, cm$^{-1}$): ν 3550, 3476, 3414, 2959, 2921, 1639, 1537, 1121, 802, 639.

**N-(2,2-dimethyloctadecyl)benzamide (2e)**

![2e](image)

White solid. mp: 71.1–71.8 ºC; **$^1$H NMR** (600 MHz, CDCl$_3$) $\delta$ 7.76 (d, $J$ = 7.8 Hz, 2H), 7.51 (t, $J$ = 7.2 Hz, 1H), 7.45 (dd, $J$ = 7.8, 7.2 Hz, 2H), 6.08 (br s, 1H), 3.30 (d, $J$ = 6.3 Hz, 2H), 1.21–1.33 (m, 30H), 0.94 (s, 6H), 0.88 (t, $J$ = 6.9 Hz, 3H). **$^{13}$C NMR** (150 MHz, CDCl$_3$) $\delta$ 167.61, 135.14, 131.25, 128.55, 126.77, 49.57, 40.13, 34.45, 31.90, 30.51, 29.67, 29.66, 29.63, 29.33, 25.04, 23.89, 22.66, 14.09. **HRMS–ESI** ($m/z$): [M+Na]$^+$ calcd. for C$_{27}$H$_{47}$NNaO, 424.3550; found, 424.3552. **IR** (KBr, cm$^{-1}$): ν 3475, 3415, 2920, 1638, 1399, 1119, 616.

**N-(5-cyclohexyl-2,2-dimethylpentyl)benzamide (2f)**

![2f](image)

White solid. mp: 112.4–113.0 ºC; **$^1$H NMR** (600 MHz, CDCl$_3$) $\delta$ 7.76 (d, $J$ = 7.5 Hz, 2H), 7.50 (t, $J$ = 7.2 Hz, 1H), 7.45 (dd, $J$ = 7.5, 7.2 Hz, 2H), 6.09 (br s, 1H), 3.29 (d, $J$ = 6.3 Hz, 2H), 1.59–1.72 (m, 5H), 1.27–1.33 (m, 2H), 1.19–1.25 (m, 5H), 1.11–1.17 (m, 3H), 0.94 (s, 6H), 0.83–0.88 (m, 2H). **$^{13}$C NMR** (150 MHz, CDCl$_3$) $\delta$ 167.59, 135.08, 131.21, 128.50, 126.74, 49.55, 45.71, 40.36, 38.25, 37.52, 34.47, 33.36, 26.65, 26.34, 25.00, 21.00, 8.55. **HRMS–ESI** ($m/z$): [M+Na]$^+$ calcd. for C$_{29}$H$_{31}$NNaO, 324.2298; found, 324.2297. **IR** (KBr, cm$^{-1}$): ν 3475, 3414, 2923, 2848, 1639, 1551, 1304, 1106, 705.
7-benzamido-6,6-dimethylheptyl benzoate (2g)

White solid. mp: 57.6–58.2 °C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.04 (d, $J = 6.0$ Hz, 2H), 7.76 (d, $J = 6.0$ Hz, 2H), 7.55 (t, $J = 6.0$ Hz, 1H), 7.50 (t, $J = 6.0$ Hz, 1H), 7.44 (dd, $J = 6.0$, 6.0 Hz, 4H), 6.12 (br s, 1H), 4.32 (t, $J = 6.0$ Hz, 2H), 3.31 (d, $J = 6.0$ Hz, 2H), 1.76–1.81 (m, 2H), 1.35–1.46 (m, 4H), 1.28–1.31 (m, 2H), 0.95 (s, 6H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 167.61, 166.54, 134.96, 132.69, 131.13, 130.32, 129.38, 128.40, 128.19, 126.75, 64.85, 49.40, 39.81, 34.49, 28.59, 26.75, 24.90, 23.50. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{23}$H$_{29}$NNaO$_3$, 390.2040; found, 390.2035. IR (KBr, cm$^{-1}$): ν 3417, 1721, 1634, 1396, 1113, 710, 617.

8-benzamido-7,7-dimethyloctyl benzoate (2h)

White solid. mp: 56.2–56.4 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.04 (d, $J = 8.0$ Hz, 2H), 7.75 (d, $J = 8.0$ Hz, 2H), 7.55 (t, $J = 8.0$ Hz, 1H), 7.50 (t, $J = 8.0$ Hz, 1H), 7.43 (dd, $J = 8.0$, 8.0 Hz, 4H), 6.08 (br s, 1H), 4.31 (t, $J = 6.0$ Hz, 2H), 3.30 (d, $J = 8.0$ Hz, 2H), 1.73–1.80 (m, 2H), 1.43–1.56 (m, 2H), 1.24–1.39 (m, 6H), 0.95(s, 6H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 167.62, 166.60, 135.02, 132.73, 131.21, 130.40, 129.44, 128.48, 128.24, 126.74, 64.96, 49.48, 39.95, 34.46, 30.05, 28.62, 25.95, 24.97, 23.75. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{24}$H$_{31}$NNaO$_3$, 404.2196; found, 404.2191. IR (KBr, cm$^{-1}$): ν 3474, 3415, 1637, 1399, 1111, 616.

7-benzamido-6,6-dimethylheptyl 4-methylbenzenesulfonate (2i)

White solid. mp: 57.6–58.2 °C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.04 (d, $J = 6.0$ Hz, 2H), 7.76 (d, $J = 6.0$ Hz, 2H), 7.55 (t, $J = 6.0$ Hz, 1H), 7.50 (t, $J = 6.0$ Hz, 1H), 7.44 (dd, $J = 6.0$, 6.0 Hz, 4H), 6.12 (br s, 1H), 4.32 (t, $J = 6.0$ Hz, 2H), 3.31 (d, $J = 6.0$ Hz, 2H), 1.76–1.81 (m, 2H), 1.35–1.46 (m, 4H), 1.28–1.31 (m, 2H), 0.95 (s, 6H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 167.61, 166.54, 134.96, 132.69, 131.13, 130.32, 129.38, 128.40, 128.19, 126.75, 64.85, 49.40, 39.81, 34.49, 28.59, 26.75, 24.90, 23.50. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{23}$H$_{29}$NNaO$_3$, 390.2040; found, 390.2035. IR (KBr, cm$^{-1}$): ν 3417, 1721, 1634, 1396, 1113, 710, 617.
White solid. mp: 58.3–59.5 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.78 (d, \(J = 6.0\) Hz, 2H), 7.76 (d, \(J = 6.0\) Hz, 2H), 7.50 (t, \(J = 6.6\) Hz, 1H), 7.44 (dd, \(J = 6.0, 6.0\) Hz, 2H), 7.33 (d, \(J = 6.0\) Hz, 2H), 6.11 (br s, 1H), 4.02 (t, \(J = 6.0\) Hz, 2H), 3.27 (d, \(J = 6.0\) Hz, 2H), 2.44 (s, 3H), 1.63–1.68 (m, 2H), 1.21–1.31 (m, 6H), 0.92 (s, 6H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 167.60, 144.61, 134.90, 133.03, 131.23, 129.75, 128.48, 127.74, 126.75, 70.50, 49.31, 39.65, 34.46, 28.65, 26.05, 24.91, 23.16, 21.53. HRMS–ESI (m/z): [M+Na]\(^+\) calcd. for C\(_{23}\)H\(_{31}\)NNaO\(_4\)S, 440.1866; found, 440.1860. IR (KBr, cm\(^{-1}\)): \(\nu\) 3475, 3415, 1636, 1400, 1171, 618.

8-benzamido-7,7-dimethyloctyl 4-methylbenzenesulfonate (2j)

White solid. mp: 67.8–69.3 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.79 (d, \(J = 8.1\) Hz, 2H), 7.76 (d, \(J = 7.5\) Hz, 2H), 7.51 (t, \(J = 7.2\) Hz, 1H), 7.45 (t, \(J = 7.5\) Hz, 2H), 7.34 (d, \(J = 8.0\) Hz, 2H), 6.09 (br s, 1H), 4.01 (t, \(J = 6.3\) Hz, 2H), 3.28 (d, \(J = 6.3\) Hz, 2H), 2.45 (s, 3H), 1.64 (quint, \(J = 6.6\) Hz, 2H), 1.30–1.35 (m, 2H), 1.19–1.29 (m, 6H), 0.93 (s, 6H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 167.47, 144.46, 134.69, 132.67, 130.93, 129.57, 128.16, 127.49, 126.66, 70.44, 49.19, 39.57, 34.37, 29.42, 28.42, 24.98, 24.70, 23.36, 21.32. HRMS–ESI (m/z): [M+Na]\(^+\) calcd. for C\(_{24}\)H\(_{33}\)NNaO\(_4\)S, 454.2023; found, 454.2020. IR (KBr, cm\(^{-1}\)): \(\nu\) 3475, 3415, 3255, 2923, 1639, 1560, 1467, 1357, 1176, 954, 813, 662.

\(N\)-(2,2-diethyloctyl)benzamide (2k)

White solid. mp: 46.8–47.6 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.73 (d, \(J = 6.0\) Hz, 2H), 7.50 (t, \(J = 6.0\) Hz, 1H), 7.44 (dd, \(J = 6.0, 6.0\) Hz, 2H), 5.95 (br s, 1H), 3.32 (d, \(J = 6.0\) Hz, 2H), 1.22–1.32 (m, 14H), 0.88 (t, \(J = 6.0\) Hz, 3H), 0.85 (t, \(J = 6.0\) Hz, 6H).
$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 167.40, 135.08, 131.07, 128.39, 126.67, 43.78, 38.63, 34.06, 31.70, 30.09, 26.78, 22.75, 22.55, 13.94, 7.42. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{19}$H$_{31}$NNaO, 312.2298; found, 312.2308. IR (KBr, cm$^{-1}$): $\nu$ 3550, 3475, 3414, 2926, 1636, 1301, 1174, 619.

$N$-(2-ethyl-2-methyloctyl)benzamide (2l)

![Structure of 2l]

White solid. mp: 57.6–58.2 °C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.75 (d, $J$ = 7.2 Hz, 2H), 7.50 (t, $J$ = 7.2 Hz, 1H), 7.44 (dd, $J$ = 7.2, 7.2 Hz, 2H), 6.02 (br s, 1H), 3.32 (d, $J$ = 6.0 Hz, 2H), 1.22–1.38 (m, 12H), 0.90 (s, 3H), 0.89–0.85 (m, 6H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 167.60, 135.00, 131.14, 128.42, 126.72, 46.99, 37.02, 36.56, 31.74, 30.11, 29.65, 23.26, 22.57, 22.56, 13.99, 7.86. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{18}$H$_{29}$NNaO, 298.2141; found, 298.2149. IR (KBr, cm$^{-1}$): $\nu$ 3752, 3550, 3475, 2926, 1639, 1550, 1383, 704.

$N$-(2,2-dipropylpentyl)benzamide (2m)

![Structure of 2m]

White solid. mp: 104.2–104.8 °C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.74 (d, $J$ = 6.0 Hz, 2H), 7.51 (t, $J$ = 6.0 Hz, 1H), 7.45 (dd, $J$ = 6.0, 6.0 Hz, 2H), 5.96 (br s, 1H), 3.32 (d, $J$ = 6.0 Hz, 2H), 1.26–1.30 (m, 6H), 1.21–1.23 (m, 6H), 0.90 (t, $J$ = 6.0 Hz, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.51, 135.18, 131.19, 128.54, 126.71, 44.86, 38.91, 37.85, 16.29, 14.97. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{18}$H$_{29}$NNaO, 298.2141; found, 298.2149. IR (KBr, cm$^{-1}$): $\nu$ 3754, 3652, 3476, 2928, 1637, 1557, 1171, 698.
N-(2-isopropyl-2-methylpentyl)benzamide (2n)

White solid. **mp**: 63.2–64.5 °C; **1H NMR** (600 MHz, CDCl₃) δ 7.75 (d, J = 7.5 Hz, 2H), 7.51 (t, J = 7.2 Hz, 1H), 7.45 (dd, J = 7.5, 7.2 Hz, 2H), 6.01 (br s, 1H), 3.39 (dd, J = 13.8, 6.0 Hz, 2H), 1.67 (sept, J = 6.6 Hz, 1H), 1.24–1.32 (m, 4H), 0.92 (d, J = 6.6 Hz, 6H), 0.91 (s, 3H), 0.86 (s, 3H). **13C NMR** (150 MHz, CDCl₃) δ 167.56, 135.14, 131.23, 128.55, 126.72, 45.29, 38.65, 38.37, 32.80, 19.47, 17.25, 17.17, 16.68, 15.09. **HRMS–ESI** (m/z): [M+Na]+ calcd. for C₁₆H₂₅NNaO, 270.1828; found, 270.1828. **IR** (KBr, cm⁻¹): ν 3551, 3476, 2960, 1634, 1317, 1183, 710, 619.

N-((1-butylecyclohexyl)methyl)benzamide (2o)

White solid. **mp**: 91.5–93.2 °C; **1H NMR** (600 MHz, CDCl₃) δ 7.75 (d, J = 7.8 Hz, 2H), 7.50 (t, J = 7.2 Hz, 1H), 7.45 (dd, J = 7.8, 7.2 Hz, 2H), 6.01 (br s, 1H), 3.38 (d, J = 6.0 Hz, 2H), 1.50–1.57 (m, 2H), 1.40–1.48 (m, 4H), 1.26–1.39 (m, 10H), 0.92 (t, J = 6.9 Hz, 3H). **13C NMR** (150 MHz, CDCl₃) δ 167.58, 135.17, 131.19, 128.52, 126.74, 45.80, 36.32, 35.55, 33.75, 26.22, 25.11, 23.57, 21.44, 14.06. **HRMS–ESI** (m/z): [M+Na]+ calcd. for C₁₈H₂₇NNaO, 296.1985; found, 296.1984. **IR** (KBr, cm⁻¹): ν 3751, 3474, 2930, 1642, 1546, 1303, 699, 613.

N-((1-octylecyclohexyl)methyl)benzamide (2p)
White solid. mp: 62.5–62.9 °C; \( ^1H \text{NMR} \) (600 MHz, CDCl\(_3\)) \( \delta \) 7.75 (d, \( J = 6.0 \) Hz, 2H), 7.50 (t, \( J = 6.0 \) Hz, 1H), 7.44 (t, \( J = 6.0 \), 6.0 Hz, 2H), 6.01 (br s, 1H), 3.38 (d, \( J = 6.0 \) Hz, 2H), 1.38–1.53 (m, 7H), 1.33–1.37 (m, 4H), 1.21–1.31 (m, 13H), 0.87 (t, \( J = 6.0 \) Hz, 3H). \( ^{13}C \text{NMR} \) (150MHz, CDCl\(_3\)) \( \delta \) 167.53, 135.10, 131.12, 128.44, 126.73, 45.80, 36.33, 35.79, 33.68, 31.82, 30.52, 29.50, 29.25, 26.18, 22.82, 22.57, 21.41, 14.02. HRMS–ESI (m/z): [M+Na]\(^+\) calcd. for C\(_{22}\)H\(_{35}\)NNaO, 352.2611; found, 352.2613. IR (KBr, cm\(^{-1}\)): ν 3474, 3415, 2926, 1637, 1549, 1301, 700, 613.

**N-(2-methylpentyl)benzamide (2q)**

![N-(2-methylpentyl)benzamide (2q)](image)

Colorless oil. \( ^1H \text{NMR} \) (600 MHz, CDCl\(_3\)) \( \delta \) 7.76 (d, \( J = 7.2 \) Hz 2H), 7.50 (t, \( J = 7.5 \) Hz, 1H), 7.44 (t, \( J = 7.2, 7.5 \) Hz, 2H), 6.14 (br s, 1H), 3.41 (ddd, \( J = 13.2, 7.2, 6.0 \) Hz, 1H), 3.27 (ddd, \( J = 13.2, 7.2, 6.0 \) Hz, 1H), 1.73–1.81 (m, 1H), 1.38–1.46 (m, 2H), 1.29–1.37 (m, 1H), 1.15–1.22 (m, 1H), 0.97 (d, \( J = 6.6 \) Hz, 3H), 0.91 (t, \( J = 7.2 \) Hz, 3H). \( ^{13}C \text{NMR} \) (150 MHz, CDCl\(_3\)) \( \delta \) 167.62, 134.72, 131.00, 128.22, 126.81, 45.90, 36.56, 32.97, 19.85, 17.44, 14.13. HRMS–ESI (m/z): [M+Na]\(^+\) calcd. for C\(_{13}\)H\(_{19}\)NNaO,228.1359; found, 228.1351. IR (KBr, cm\(^{-1}\)): ν 3317, 2961, 1643, 1543, 1300, 702.

**N-(2-propylpentyl)benzamide (2r)**

![N-(2-propylpentyl)benzamide (2r)](image)

White solid. mp: 63.7–64.2 °C; \( ^1H \text{NMR} \) (600 MHz, CDCl\(_3\)) \( \delta \) 7.75 (d, \( J = 6.0 \) Hz, 2H), 7.50 (t, \( J = 6.0 \) Hz, 1H), 7.44 (dd, \( J = 6.0, 6.0 \) Hz, 2H), 6.05 (br s, 1H), 3.41 (t, \( J = 6.0 \) Hz, 2H), 1.65 (sept, \( J = 6.0 \) Hz, 1H), 1.34–1.41 (m, 4H), 1.30–1.33 (m, 4H), 0.92 (t, \( J = 6.0 \) Hz, 6H). \( ^{13}C \text{NMR} \) (150 MHz, CDCl\(_3\)) \( \delta \) 167.57, 134.89, 131.16,
128.43, 126.77, 43.24, 37.54, 34.16, 19.74, 14.37. **HRMS–ESI** (m/z): [M+Na]+ calcd. for C₁₅H₂₃NNaO, 256.1672; found, 256.1676. **IR** (KBr, cm⁻¹): ν 3752, 3551, 3476, 2956, 2925, 1631, 1540, 1301, 695.

**N-(2-isopropylpentyl)benzamide (2s)**

White solid. mp: 69.6–71.3 °C; **¹H NMR** (600 MHz, CDCl₃) δ 7.75 (d, J = 6.0 Hz, 2H), 7.50 (t, J = 6.0 Hz, 1H), 7.44 (dd, J = 6.0, 6.0 Hz, 2H), 6.03 (s, 1H), 3.38–3.47 (m, 2H), 1.75–1.81 (m, 1H), 1.44–1.50 (m, 1H), 1.32–1.44 (m, 3H), 1.18–1.25 (m, 1H), 0.95 (d, J = 6.0, 3H), 0.94 (d, J = 6.0, 3H), 0.92 (t, J = 6.0, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 167.49, 134.96, 131.20, 128.49, 126.76, 43.90, 41.14, 31.16, 28.61, 20.82, 19.42, 19.06, 14.42. **HRMS–ESI** (m/z): [M+Na]+ calcd. for C₁₅H₂₃NNaO, 256.1672; found, 256.1675. **IR** (KBr, cm⁻¹): ν 3474, 3415, 1633, 1549, 1315, 1122, 705, 617.

**N-octylbenzamide (2t)**

White solid. mp: 41.6–42.0 °C; **¹H NMR** (600 MHz, CDCl₃) δ 7.76 (d, J = 7.2 Hz, 2H), 7.49 (t, J = 7.5 Hz, 1H), 7.43 (dd, J = 7.5, 7.5 Hz, 2H), 6.13 (br s, 1H), 3.43–3.47 (m, 2H), 1.58–1.66 (m, 2H), 1.27–1.40 (m, 10H), 0.88 (t, J = 6.9 Hz, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 167.49, 134.73, 131.00, 128.23, 126.83, 40.01, 31.65, 29.52, 29.17, 29.07, 26.90, 22.48, 13.93. **HRMS–ESI** (m/z): [M+Na]+ calcd. for C₁₅H₂₃NNaO, 256.1672; found, 256.1672. **IR** (KBr, cm⁻¹): ν 3474, 3415, 2921, 1631, 1532, 1121, 615.

**N-(2,2,4-trimethylpentyl)benzamide (2u)**
White solid. mp: 58.0–58.5 ºC; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.76 (d, \(J = 7.5\) Hz, 2H), 7.51 (t, \(J = 7.2\) Hz, 1H), 7.45 (dd, \(J = 7.5, 7.2\) Hz, 2H), 6.11 (br s, 1H), 3.31 (d, \(J = 6.3\) Hz, 2H), 1.75 (sept, \(J = 6.0\) Hz, 1H), 1.23 (d, \(J = 5.4\) Hz, 2H), 0.98 (s, 6H), 0.95 (d, \(J = 6.6\) Hz, 6H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 167.59, 135.01, 131.24, 128.52, 126.75, 50.04, 48.85, 35.17, 25.44, 23.98. HRMS–ESI (m/z): [M+Na]\(^+\) calcd. for C\(_{15}\)H\(_{23}\)NNaO, 256.1672; found, 256.1665. IR (KBr, cm\(^{-1}\)): ν 3474, 3415, 2958, 1638, 1398, 1178, 614.

\(N\)-(2-heptanyl)benzamide (2v)

White solid. mp: 64.7–65.3 ºC; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.75 (d, \(J = 8.0\) Hz, 2H), 7.49 (t, \(J = 8.0\) Hz, 1H), 7.42 (dd, \(J = 8.0, 8.0\) Hz, 2H), 5.86 (d, \(J = 8.0\) Hz, 1H), 4.14–4.24 (m, 1H), 1.50–1.57 (m, 2H), 1.27–1.40 (m, 6H), 1.23 (d, \(J = 8.0\) Hz, 3H), 0.88 (t, \(J = 6.0\) Hz, 3H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 166.77, 135.07, 131.15, 128.44, 126.77, 45.73, 36.98, 31.67, 25.73, 22.52, 20.98, 13.96. HRMS–ESI (m/z): [M+Na]\(^+\) calcd. for C\(_{14}\)H\(_{21}\)NNaO, 242.1515; found, 242.1518. IR (KBr, cm\(^{-1}\)): ν 3415, 2923, 1633, 1457, 1162, 889, 698.

\(N\)-(1-octylcyclopentyl)benzamide (2w)

White solid. mp: 89.1–89.7 ºC; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.71 (d, \(J = 8.0\) Hz, 2H), 7.48 (t, \(J = 8.0\) Hz, 1H), 7.42 (dd, \(J = 8.0, 8.0\) Hz, 2H), 5.84 (br s, 1H), 2.05–2.11 (m, 2H), 1.90–1.94 (m, 2H), 1.68–1.77 (m, 6H), 1.24–1.29 (m, 12H), 0.86 (t, \(J = 6.0\) Hz, 3H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 166.89, 135.92, 131.02, 128.46, 126.65, 820.
65.19, 38.12, 37.35, 31.82, 29.97, 29.26, 25.10, 23.75, 22.62, 14.06. **HRMS–ESI** (m/z): [M+Na]⁺ calcd. for C₂₀H₃₁NNaO, 324.2298; found, 324.2288. **IR** (KBr, cm⁻¹): v 3416, 2924, 1636, 1400, 1119, 617.

(±)2-benzamidoheptyl pivalate (2x)

White solid. mp: 71.8–73.3 °C; **¹H NMR** (600 MHz, CDCl₃) δ 7.75 (d, J = 7.2 Hz, 2H), 7.50 (t, J = 7.5 Hz, 1H), 7.44 (dd, J = 7.2, 7.5 Hz, 2H), 6.21 (d, J = 7.5 Hz, 1H), 4.40–4.46 (m, 1H), 4.32 (dd, J = 11.4, 6.3 Hz, 1H), 4.12 (dd, J = 11.4, 4.2 Hz, 1H), 1.53–1.64 (m, 2H), 1.33–1.42 (m, 4H), 1.19 (s, 9H), 0.90 (t, J = 6.9 Hz, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 178.72, 167.01, 134.40, 131.30, 128.41, 126.77, 65.58, 49.01, 38.77, 31.25, 27.82, 27.03, 22.41, 13.81. **HRMS–ESI** (m/z): [M+Na]⁺ calcd. for C₁₈H₂₇NNaO₃, 328.1883; found, 328.1887. **IR** (KBr, cm⁻¹): v 3417, 2925, 1637, 1400, 1173, 614.

(±) 2-benzamidoheptyl acetate (2y)

White solid. mp: 63.7–64.3 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.76 (d, J = 8.0 Hz, 2H), 7.51 (t, J = 8.0 Hz, 1H), 7.44 (dd, J = 8.0, 8.0 Hz, 2H), 6.20 (d, J = 8.0 Hz, 1H), 4.36–4.44 (m, 1H), 4.30 (dd, J = 12.0, 4.0 Hz, 1H), 4.14 (dd, J = 12.0, 4.0 Hz, 1H), 2.08 (s, 3H), 1.52–1.66 (m, 2H), 1.32–1.43 (m, 4H), 0.91 (t, J = 8.0 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 171.25, 167.14, 134.47, 131.37, 128.45, 126.85, 65.93, 48.95, 31.27, 27.94, 22.44, 20.75, 13.84. **HRMS–ESI** (m/z): [M+Na]⁺ calcd. for
C₁₃H₂₁NNaO₃, 286.1414; found, 286.1418. **IR** (KBr, cm⁻¹): ν 3415, 2926, 1732, 1637, 1399, 1121, 695, 616.

(±)-2-benzamidohexyl benzoate (2z)

![Chemical structure of 2z](image)

White solid. mp: 117.0–118.0 °C; **¹H NMR** (600 MHz, CDCl₃)  δ 8.02 (d,  J = 7.8 Hz, 2H), 7.76 (d,  J = 7.8 Hz, 2H), 7.56 (t,  J = 7.2 Hz, 1H), 7.49 (t,  J = 7.5 Hz, 1H), 7.44 (dd,  J = 7.8, 7.2 Hz, 2H), 7.42 (dd,  J = 7.8, 7.5 Hz, 2H), 6.32 (d,  J = 7.2 Hz, 1H), 4.53–4.57 (m, 1H), 4.52 (dd,  J = 11.1, 6.0 Hz, 1H), 4.43 (dd,  J = 11.1, 3.3 Hz, 1H), 1.71–1.76 (m, 1H), 1.64–1.69 (m, 1H), 1.42–1.50 (m, 2H), 0.92 (t,  J = 7.2 Hz, 3H). **¹³C NMR** (150 MHz, CDCl₃)  δ 167.23, 166.90, 134.59, 133.20, 131.47, 129.81, 129.66, 128.59, 128.47, 126.87, 66.51, 49.28, 31.55, 28.07, 22.56, 13.93. **HRMS–ESI** (m/z): [M+Na]⁺ calcd. for C₂₀H₂₁NNaO₃, 348.1570; found, 348.1576. **IR** (KBr, cm⁻¹): ν 3416, 2956, 1719, 1635, 1399, 1127, 706, 615.

(±)-2-benzamidohexyl 2,3,4,5,6-pentafluorobenzoate (2aa)

![Chemical structure of 2aa](image)

White solid. mp: 96.0–97.6 °C; **¹H NMR** (600 MHz, CDCl₃)  δ 7.76 (d,  J = 7.2 Hz, 2H), 7.52 (t,  J = 7.5 Hz, 1H), 7.45 (dd,  J = 7.2, 7.5 Hz, 2H), 6.15 (d,  J = 7.8 Hz, 1H), 4.57 (dd,  J = 10.5, 4.2 Hz, 1H), 4.49–4.54 (m, 2H), 1.62–1.73 (m, 2H), 1.34–1.45 (m, 4H), 0.92 (t,  J = 7.2 Hz, 3H). **¹³C NMR** (150 MHz, CDCl₃)  δ 167.20, 158.90, 134.12, 131.42, 128.37, 126.79, 67.89, 48.42, 31.04, 27.94, 22.35, 13.74. **HRMS–ESI** (m/z): [M+Na]⁺ calcd. for C₂₀H₁₈F₅NNaO₃, 438.1099; found, 438.1089. **IR** (KBr, cm⁻¹): ν 3416, 2956, 1719, 1635, 1399, 1127, 706, 615.
3475, 3415, 1734, 1531, 1396, 1106, 696.

(±)-methyl 2-benzamidohexanoate (2ab)

White solid. mp: 69.5–71.3 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.81 (d, \(J = 7.5\) Hz, 2H), 7.53 (t, \(J = 7.5\) Hz, 1H), 7.46 (dd, \(J = 7.5, 7.5\) Hz, 2H), 6.65 (d, \(J = 7.2\) Hz, 1H), 4.84 (dd, \(J = 13.2, 7.2\) Hz, 1H), 3.79 (s, 3H), 1.95–1.99 (m, 1H), 1.76–1.82 (m, 1H), 1.30–1.41 (m, 4H), 0.90 (t, \(J = 6.9\) Hz, 3H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 173.06, 166.95, 133.65, 131.37, 128.20, 126.91, 52.39, 52.06, 31.79, 27.29, 22.05, 13.61. HRMS–ESI (m/z): [M+Na]^+ calcd. for C\(_{14}\)H\(_{19}\)NNaO\(_3\), 272.1257; found, 272.1252. IR (KBr, cm\(^{-1}\)): \(\nu\) 3415, 2954, 1752, 1634, 1363, 1157, 720, 633.

(±)-ethyl 2-benzamidohexanoate (2ac)

White solid. mp: 79.4–81.1 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.82 (d, \(J = 7.8\) Hz, 2H), 7.52 (t, \(J = 7.5\) Hz, 1H), 7.45 (dd, \(J = 7.8, 7.5\) Hz, 2H), 6.68 (d, \(J = 7.2\) Hz, 1H), 4.82 (dt, \(J = 13.2, 7.2\) Hz, 1H), 4.25 (dq, \(J = 7.2, 1.8\) Hz, 2H), 1.95–2.00 (m, 1H), 1.76–1.82 (m, 1H), 1.30–1.44 (m, 4H), 1.31 (t, \(J = 7.2\) Hz, 3H), 0.90 (t, \(J = 7.0\) Hz, 3H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 172.68, 166.92, 133.95, 131.47, 128.37, 126.95, 61.27, 52.51, 32.15, 27.25, 22.19, 14.04, 13.71. HRMS–ESI (m/z): [M+Na]^+ calcd. for C\(_{15}\)H\(_{21}\)NNaO\(_3\), 286.1414; found, 286.1410. IR (KBr, cm\(^{-1}\)): \(\nu\) 3415, 2924, 1745, 1637, 1399, 1157, 720, 618.

(±)-methyl 2-benzamidodecanoate (2ad)
(±)-methyl 2-benzamido-5-cyclohexylpentanoate (2ae)

White solid. mp: 61.4–63.2 °C; \(^1H\) NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.81 (d, \(J = 7.2\) Hz, 2H), 7.52 (t, \(J = 7.5\) Hz, 1H), 7.45 (t, \(J = 7.2, 7.5\) Hz, 2H), 6.65 (d, \(J = 7.5\) Hz, 1H), 4.83 (td, \(J = 7.5, 5.7\) Hz, 1H), 3.78 (s, 3H), 1.90–1.96 (m, 1H), 1.73–1.79 (m, 1H), 1.61–1.68 (m, 5H), 1.38–1.45 (m, 1H), 1.30–1.37 (m, 1H), 1.09–1.24 (m, 6H), 0.80–0.90 (m, 2H). \(^{13}C\) NMR (150 MHz, CDCl\(_3\)) \(\delta\) 173.30, 166.99, 134.04, 131.71, 128.60, 127.04, 52.59, 52.41, 37.40, 36.98, 33.31, 33.24, 32.97, 26.62, 26.32, 22.52. HRMS–ESI (m/z): [M+Na]^+ calcd. for C\(_{19}\)H\(_{27}\)NNaO\(_3\), 340.1883; found, 340.1881. IR (KBr, cm\(^{-1}\)): v 3416, 2922, 1749, 1637, 1400, 1169, 614.

7-benzamido-8-methoxy-8-oxooctyl benzoate (2af)

White solid. mp: 61.9–62.8 °C; \(^1H\) NMR (600 MHz, CDCl\(_3\)) \(\delta\) 8.03 (d, \(J = 7.8\) Hz, 2H), 7.49 (t, \(J = 7.4\) Hz, 1H), 6.07 (t, \(J = 7.4\) Hz, 1H), 5.77 (br s, 1H), 4.83 (ddt, \(J = 9.0, 6.0, 2.4\) Hz, 1H), 4.12 (dt, \(J = 6.0, 2.4\) Hz, 1H), 3.81 (s, 3H), 1.70–1.75 (m, 1H), 1.50–1.55 (m, 1H), 1.30–1.40 (m, 12H), 0.86 (t, \(J = 6.0\) Hz, 3H).
2H), 7.81 (d, $J = 7.5$ Hz, 2H), 7.55 (t, $J = 7.5$ Hz, 1H), 7.52 (dd, $J = 7.5$, 7.5 Hz, 1H), 7.42–7.46 (m, 4H), 6.67 (t, $J = 6.9$ Hz, 1H), 4.85 (dd, $J = 13.2$, 6.5 Hz, 1H), 4.30 (t, $J = 6.6$ Hz, 2H), 3.79 (s, 3H), 1.95–2.02 (m, 1H), 1.71–1.84 (m, 3H), 1.33–1.44 (m, 6H), 7.42–7.46 (m, 4H), 6.67 (t, $J = 6.9$ Hz, 1H), 4.85 (dd, $J = 13.2$, 6.5 Hz, 1H), 4.30 (t, $J = 6.6$ Hz, 2H), 3.79 (s, 3H), 1.95–2.02 (m, 1H), 1.71–1.84 (m, 3H), 1.33–1.44 (m, 6H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 173.05, 166.96, 166.49, 133.77, 132.69, 131.56, 130.25, 129.35, 128.39, 128.18, 126.95, 64.75, 52.39, 52.28, 32.30, 28.70, 28.43, 25.67, 25.08. HRMS–ESI ($m/z$): [M+Na]$^+$ calcd. for C$_{23}$H$_{27}$NNaO$_5$, 420.1781; found, 420.1780.

IR (KBr, cm$^{-1}$): $\nu$ 3416, 2924, 1636, 1400, 1118, 617.

17-(-7-benzamido-6,6-dimethyl-2-heptanyl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-yl benzoate (2ag)

Yellow oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.05 (d, $J = 6.6$ Hz, 2H), 7.76 (d, $J = 7.2$ Hz, 2H), 7.55 (t, $J = 7.5$ Hz, 1H), 7.51 (t, $J = 7.5$ Hz, 1H), 7.44 (d, $J = 7.8$ Hz, 2H), 7.43 (d, $J = 7.8$ Hz, 2H), 6.10 (t, $J = 5.7$ Hz, 1H), 4.95–5.00 (m, 1H), 3.30 (d, $J = 6.3$ Hz, 2H), 1.98 (t, $J = 11.1$ Hz, 2H), 1.86–1.88 (m, 2H), 1.77–1.83 (m, 2H), 1.67–1.69 (m, 1H), 1.51–1.57 (m, 3H), 1.32–1.48 (m, 8H), 1.16–1.29 (m, 8H), 1.08–1.13 (m, 4H), 0.96 (s, 3H), 0.95 (s, 6H), 0.92 (d, $J = 6.5$ Hz, 3H), 0.65 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 167.62, 166.13, 135.11, 132.66, 131.31, 130.90, 129.50, 128.59, 128.23, 126.77, 74.99, 56.49, 56.26, 49.63, 42.69, 41.94, 40.65, 40.47, 40.15, 36.75, 35.79, 35.73, 35.06, 34.62, 34.51, 32.33, 28.33, 27.04, 26.74, 26.34, 25.11, 25.05, 24.19, 23.36, 20.87, 20.26, 18.68, 12.04. HRMS–ESI ($m/z$): [M+Na]$^+$ calcd. for C$_{42}$H$_{59}$N$_2$NaO$_5$, 648.4387; found, 648.4377. IR (KBr, cm$^{-1}$): $\nu$ 3750, 3474, 2924, 1637, 1460, 1399, 615.

Procedures for Site-Selective Oxidation Trifluoroacetoxylation of Aliphatic Amines
**Procedure A:** To an oven-dried 25 mL Schlenk tube, 2a (23.3 mg, 0.10 mmol, 1.0 equiv), TBAB (16.2 mg, 0.05 mmol, 50 mol%), Br₂ (6.0 μL, 0.12 mmol, 1.2 equiv), 1.0 mL DCM were added sequentially. The reaction mixture was stirred at room temperature for 15 min. After that, CuI (3.8 mg, 0.02 mmol, 20 mol%), PhI(OTFA)₂ (95.0 mg, 0.22 mmol, 2.2 equiv) were added, the tube was sealed and placed in a 100 °C parallel synthesizer and stirred for 5 h. After completion, the reaction mixture was cooled down to room temperature and the solvent was removed under reduced pressure. Flash Silica gel column purification (EtOAc/petroleum ether/DCM = 1:25:0.5 as eluent) of the crude product provided 3a (21.4 mg, 0.08 mmol) in 72% isolated yield.

**Procedure B:** Changed: AgOAc (3.3 mg, 0.02 mmol, 20 mol%). Other process is the same as the Procedure A.

**Characterization Data for Product**

6-benzamido-5,5-dimethylhexan-3-yl 2,2,2-trifluoroacetate (3a)

![Image of 3a](image)

Colourless oil. **¹H NMR** (600 MHz, CDCl₃) δ 7.77 (d, J = 6.0 Hz, 2H), 7.52 (t, J = 9.0 Hz, 1H), 7.46 (dd, J = 6.0, 9.0 Hz, 2H), 6.29 (br s, 1H), 5.19–5.23 (m, 1H), 3.53 (dd, J = 12.0, 6.0 Hz, 1H), 3.10 (dd, J = 12.0, 6.0 Hz, 1H), 1.81 (dd, J = 12.0, 9.0 Hz, 1H), 1.71 (td, J = 9.0, 6.0 Hz, 2H), 1.56 (dd, J = 12.0, 1.8 Hz, 1H), 0.98 (s, 6H), 0.92 (t, J = 9.0 Hz, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 167.68, 157.24 (q, J = 42.0 Hz) 134.64, 131.52, 128.65, 126.77, 114.55 (q, J = 285.0 Hz), 78.35, 49.33, 42.31, 34.54, 28.66, 25.34, 25.19, 9.06. **HRMS–ESI** (m/z): [M+Na]⁺ calcd. for C₁₁H₂₂F₃NNaO₃, 368.1444; found, 368.1442. **IR** (KBr, cm⁻¹): ν 3415, 1679, 1544, 1205, 800, 716.

5,5-dimethyl-6-(4-methylbenzamido)hexan-3-yl 2,2,2-trifluoroacetate (3-PG 2)
Colourless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.94 (s, 1H), 7.59 (d, $J = 7.8$ Hz, 1H), 7.30 (d, $J = 7.8$ Hz, 1H), 6.22 (s, 1H), 5.18-5.21 (m, 1H), 3.52 (dd, $J = 13.8$, 7.8 Hz, 1H), 3.08 (dd, $J = 13.8$, 5.4 Hz, 1H), 2.45 (s, 3H), 1.79 (dd, $J = 15.3$, 8.4 Hz, 1H), 1.66–1.75 (m, 2H), 1.55 (dd, $J = 15.3$, 1.8 Hz, 1H), 0.98 (s, 6H), 0.93 (t, $J = 7.5$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.14, 157.27 (q, $J = 42.0$ Hz), 141.74, 133.81, 130.89, 130.87, 125.52, 125.15, 114.54 (q, $J = 285.0$ Hz), 78.37, 49.32, 42.31, 34.57, 28.65, 25.42, 25.22, 22.99, 9.09. HRMS–ESI ($m/z$): [M+Na]$^+$ calcd. for C$_{18}$H$_{23}$BrF$_3$NNaO$_3$, 460.0706; found, 460.0700. IR (KBr, cm$^{-1}$): ν 3415, 1637, 1400, 1172, 617.

6-(4-chlorobenzamido)-5,5-dimethylhexan-3-yl 2,2,2-trifluoroacetate (3-PG 3)

Colourless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.71 (d, $J = 8.4$ Hz, 2H), 7.42 (d, $J = 8.4$ Hz, 2H), 6.27 (br s, 1H), 5.16–5.23 (m, 1H), 3.52 (dd, $J = 13.8$, 7.8 Hz, 1H), 3.09 (dd, $J = 13.8$, 5.4 Hz, 1H), 1.80 (dd, $J = 15.4$, 8.4 Hz, 1H), 1.67–1.75 (m, 2H), 1.55 (d, $J = 15.4$ Hz, 1H), 0.98 (s, 6H), 0.93 (t, $J = 7.5$ Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 166.62, 157.27 (q, 42.0 Hz), 137.78, 132.96, 128.90, 128.22, 114.55, 78.38, 49.32, 42.37, 34.54, 28.65, 25.48, 25.21, 9.07. HRMS–ESI ($m/z$): [M+Na]$^+$ calcd. for C$_{17}$H$_{21}$F$_3$NClNaO$_3$, 402.1054; found, 402.1041. IR (KBr, cm$^{-1}$): ν 3415, 1637, 1400, 1120, 617.

5,5-dimethyl-6-(4-nitrobenzamido)hexan-3-yl 2,2,2-trifluoroacetate (3-PG 5)
Colourless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.30 (d, $J = 8.4$ Hz, 2H), 7.93 (d, $J = 8.4$ Hz, 2H), 6.46 (br s, 1H), 5.15–5.23 (m, 1H), 3.57 (dd, $J = 13.8$, 7.8 Hz, 1H), 3.13 (dd, $J = 13.8$, 5.4 Hz, 1H), 1.82 (dd, $J = 15.3$, 8.1 Hz, 1H), 1.69–1.78 (m, 2H), 1.58 (dd, $J = 15.4$, 2.1 Hz, 1H), 1.00 (s, 6H), 0.94 (t, $J = 7.5$ Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 165.73, 157.31 (q, $J = 42.0$ Hz), 149.60, 140.16, 128.01, 123.87, 114.53 (q, $J = 285.0$ Hz), 78.41, 49.44, 42.43, 34.57, 28.64, 25.64, 25.20, 9.07. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{17}$H$_{21}$F$_3$N$_2$NaO$_5$, 413.1295; found, 413.1282. IR (KBr, cm$^{-1}$): v 3416, 1638, 1400, 1120, 616, 480.

5,5-dimethyl-6-(2-nitrobenzamido)hexan-3-yl 2,2,2-trifluoroacetate (3-PG 6)

Colourless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.05 (d, $J = 8.1$ Hz, 1H), 7.68 (t, $J = 7.5$ Hz, 1H), 7.59 (t, $J = 7.8$ Hz, 1H), 7.50 (d, $J = 7.5$ Hz, 1H), 6.03 (br s, 1H), 5.21–5.24 (m, 1H), 3.49–3.52 (m, 1H), 3.09 (dd, $J = 13.8$, 5.7 Hz, 1H), 1.83 (dd, $J = 15.6$, 8.7 Hz, 1H), 1.69–1.77 (m, 2H), 1.66 (d, $J = 15.3$ Hz, 1H), 1.01 (s, 3H), 0.98 (s, 3H), 0.93 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 166.63, 157.23 (q, $J = 42.0$ Hz), 146.61, 133.62, 133.03, 130.53, 128.64, 124.56, 114.58 (q, $J = 285.0$ Hz), 78.49, 49.89, 42.16, 34.53, 28.65, 25.26, 25.21, 8.98. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{17}$H$_{21}$F$_3$N$_2$NaO$_5$, 413.1295; found, 413.129. IR (KBr, cm$^{-1}$): v 3415, 1638, 1400, 1120, 616, 480.

5,5-dimethyl-6-(perfluorobenzamido)hexan-3-yl 2,2,2-trifluoroacetate (3-PG 8)
5,5-dimethyl-6-(picolinamido)hexan-3-yl 2,2,2-trifluoroacetate (3-PG 9)

Colourless oil. \textbf{\textsuperscript{1}H NMR} (600 MHz, CDCl\textsubscript{3}) $\delta$ 8.57 (d, $J = 4.5$ Hz, 1H), 8.23 (br s, 1H), 8.20 (d, $J = 7.8$ Hz, 1H), 7.86 (t, $J = 7.5$ Hz, 1H), 7.44 (dd, $J = 6.9$, 5.4 Hz, 1H), 5.21–5.25 (m, 1H), 3.44 (dd, $J = 13.5$, 7.5 Hz, 1H), 3.19 (dd, $J = 13.5$, 6.0 Hz, 1H), 1.81 (dd, $J = 15.3$, 8.7 Hz, 1H), 1.65–1.76 (m, 2H), 1.58 (d, $J = 13.2$ Hz, 1H), 0.99 (d, $J = 3.6$ Hz, 6H), 0.91 (t, $J = 7.5$ Hz, 3H). \textbf{\textsuperscript{13}C NMR} (100 MHz, CDCl\textsubscript{3}) $\delta$ 157.64, 157.25 (q, $J = 42.0$ Hz), 114.51 (q, $J = 285.0$ Hz), 78.17, 49.65, 42.14, 34.43, 28.62, 25.29, 24.99, 8.97. \textbf{HRMS–ESI} (m/z): [M+Na]$^+$ calcd. for C\textsubscript{17}H\textsubscript{17}F\textsubscript{8}NNaO\textsubscript{7}, 458.0973; found, 458.0960. \textbf{IR} (KBr, cm\textsuperscript{-1}): $\nu$ 3415, 2960, 1621, 1533, 1399, 1170, 619, 480.

5,5-dimethyl-6-pivalamidohexan-3-yl 2,2,2-trifluoroacetate (3-PG-10)

Colourless oil. \textbf{\textsuperscript{1}H NMR} (600 MHz, CDCl\textsubscript{3}) $\delta$ 8.57 (d, $J = 4.5$ Hz, 1H), 8.23 (br s, 1H), 8.20 (d, $J = 7.8$ Hz, 1H), 7.86 (t, $J = 7.5$ Hz, 1H), 7.44 (dd, $J = 6.9$, 5.4 Hz, 1H), 5.21–5.25 (m, 1H), 3.44 (dd, $J = 13.5$, 7.5 Hz, 1H), 3.19 (dd, $J = 13.5$, 6.0 Hz, 1H), 1.81 (dd, $J = 15.3$, 8.7 Hz, 1H), 1.65–1.76 (m, 2H), 1.58 (d, $J = 13.2$ Hz, 1H), 0.99 (d, $J = 3.6$ Hz, 6H), 0.91 (t, $J = 7.5$ Hz, 3H). \textbf{\textsuperscript{13}C NMR} (150 MHz, CDCl\textsubscript{3}) $\delta$ 164.47, 149.78, 148.07, 137.38, 126.18, 122.31, 78.12, 49.37, 42.39, 34.53, 28.70, 25.20, 24.96, 9.03 (OCOCF\textsubscript{3} is difficult to detect). \textbf{HRMS–ESI} (m/z): [M+Na]$^+$ calcd. for C\textsubscript{18}H\textsubscript{21}F\textsubscript{3}N\textsubscript{2}NaO\textsubscript{3}, 369.1396; found, 369.1389. \textbf{IR} (KBr, cm\textsuperscript{-1}): $\nu$ 3415, 2960, 2961, 1621, 1533, 1399, 1170, 619, 480.
Colourless oil. \textit{^{1}H NMR} (600 MHz, CDCl$_3$) $\delta$ 5.76 (br s, 1H), 5.15–5.18 (m, 1H), 3.32 (dd, $J = 13.8$, 7.8 Hz, 1H), 2.85 (dd, $J = 13.8$, 5.4 Hz, 1H), 1.64–1.73 (m, 3H), 1.46 (dd, $J = 15.3$, 2.1 Hz, 1H), 1.21 (s, 9H), 0.91 (t, $J = 7.8$ Hz, 3H), 0.90 (s, 3H), 0.89 (s, 3H). \textit{^{13}C NMR} (150 MHz, CDCl$_3$) $\delta$ 178.38, 157.19 (q, $J = 42.0$ Hz), 114.59 (q, 285.0 Hz), 78.34, 48.57, 42.24, 38.88, 34.38, 28.62, 27.62, 25.31, 25.14, 8.99. \textit{HRMS–ESI} (m/z): [M+Na]$^+$ calcd. for C$_{15}$H$_{26}$F$_3$NNaO$_3$, 348.1757; found, 348.1762. \textit{IR} (KBr, cm$^{-1}$): v 3415, 2962, 1778, 1541, 1165, 702.

6-((methoxycarbonyl)amino)-5,5-dimethylhexan-3-yl-2,2,2-trifluoroacetate (3-PG 12)

Colourless oil. \textit{^{1}H NMR} (400 MHz, CDCl$_3$) $\delta$ 5.12–5.15 (m, 1H), 4.75 (br s, 1H), 3.67 (s, 3H), 3.12 (dd, $J = 13.8$, 7.5 Hz, 1H), 2.90 (dd, $J = 13.8$, 5.7 Hz, 1H), 1.73 (dd, $J = 15.5$, 8.7 Hz, 1H), 1.64–1.68 (m, 2H), 1.48 (d, $J = 15.3$ Hz, 1H), 0.91 (t, $J = 11.1$ Hz, 3H), 0.90 (s, 3H), 0.86 (s, 3H). \textit{^{13}C NMR} (150 MHz, CDCl$_3$) $\delta$ 157.36, 157.18 (q, $J = 42.0$ Hz), 114.58 (q, $J = 285.0$ Hz), 78.13, 52.18, 51.15, 42.08, 34.18, 28.68, 24.94, 24.83, 8.98. \textit{HRMS–ESI} (m/z): [M+Na]$^+$ calcd. for C$_{12}$H$_{20}$F$_3$NNaO$_4$, 322.1237; found, 322.1243. \textit{IR} (KBr, cm$^{-1}$): v 3753, 3416, 2926, 1622, 1400, 1172, 615, 472.

5-benzamido-4,4-dimethylpentan-2-yl 2,2,2-trifluoroacetate (3b)

Colourless oil. \textit{^{1}H NMR} (600 MHz, CDCl$_3$) $\delta$ 7.36 (s, 5H), 4.15 (s, 2H), 3.94 (s, 2H), 1.93 (s, 9H), 1.21 (s, 9H), 0.91 (t, $J = 11.1$ Hz, 3H), 0.90 (s, 3H), 0.89 (s, 3H). \textit{^{13}C NMR} (150 MHz, CDCl$_3$) $\delta$ 178.03, 157.29 (q, $J = 45.0$ Hz), 114.66 (q, 285.0 Hz), 78.20, 52.54, 51.21, 42.09, 34.18, 28.70, 24.94, 24.83, 8.98. \textit{HRMS–ESI} (m/z): [M+Na]$^+$ calcd. for C$_{15}$H$_{24}$F$_3$NNaO$_4$, 356.1866; found, 356.1876. \textit{IR} (KBr, cm$^{-1}$): v 3754, 3480, 3417, 2926, 1622, 1400, 1172, 615, 472.
Colourless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.77 (d, $J$ = 7.2 Hz, 2H), 7.51 (t, $J$ = 7.5 Hz, 1H), 7.45 (dd, $J$ = 7.2, 7.5 Hz, 2H), 6.33 (br s, 1H), 5.28–5.33 (m, 1H), 3.54 (dd, $J$ = 13.8, 7.8 Hz, 1H), 3.09 (dd, $J$ = 13.8, 5.7 Hz, 1H), 1.87 (dd, $J$ = 15.3, 8.4 Hz, 1H), 1.52 (dd, $J$ = 15.3, 2.7 Hz, 1H), 1.38 (d, $J$ = 6.0 Hz, 3H), 0.99 (d, $J$ = 6.6 Hz, 6H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 167.68, 157.00 (q, $J$ = 42.0 Hz), 134.61, 131.52, 128.63, 126.77, 114.46 (q, $J$ = 285.0 Hz), 74.24, 49.27, 44.50, 34.63, 25.41, 25.26, 21.61. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{11}$H$_{20}$F$_3$NNaO$_3$, 354.1287; found, 354.1282. IR (KBr, cm$^{-1}$): ν 3415, 2960, 1638, 1399, 1173, 616.

1-benzamido-2,2-dimethyldecan-4-yl 2,2,2-trifluoroacetate (3c)

![chemical structure]

Colourless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.77 (d, $J$ = 7.2 Hz, 2H), 7.51 (t, $J$ = 7.5 Hz, 1H), 7.45 (dd, $J$ = 7.2, 7.5 Hz, 2H), 6.31 (br s, 1H), 5.22–5.26 (m, 1H), 3.51 (dd, $J$ = 13.8, 7.5 Hz, 1H), 3.10 (dd, $J$ = 13.8, 5.7 Hz, 1H), 1.80 (dd, $J$ = 15.4, 8.4 Hz, 1H), 1.61–1.68 (m, 2H), 1.57 (dd, $J$ = 15.4, 2.4 Hz, 1H), 1.21–1.33 (m, 8H), 0.98 (d, $J$ = 1.8 Hz, 6H), 0.87 (t, $J$ = 6.9 Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 167.69, 157.16 (q, $J$ = 42.0 Hz), 134.63, 131.43, 128.55, 126.78, 114.52 (q, $J$ = 285.0 Hz) 77.40, 49.38, 42.77, 35.66, 34.56, 31.49, 28.83, 25.27, 25.14, 24.68, 22.41, 13.92.

HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{21}$H$_{30}$F$_3$NNaO$_3$, 424.2070; found, 424.2066. IR (KBr, cm$^{-1}$): ν 3415, 2960, 1680, 1538, 1465, 1167, 711.

1-benzamido-2,2-dimethyltetradecan-4-yl 2,2,2-trifluoroacetate (3d)

![chemical structure]

Colourless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.76 (d, $J$ = 7.5 Hz, 2H), 7.51 (t, $J$ = 7.2 Hz, 1H), 7.45 (dd, $J$ = 7.5, 7.2 Hz, 2H), 6.29 (br s, 1H), 5.22–5.26 (m, 1H), 3.51 (dd, $J$ = 13.8, 7.5 Hz, 1H), 3.10 (dd, $J$ = 13.8, 5.4 Hz, 1H), 1.80 (dd, $J$ = 15.4, 8.4 Hz,
1H), 1.58–1.73 (m, 2H), 1.57 (dd, \(J = 15.4, 1.8\) Hz, 1H), 1.14–1.34 (m, 16H), 0.98 (s, 6H), 0.88 (t, \(J = 6.9\) Hz, 3H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 167.67, 157.22 (q, \(J = 42.0\) Hz), 134.68, 131.50, 128.63, 126.79, 114.57 (q, \(J = 285.0\) Hz), 77.45, 49.40, 42.84, 35.71, 34.59, 31.86, 29.52, 29.44, 29.35, 29.26, 29.22, 25.40, 25.19, 24.78, 22.65, 14.07. HRMS–ESI (m/z): [M+Na]\(^+\) calcd. for C\(_{25}\)H\(_{38}\)F\(_3\)NNaO\(_3\), 480.2696; found, 480.2691. IR (KBr, cm\(^{-1}\)): v 3415, 2926, 1638, 1400, 1172, 617.

1-benzamido-2,2-dimethyloctadecan-4-yl 2,2,2-trifluoroacetate (3e)

![3e](image)

Colourless oil. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.77 (d, \(J = 7.2\) Hz, 2H), 7.52 (t, \(J = 7.2\) Hz, 1H), 7.46 (dd, \(J = 7.2, 7.2\) Hz, 2H), 6.25 (br s, 1H), 5.22–5.26 (m, 1H), 3.53 (dd, \(J = 13.8, 7.5\) Hz, 1H), 3.10 (dd, \(J = 13.8, 5.4\) Hz, 1H), 1.81 (dd, \(J = 15.4, 8.4\) Hz, 1H), 1.60–1.71 (m, 2H), 1.57 (dd, \(J = 15.0, 2.4\) Hz, 1H), 1.20–1.34 (m, 24H), 0.98 (s, 3H), 0.97 (s, 3H), 0.88 (t, \(J = 6.9\) Hz, 3H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 167.66, 157.24 (q, \(J = 42.0\) Hz), 134.70, 131.53, 128.67, 126.80, 114.59 (q, \(J = 285.0\) Hz), 77.47, 49.40, 42.85, 35.74, 34.61, 31.93, 29.69, 29.68, 29.66, 29.64, 29.60, 29.48, 29.39, 29.36, 29.26, 25.46, 25.22, 24.82, 22.70, 14.12. HRMS–ESI (m/z): [M+Na]\(^+\) calcd. for C\(_{29}\)H\(_{46}\)F\(_3\)NNaO\(_3\), 536.3322; found, 536.3321. IR (KBr, cm\(^{-1}\)): v 3416, 1636, 1400, 1119, 616.

(5-benzamido-1-cyclohexyl-4,4-dimethylpentan-2-yl 2,2,2-trifluoroacetate (3f)

![3f](image)

Colourless oil. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.77 (d, \(J = 7.8\) Hz, 2H), 7.52 (t, \(J = 7.2\) Hz, 1H), 7.46 (dd, \(J = 7.8, 7.2\) Hz, 2H), 6.31 (br s, 1H), 5.30–5.36 (m, 1H), 3.52 (dd, \(J = 13.8, 7.5\) Hz, 1H), 3.12 (dd, \(J = 13.8, 5.4\) Hz, 1H), 1.76–1.80 (m, 2H), 1.62–
1.69 (m, 5H), 1.56–1.61 (m, 2H), 1.43–1.49 (m, 1H), 1.12–1.22 (m, 5H), 0.99 (s, 6H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 167.64, 157.22 (q, $J = 42.0$ Hz), 134.64, 131.52, 128.64, 126.79, 114.53 (q, $J = 285.0$ Hz), 75.62, 49.37, 43.48, 43.31, 34.66, 34.00, 33.29, 33.02, 26.27, 26.03, 25.97, 25.57, 25.21. HRMS–ESI (m/z): $[M+Na]^+$ calcd. for C$_{22}$H$_{30}$F$_3$NaO$_3$, 436.2070; found, 436.2084. IR (KBr, cm$^{-1}$): $\nu$ 3415, 2925, 1638, 1400, 1120, 616.

7-benzamido-6,6-dimethyl-4-(2,2,2-trifluoroacetoxy)heptyl benzoate (3g)

Colourless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.02 (d, $J = 7.2$ Hz, 2H), 7.76 (d, $J = 7.5$ Hz, 2H), 7.56 (t, $J = 7.5$ Hz, 1H), 7.51 (t, $J = 7.5$ Hz, 1H), 7.43 (dd, $J = 7.2$, 7.5 Hz, 4H), 6.32 (br s, 1H), 5.35–5.40 (m, 1H), 4.29–4.38 (m, 2H), 3.55 (dd, $J = 13.8$, 7.5 Hz, 1H), 3.11 (dd, $J = 13.8$, 5.4 Hz, 1H), 1.75–1.87 (m, 5H), 1.60 (dd, $J = 15.4$, 2.4 Hz, 1H), 0.99 (s, 6H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 167.70, 166.51, 157.26 (q, $J = 42.0$ Hz), 134.61, 133.00, 131.53, 130.07, 129.55, 128.65, 128.38, 126.79, 114.53 (q, $J = 285.0$ Hz), 76.70, 64.00, 49.28, 42.72, 34.67, 32.36, 25.41, 25.26, 24.21. HRMS–ESI (m/z): $[M+Na]^+$ calcd. for C$_{25}$H$_{28}$F$_3$NaO$_5$, 502.1812; found, 502.1808. IR (KBr, cm$^{-1}$): $\nu$ 3416, 1636, 1400, 1120, 616.

8-benzamido-7,7-dimethyl-5-(2,2,2-trifluoroacetoxy)octyl benzoate (3h)

Yellow oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.02 (d, $J = 7.5$ Hz, 2H), 7.76 (d, $J = 7.5$ Hz, 2H), 7.56 (t, $J = 7.5$ Hz, 1H), 7.51 (t, $J = 7.2$ Hz, 1H), 7.42–7.45 (m, 4H), 6.27 (br s, 1H), 5.28–5.32 (m, 1H), 4.31 (t, $J = 6.3$ Hz, 2H), 3.54 (dd, $J = 13.8$, 7.8 Hz, 1H), 3.10 (dd, $J = 13.8$, 5.4 Hz, 1H), 1.73–1.84 (m, 5H), 1.58 (dd, $J = 15.4$, 2.1 Hz, 1H), 1.45–1.52 (m, 2H), 0.98 (s, 6H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 167.70, 166.58,
157.23 (q, $J = 42.0$ Hz), 134.57, 132.92, 131.56, 130.23, 129.51, 128.66, 128.34, 126.78, 114.53 (q, $J = 285.0$ Hz), 64.34, 49.35, 42.81, 35.39, 34.62, 28.34, 25.30, 21.38. **HRMS–ESI** ($m/z$): [M+Na]$^+$ calcd. for C$_{26}$H$_{30}$F$_3$NNaO$_5$, 516.1968; found: 516.1964. **IR** (KBr, cm$^{-1}$): ν 3418, 1637, 1400, 1120, 615.

**1-benzamido-2,2-dimethyl-7-(tosyloxy)heptan-4-yl 2,2,2-trifluoroacetate(3i)**

![Structure 3i]

Colourless oil. **$^1$H NMR** (600 MHz, CDCl$_3$) δ 7.77 (d, $J = 7.8$ Hz, 2H), 7.76 (d, $J = 7.5$ Hz, 1H), 7.52 (d, $J = 7.5$ Hz, 2H), 7.46 (dd, $J = 7.5$, 7.5 Hz, 2H), 7.34 (d, $J = 7.8$ Hz, 2H), 6.27 (br s, 1H), 5.25–5.29 (m, 1H), 4.00–4.08 (m, 2H), 3.50 (dd, $J = 13.8$, 7.5 Hz, 1H), 3.05 (dd, $J = 13.8$, 5.7 Hz, 1H), 2.45 (s, 3H), 1.77 (dd, $J = 15.4$, 8.4 Hz, 1H), 1.64–1.73 (m, 4H), 1.53 (dd, $J = 15.3$, 2.4 Hz, 1H), 0.96 (s, 6H). **$^{13}$C NMR** (100 MHz, CDCl$_3$) δ 167.73, 157.20 (q, $J = 42.0$ Hz), 144.96, 134.51, 132.85, 131.58, 129.91, 128.68, 127.86, 126.81, 114.44 (q, $J = 285.0$ Hz), 76.19, 69.45, 49.23, 42.66, 34.66, 31.84, 25.42, 25.16, 24.31, 21.62. **HRMS–ESI** ($m/z$): [M+Na]$^+$ calcd. for C$_{25}$H$_{30}$F$_3$NNaO$_6$S, 552.1638; found, 552.1633. **IR** (KBr, cm$^{-1}$): ν 3417, 1637, 1400, 1120, 615.

**1-benzamido-2,2-dimethyl-8-(tosyloxy)octan-4-yl 2,2,2-trifluoroacetate (3j)**

![Structure 3j]

Colourless oil. **$^1$H NMR** (600 MHz, CDCl$_3$) δ 7.77 (d, $J = 8.1$ Hz, 4H), 7.52 (t, $J = 7.2$ Hz, 1H), 7.46 (dd, $J = 8.1$, 7.5 Hz, 2H), 7.34 (d, $J = 8.1$ Hz, 2H), 6.28 (br s, 1H), 5.20–5.24 (m, 1H), 4.00 (t, $J = 6.3$ Hz, 2H), 3.53 (dd, $J = 13.8$, 7.8 Hz, 1H), 3.07 (dd, $J = 13.8$, 5.4 Hz, 1H), 2.45 (s, 3H), 1.77 (dd, $J = 15.3$, 8.7 Hz, 1H), 1.62–1.66 (m, 4H), 1.53 (d, $J = 15.3$ Hz, 1H), 1.31–1.38 (m, 2H), 0.96 (s, 6H). **$^{13}$C NMR** (150 MHz, CDCl$_3$) δ 167.72, 157.19 (q, $J = 42.0$ Hz), 144.85, 134.59, 132.97, 131.60, 129.89.
128.70, 127.87, 126.82, 114.51 (q, J = 285.0 Hz), 76.78, 69.88, 49.34, 42.65, 34.99, 34.64, 28.40, 25.38, 25.23, 21.64, 20.77. **HRMS–ESI** (m/z): [M+Na]⁺ calcd. for C₂₆H₃₂F₃NNaO₆S, 566.1795; found: 566.1793. **IR** (KBr, cm⁻¹): ν 3417, 1636, 1400, 1119, 616.

3-(benzamidomethyl)-3-ethylnonan-5-yl 2,2,2-trifluoroacetate (3k)

![Chemical structure of 3k](image)

Yellow oil. **¹H NMR** (600 MHz, CDCl₃) δ 7.75 (d, J = 7.5 Hz, 2H), 7.52 (t, J = 7.2 Hz, 1H), 7.45 (dd, J = 7.2, 7.5 Hz, 2H), 6.18 (br s, 1H), 5.26–5.29 (m, 1H), 3.69 (dd, J = 14.4, 8.4 Hz, 1H), 2.97 (dd, J = 14.4, 4.8 Hz, 1H), 1.78 (dd, J = 16.2, 9.0 Hz, 1H), 1.65–1.70 (m, 2H), 1.60 (d, J = 18.9 Hz, 1H), 1.23–1.37 (m, 8H), 0.87–0.91 (m, 9H).

**¹³C NMR** (150 MHz, CDCl₃) δ 167.45, 156.63 (q, J = 42.0 Hz), 134.67, 131.47, 128.63, 126.74, 114.55 (q, J = 285.0 Hz), 77.16, 43.73, 39.22, 37.58, 35.56, 26.92, 26.64, 22.39, 13.83, 7.43, 7.38. **HRMS–ESI** (m/z): [M+Na]⁺ calcd. for C₂₁H₂₉F₃NO₃Na, 424.2070; found: 424.2064. **IR** (KBr, cm⁻¹): ν 3751, 3415, 2927, 1640, 1400, 1126, 704, 614.

3-(benzamidomethyl)-3-methylnonan-5-yl -2,2,2-trifluoroacetate (3l)

![Chemical structure of 3l](image)

Colourless oil. **¹H NMR** (600 MHz, CDCl₃) δ 7.76 (d, J = 8.1 Hz, 1/2×4H, 1/2×4H), 7.51 (t, J = 6.9 Hz, 1/2×2H, 1/2×2H), 7.45 (dd, J = 8.1, 6.9 Hz, 1/2×4H, 1/2×4H), 6.22 (br s, 1/2×2H, 1/2×2H), 5.21–5.29 (m, 1/2×2H, 1/2×2H), 3.60 (t, J = 6.9 Hz, 1H), 3.58 (t, J = 6.9 Hz, 1H), 3.09 (t, J = 4.8 Hz, 1H), 3.06 (t, J = 4.8 Hz, 1H), 1.82 (dd, J = 15.6, 8.4 Hz, 1H), 1.78 (dd, J = 15.6, 8.4 Hz, 1H), 1.63–1.67 (m, 1/2×4H, 1/2×4H), 1.61 (dd, J = 15.6, 2.4 Hz, 1H), 1.55 (dd, J = 15.6, 2.4 Hz, 1H), 1.27–1.38 (m, 1/2×12H, 1/2×12H), 0.93 (s, 3H), 0.91 (s, 3H), 0.91 (t, J = 7.2 Hz, 3H), 0.90 (t, J
= 7.2 Hz, 3H), 0.89 (t, J = 6.9 Hz, 3H), 0.88 (t, J = 6.9 Hz, 3H). \textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}) \( \delta \) 167.60, 167.57, 157.24 (q, J = 42.0 Hz), 157.15 (q, J = 42.0 Hz), 134.70, 134.68, 131.50, 131.49, 128.65, 128.64, 126.77, 126.75, 114.57 (q, J = 285.0 Hz), 114.55 (q, J = 285.0 Hz), 77.29, 77.26, 46.86, 46.84, 40.46, 39.98, 37.02, 36.89, 35.52, 35.48, 30.40, 30.17, 26.94, 26.90, 22.68, 22.44, 22.36, 13.83, 7.90, 7.88.

\textbf{HRMS–ESI} (m/z): [M+Na]\textsuperscript{+} calcd. for C\textsubscript{20}H\textsubscript{28}F\textsubscript{3}NNaO\textsubscript{3}, 410.1913; found, 410.1913.

\textbf{IR} (KBr, cm\textsuperscript{-1}): \( \nu \) 3417, 1638, 1400, 1122, 616.

\textbf{4-(benzamidomethyl)-4-propylheptan-2-yl 2,2,2-trifluoroacetate (3m)}

Yellow oil. \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) \( \delta \) 7.75 (d, J = 7.2 Hz, 2H), 7.52 (t, J = 7.5 Hz, 1H), 7.46 (dd, J = 7.5, 7.2 Hz, 2H), 6.19 (br s, 1H), 5.29–5.34 (m, 1H), 3.71 (dd, J = 14.1, 8.1 Hz, 1H), 2.97 (dd, J = 14.1, 4.8 Hz, 1H), 1.85 (dd, J = 15.8, 8.7 Hz, 1H), 1.53 (dd, J = 15.9, 2.1 Hz, 1H), 1.38 (d, J = 6.3 Hz, 3H), 1.13–1.35 (m, 9H), 0.92 (t, J = 6.9 Hz, 3H), 0.88 (t, J = 7.2 Hz, 3H). \textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}) \( \delta \) 167.48, 156.97 (q, J = 42.0 Hz), 134.74, 131.46, 128.65, 126.72, 114.46 (q, J = 285.0 Hz) 74.09, 44.63, 40.49, 39.35, 37.67, 37.43, 21.72, 16.28, 14.76, 14.72. \textbf{HRMS–ESI} (m/z): [M+Na]\textsuperscript{+} calcd. for C\textsubscript{20}H\textsubscript{28}F\textsubscript{3}NNaO\textsubscript{3}, 410.1913; found, 410.1903. \textbf{IR} (KBr, cm\textsuperscript{-1}): \( \nu \) 3417, 1636, 1400, 1120, 616.

\textbf{4-(benzamidomethyl)-4,5-dimethylhexan-2-yl 2,2,2-trifluoroacetate (3n)}

Yellow oil. \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) \( \delta \) 7.76 (t, J = 6.9 Hz, 1/2×4H, 1/2×4H), 7.51 (t, J = 7.8 Hz, 1/2×2H, 1/2×2H), 7.46 (dd, J = 6.9, 7.8 Hz , 1/2×4H, 1/2×4H), 6.22 (br s, 1/2×2H, 1/2×2H), 5.31–5.37 (m, 1/2×2H, 1/2×2H), 3.85 (dd, J = 14.1, 8.4
1-(1-(benzamidomethyl)cyclohexyl)butan-2-yl 2,2,2-trifluoroacetate (3o)  

Colourless oil. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.76 (d, \(J = 7.2\) Hz, 2H), 7.51 (t, \(J = 7.5\) Hz, 1H), 7.45 (dd, \(J = 7.2, 7.5\) Hz, 2H), 6.32 (br s, 1H), 5.25–5.29 (m, 1H), 3.92 (dd, \(J = 14.1, 8.7\) Hz, 1H), 2.93 (dd, \(J = 14.1, 4.5\) Hz, 1H), 1.85 (dd, \(J = 15.8, 8.1\) Hz, 1H), 1.65–1.78 (m, 2H), 1.58–1.65 (m, 1H), 1.61 (dd, \(J = 15.8, 3.6\) Hz, 1H), 1.51–1.58 (m, 1H), 1.42–1.51 (m, 4H), 1.25–1.41 (m, 4H), 0.94 (t, \(J = 7.5\) Hz, 3H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 167.57, 157.21 (q, \(J = 42.0\) Hz), 134.64, 131.44, 128.60, 126.75, 114.57 (q, \(J = 285.0\) Hz), 78.32, 36.69, 34.12, 34.00, 28.73, 25.97, 21.40, 21.24, 9.09. HRMS–ESI (m/z): [M+H]\(^+\) calcd. for C\(_{20}\)H\(_{27}\)F\(_3\)NO\(_3\), 386.1938; found, 386.1943. IR (KBr, cm\(^{-1}\)) : ν 3415, 2930, 1777, 1642, 1398, 1172, 710.

1-(1-(benzamidomethyl)cyclohexyl)octan-2-yl 2,2,2-trifluoroacetate (3p)
Colourless oil. **\(^1\)H NMR** (600 MHz, CDCl\(_3\)) \(\delta\) 7.76 (d, \(J = 7.5\) Hz, 2H), 7.51 (t, \(J = 7.5\) Hz, 1H), 7.45 (dd, \(J = 7.5\), 7.5 Hz, 2H), 6.31 (br s, 1H), 5.25–5.32 (m, 1H), 3.92 (dd, \(J = 14.1\), 8.7 Hz, 1H), 2.93 (dd, \(J = 14.1\), 4.5 Hz, 1H), 1.85 (dd, \(J = 15.7\), 8.1 Hz, 1H), 1.61–1.73 (m, 3H), 1.51–1.58 (m, 1H), 1.20–1.51 (m, 17H), 0.87 (t, \(J = 6.9\) Hz, 3H). **\(^{13}\)C NMR** (150 MHz, CDCl\(_3\)) \(\delta\) 167.51, 157.20 (q, \(J = 42.0\) Hz), 134.64, 131.45, 128.61, 126.77, 114.56 (q, \(J = 285.0\) Hz), 77.42, 36.74, 35.77, 34.13, 34.10, 31.56, 28.92, 25.99, 24.81, 22.46, 21.42, 21.26, 14.00. **HRMS–ESI** (m/z): [M+Na\(^+\)] calcd. for C\(_{24}\)H\(_{34}\)F\(_3\)NNaO\(_3\), 464.2383; found, 464.2380. **IR** (KBr, cm\(^{-1}\)): \(\nu\) 3414, 2925, 1641, 1400, 1128, 699.

5-benzamido-4-methylpentan-2-yl 2,2,2-trifluoroacetate (3q)

Colourless oil. **\(^1\)H NMR** (600 MHz, CDCl\(_3\)) \(\delta\) 7.77 (d, \(J = 7.5\) Hz, 2H), 7.51 (d, \(J = 7.2\) Hz, 1H), 7.45 (dd, \(J = 7.5\), 7.1 Hz, 2H), 6.28 (br s, 1H), 5.24–5.30 (m, 1H), 3.39–3.44 (m, 1H), 3.33–3.38 (m, 1H), 1.85–1.91 (m, 1H), 1.65–1.72 (m, 2H), 1.37 (d, \(J = 6.3\) Hz, 3H), 1.02 (t, \(J = 6.9\) Hz, 3H). **\(^{13}\)C NMR** (150 MHz, CDCl\(_3\)) \(\delta\) 167.73, 157.20 (q, \(J = 42.0\) Hz), 134.51, 131.53, 128.63, 126.80, 114.53 (q, \(J = 285.0\) Hz), 75.11, 45.40, 40.02, 30.55, 19.77, 17.94. **HRMS–ESI** (m/z): [M+Na\(^+\)] calcd. for C\(_{15}\)H\(_{18}\)F\(_3\)NNaO\(_3\), 340.1131; found, 340.1122. **IR** (KBr, cm\(^{-1}\)): \(\nu\) 3415, 2959, 1640, 1400, 1150, 803, 700.

4-(benzamidomethyl)heptan-2-yl 2,2,2-trifluoroacetate (3r)
Colourless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.75 (d, $J = 7.2$ Hz, 2H), 7.51 (t, $J = 7.2$ Hz, 1H), 7.44 (dd, $J = 7.2$, 7.2 Hz, 2H), 6.23 (br s, 1H), 5.29–5.35 (m, 1H), 3.56–3.60 (m, 1H), 3.29–3.34 (m, 1H), 1.76–1.80 (m, 1H), 1.67–1.74 (m, 1H), 1.55–1.62 (m, 1H), 1.38–1.43 (m, 3H), 1.37 (d, $J = 12.0$ Hz, 3H), 1.28–1.32 (m, 1H), 0.92 (t, $J = 6.6$ Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 167.77, 157.23 (q, $J = 42.0$ Hz), 134.54, 131.51, 128.63, 126.78, 114.56 (q, $J = 285.0$ Hz), 75.15, 42.99, 38.04, 34.91, 34.56, 20.15, 19.69, 14.14. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{17}$H$_{22}$F$_3$NNaO$_3$, 368.1444; Found: 368.1441. IR (KBr, cm$^{-1}$): ν 3415, 2961, 1780, 1639, 1399, 1170, 703, 616.

4-(benzamidomethyl)-5-methylhexan-2-yl 2,2,2-trifluoroacetate (3s)

Colourless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.77 (d, $J = 7.8$ Hz, 2H), 7.51 (t, $J = 7.5$ Hz, 1H), 7.45 (dd, $J = 7.8$, 7.5 Hz, 2H), 6.16 (br s, 1H), 5.27–5.33 (m, 1H), 3.52–3.58 (m, 1H), 3.39–3.45 (m, 1H), 1.83 (sept, $J = 7.8$ Hz, 1H), 1.77–1.80 (m, 1H), 1.52 (d, $J = 3.6$ Hz, 1H), 1.50 (d, $J = 3.6$ Hz, 1H), 1.38 (d, $J = 6.3$ Hz, 3H), 0.96 (d, $J = 6.9$ Hz, 3H), 0.94 (d, $J = 6.9$ Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 167.66, 157.40 (q, $J = 42.0$ Hz), 134.51, 131.51, 128.64, 126.79, 114.59 (q, $J = 285.0$ Hz) 75.51, 41.53, 40.87, 35.41, 29.10, 20.32, 19.63, 18.46. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{17}$H$_{22}$F$_3$NNaO$_3$, 368.1444; found, 368.1443. IR (KBr, cm$^{-1}$): ν 3415, 1622, 1400, 1122, 616.

1-benzamidoctan-4-yl 2,2,2-trifluoroacetate (3t)
Colourless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.76 (d, $J = 7.8$ Hz, 2H), 7.51 (t, $J = 7.2$ Hz, 1H), 7.44 (t, $J = 7.5$ Hz, 2H), 6.18 (br s, 1H), 5.08–5.14 (m, 1H), 3.44–3.53 (m, 2H), 1.73–1.79 (m, 2H), 1.60–1.72 (m, 4H), 1.27–1.36 (m, 4H), 0.90 (t, $J = 6.5$ Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 167.58, 157.41 (q, $J = 42.0$ Hz), 134.49, 131.51, 128.61, 126.81, 114.63 (q, $J = 285.0$ Hz), 79.50, 39.51, 33.35, 31.11, 27.09, 25.49, 22.32, 13.82. HRMS–ESI ($m/z$): [M+Na]$^+$ calcd. for C$_{17}$H$_{22}$F$_3$NNaO$_3$, 368.1444; found, 368.1442. IR (KBr, cm$^{-1}$): $\nu$ 3415, 2960, 1465, 1174, 618.

6-benzamidoheptan-3-yl 2,2,2-trifluoroacetate (3v)

Colourless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.75 (d, $J = 6.6$ Hz, 2H), 7.51 (t, $J = 7.5$ Hz, 1H), 7.44 (dd, $J = 7.5$, 6.6 Hz, 2H), 5.87 (d, $J = 8.4$ Hz, 1H), 5.04–5.09 (m, 1H), 4.22–4.28 (m, 1H), 1.75–1.78 (m, 2H), 1.68–1.73 (m, 2H), 1.53–1.61 (m, 2H), 1.26 (d, $J = 6.6$ Hz, 3H), 0.92 (t, $J = 7.5$ Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 166.97, 157.38 (q, $J = 42.0$ Hz), 134.67, 131.45, 128.58, 126.77, 114.69 (q, $J = 285.0$ Hz), 80.70, 45.15, 32.70, 29.91, 26.71, 21.19, 9.23. HRMS–ESI ($m/z$): [M+Na]$^+$ calcd. for C$_{16}$H$_{20}$F$_3$NNaO$_3$, 354.1287; found, 354.1294. IR (KBr, cm$^{-1}$): $\nu$ 3416, 1637, 1400, 1172, 616.

(1-benzamidocyclopentyl)octan-3-yl 2,2,2-trifluoroacetate (3w)

Colourless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.70 (d, $J = 7.2$ Hz, 2H), 7.50 (t, $J =$...
7.5 Hz, 1H), 7.43 (dd, J = 7.2, 7.5 Hz, 2H), 5.81 (br s, 1H), 5.04 (quint, J = 6.0 Hz, 1H), 2.08–2.14 (m, 2H), 2.01–2.03 (m, 1H), 1.89–1.94 (m, 1H), 1.62–1.75 (m, 10H), 1.23–1.33 (m, 6H), 0.85 (t, J = 6.6 Hz, 3H). $^1$H NMR (150 MHz, CDCl$_3$) δ 167.00, 157.28 (q, J = 42.0 Hz), 135.52, 131.30, 128.59, 126.65, 114.65 (q, J = 285.0), 80.12, 64.69, 38.33, 38.24, 33.19, 32.16, 31.35, 29.31, 24.59, 23.56, 22.38, 13.86. $^{13}$C NMR (150 MHz, CDCl$_3$) δ 167.00, 157.28 (q, J = 42.0 Hz), 135.52, 131.30, 128.59, 126.65, 114.65 (q, J = 285.0), 80.12, 64.69, 38.33, 38.24, 33.19, 32.16, 31.35, 29.31, 24.59, 23.56, 22.38, 13.86. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{22}$H$_{30}$F$_3$NNaO$_3$, 436.2070; found, 430.2064. IR (KBr, cm$^{-1}$): ν 3415, 1637, 1400, 1175, 618.

2-benzamido-5-(2,2,2-trifluoroacetoxy)hexyl pivalate (3x)

![Chemical Structure](image)

Colourless oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.76 (d, J = 7.8 Hz, 2H), 7.53 (t, J = 7.2 Hz, 1H), 7.46 (dd, J = 7.5 Hz, 2H), 6.35 (d, J = 8.7 Hz, 1H), 5.15–5.20 (m, 1H), 4.45–4.51 (m, 1H), 4.34 (dd, J = 11.7, 6.3 Hz, 1H), 4.12 (dd, J = 11.7, 3.6 Hz, 1H), 1.75–1.87 (m, 2H), 1.59–1.65 (m, 2H), 1.37 (d, J = 6.3 Hz, 3H), 1.19 (s, 9H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 178.97, 167.13, 157.09 (q, J = 42.0 Hz), 134.01, 131.73, 128.68, 126.83, 114.51 (q, J = 285.0 Hz), 75.93, 65.61, 48.78, 38.93, 31.78, 27.54, 27.09, 19.59. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{20}$H$_{26}$F$_3$NNaO$_5$, 440.1655; found, 440.1662. IR (KBr, cm$^{-1}$): ν 3416, 1638, 1400, 1168, 617.

6-acetoxy-5-benzamidohexan-2-yl 2,2,2-trifluoroacetate (3y)

![Chemical Structure](image)

Colourless oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.77 (d, J = 7.5 Hz, 2H), 7.53 (t, J = 6.9 Hz, 1H), 7.46 (dd, J = 7.5, 6.9 Hz, 2H), 6.34 (d, J = 9.0 Hz, 1H), 5.15–5.20 (m, 1H), 4.45–4.51 (m, 1H), 4.34 (dd, J = 11.7, 6.3 Hz, 1H), 4.12 (dd, J = 11.7, 3.6 Hz, 1H), 1.75–1.87 (m, 2H), 1.59–1.65 (m, 2H), 1.37 (d, J = 6.3 Hz, 3H), 1.19 (s, 9H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 178.97, 167.13, 157.09 (q, J = 42.0 Hz), 134.01, 131.73, 128.68, 126.83, 114.51 (q, J = 285.0 Hz), 75.93, 65.61, 48.78, 38.93, 31.78, 27.54, 27.09, 19.59. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{20}$H$_{26}$F$_3$NNaO$_5$, 440.1655; found, 440.1662. IR (KBr, cm$^{-1}$): ν 3416, 1638, 1400, 1168, 617.
1H), 4.39–4.50 (m, 1H), 4.32 (dd, J = 11.5, 5.4 Hz, 1H), 4.10–4.17 (m, 1H), 2.09 (s, 3H), 1.89–1.95 (m, 1H), 1.81–1.86 (m, 1H), 1.74–1.79 (m, 1H), 1.63–1.67 (m, 1H), 1.37 (d, J = 6.0 Hz, 3H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 171.40, 167.23, 157.10 (q, J = 42.0 Hz), 134.05, 131.76, 128.69, 126.88, 114.53 (q, J = 285.0 Hz), 75.89, 65.87, 48.54, 31.78, 27.45, 20.75, 19.58. HRMS–ESI (m/z): [M+Na]\(^+\) calcd. for C\(_{17}\)H\(_{20}\)F\(_3\)NNaO\(_5\), 398.1186; found, 398.1192. IR (KBr, cm\(^{-1}\)): \(\nu\) 3415, 1638, 1398, 1171, 616.

2-benzamido-5-(2,2,2-trifluoroacetoxy)hexyl benzoate (3z)

![Structure 3z](image)

Colourless oil. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 8.02 (d, J = 7.8 Hz, 2H), 7.77 (d, J = 7.5 Hz, 2H), 7.59 (t, J = 7.1 Hz, 1H), 7.51 (t, J = 6.9 Hz, 1H), 7.45 (dd, J = 7.5, 7.1 Hz, 4H), 6.45 (d, J = 8.4 Hz, 1H), 5.17–5.22 (m, 1H), 4.57–4.63 (m, 1H), 4.53 (dt, J = 11.4, 6.0 Hz, 1H), 4.43–4.47 (m, 1H), 1.96–2.00 (m, 1H), 1.81–1.86 (m, 1H), 1.75–1.80 (m, 2H), 1.38 (d, J = 6.3 Hz, 3H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 167.34, 166.93, 157.12 (q, J = 42.0 Hz), 134.09, 133.42, 131.73, 129.65, 129.45, 128.68, 128.53, 126.89, 114.53 (q, J = 285.0 Hz), 75.92, 66.38, 48.80, 31.84, 27.59, 19.60. HRMS–ESI (m/z): [M+Na]\(^+\) calcd. for C\(_{22}\)H\(_{22}\)F\(_3\)NNaO\(_5\), 460.1342; found, 460.1333. IR (KBr, cm\(^{-1}\)): \(\nu\) 3417, 1636, 1400, 1119, 615.

2-benzamido-5-(2,2,2-trifluoroacetoxy)hexyl-2,3,4,5,6-pentafluorobenzoate (3aa)

![Structure 3aa](image)
Yellow oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.77 (d, $J$ = 7.5 Hz, 2H), 7.53 (t, $J$ = 7.2 Hz, 1H), 7.46 (dd, $J$ = 7.5, 7.3 Hz, 2H), 6.29 (d, $J$ = 8.2 Hz, 1H), 4.58 (dd, $J$ = 10.8, 3.6 Hz, 1H), 4.52–4.56 (m, 1H), 4.50 (dd, $J$ = 10.2, 3.0 Hz, 1H), 4.16 (dd, $J$ = 12.7, 6.4 Hz, 1H), 1.88–2.02 (m, 3H), 1.72–1.82 (m, 1H), 1.72 (d, $J$ = 6.6 Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 167.13, 133.95, 131.83, 128.70, 126.88, 67.99, 53.39, 50.91, 48.40, 37.46, 29.95, 26.37. (OCOCF$_3$ is difficult to detect). HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{22}$H$_{17}$F$_8$NNaO$_5$, 550.0871; Found: 550.0860. IR (KBr, cm$^{-1}$): $\nu$ 3417, 1638, 1400, 1118, 616.

methyl-2-benzamido-5-(2,2,2-trifluoroacetoxy)hexanoate (3ab)

\[
\begin{align*}
\text{Ph} & \quad \text{O} \\
\text{N} & \quad \text{COOMe} \\
\text{(±)} & \quad \text{OTFA}
\end{align*}
\]

Colourless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J$ = 7.5 Hz, 2H), 7.54 (t, $J$ = 7.2 Hz, 1H), 7.47 (dd, $J$ = 7.5, 7.2 Hz, 2H), 6.75 (d, $J$ = 6.9 Hz, 1H), 5.13–5.18 (m, 1H), 4.86–4.89 (m, 1H), 3.81 (s, 3H), 2.03–2.11 (m, 1H), 1.71–1.84 (m, 3H), 1.36 (d, $J$ = 6.3 Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 172.62, 167.10, 157.05 (q, $J$ = 42.0 Hz) 133.62, 131.96, 128.68, 127.03, 114.50 (q, $J$ = 285.0 Hz), 75.66, 52.77, 51.86, 31.21, 28.63, 19.56. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{16}$H$_{18}$F$_3$NNaO$_5$, 384.1029; found: 384.1029. IR (KBr, cm$^{-1}$): $\nu$ 3415, 1620, 1400, 1121, 617.

(±)-ethyl-2-benzamido-5-(2,2,2-trifluoroacetoxy)hexanoate (3ac)

\[
\begin{align*}
\text{Ph} & \quad \text{O} \\
\text{N} & \quad \text{COOEt} \\
\text{(±)} & \quad \text{OTFA}
\end{align*}
\]

Colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J$ = 7.2 Hz, 2H), 7.53 (t, $J$ = 7.2 Hz, 1H), 7.47 (dd, $J$ = 7.2, 7.2 Hz, 2H), 6.74 (d, $J$ = 7.5 Hz, 1H), 4.79–4.87 (m, 1H), 4.26 (q, $J$ = 7.2 Hz, 2H), 4.10–4.18 (m, 1H), 2.20–2.28 (m, 1H), 1.83–1.99 (m, 3H), 1.36 (d, $J$ = 6.3 Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 172.62, 167.10, 157.05 (q, $J$ = 42.0 Hz) 133.62, 131.96, 128.68, 127.03, 114.50 (q, $J$ = 285.0 Hz), 75.66, 52.77, 51.86, 31.21, 28.63, 19.56. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{16}$H$_{18}$F$_3$NNaO$_5$, 384.1029; found: 384.1029. IR (KBr, cm$^{-1}$): $\nu$ 3415, 1620, 1400, 1121, 617.
3H), 1.71 (d, \( J = 6.6 \) Hz, 3H), 1.32 (t, \( J = 7.2 \) Hz, 3H). \( ^{13}C \) NMR (150 MHz, CDCl\(_3\)) \( \delta \) 172.15, 167.09, 157.04 (q, \( J = 42.0 \) Hz), 133.68, 131.92, 128.67, 127.02, 114.50 (q, \( J = 285.0 \) Hz), 75.68, 61.97, 51.87, 31.14, 28.62, 19.58, 14.08. HRMS–ESI (m/z): \([\text{M+Na}^+]\) calcd. for C\(_{17}\)H\(_{20}\)F\(_3\)NNaO\(_5\), 398.1186; found, 398.1183. IR (KBr, cm\(^{-1}\)): \( \nu \) 3416, 1637, 1400, 1172, 616.

**methyl-2-benzamido-5-(2,2,2-trifluoroacetoxy)decanoate (3ad)**

![structure of 3ad]

Colourless oil. \(^1H\) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.81 (d, \( J = 6.9 \) Hz, 2/5×2 H, 3/5×2 H), 7.53 (t, \( J = 7.2 \) Hz, 2/5×1 H, 3/5×1 H), 7.45 (dd, \( J = 7.2, 6.9 \) Hz, 2/5×2 H, 3/5×2H), 6.68–6.78 (m, 2/5×1H, 3/5×1H), 5.08–5.14(m, 2/5×1H), 4.81–4.89 (m, 2/5×1H, 3/5×1H), 3.98–4.05 (m, 3/5×1H), 3.79 (s, 2/5×3 H, 3/5×3H), 2.24–2.29 (m, 2/5×1H), 1.99–2.07 (m, 3/5×1H), 1.25–2.00 (m, 2/5×11H, 3/5×11H), 0.88 (t, \( J = 6.0 \) Hz, 2/5×3H, 3/5×3H). \( ^{13}C \) NMR (150 MHz, CDCl\(_3\)) \( \delta \) 172.64, 172.56, 167.10, 167.06, 133.65, 133.63, 131.95 (C×2), 128.68 (C×2), 127.03 (C×2), 79.17, 79.06, 52.76, 52.74, 52.17, 51.88, 33.61, 33.32, 31.32, 31.29, 29.51, 29.45, 28.59, 28.18, 24.56, 24.53, 22.35 (C×2), 13.86 (C×2). (OCOCF\(_3\) is difficult to detect). HRMS–ESI (m/z): \([\text{M+Na}^+]\) calcd. for C\(_{20}\)H\(_{26}\)F\(_3\)NNaO\(_5\), 440.1655; found, 440.1662. IR (KBr, cm\(^{-1}\)): \( \nu \) 3416, 1636, 1400, 1119, 616.

**methyl-2-benzamido-5-cyclohexyl-5-(2,2,2-trifluoroacetoxy)pentanoate (3ae)**

![structure of 3ae]

Colourless oil. \(^1H\) NMR (600 MHz, CDCl\(_3\)) \( \delta \) 7.76 (d, \( J = 7.8 \) Hz, 2/5×2 H, 3/5×2
H), 7.54 (t, J = 6.9 Hz, 2/5×1 H, 3/5×1 H), 7.46 (dd, J = 8.1, 6.9 Hz, 2/5×2 H, 3/5×2 H), 6.70 (d, J = 7.2 Hz, 3/5×1 H), 6.68 (d, J = 7.2 Hz, 2/5×1 H), 4.86–4.89 (m, 2/5×1 H), 4.81–4.86 (m, 3/5×1 H), 3.97–4.00 (m, 2/5×1 H), 3.92–3.96 (m, 3/5×1 H), 3.80 (s, 2/5×3 H, 3/5×3 H), 2.28–2.33 (m, 3/5×1 H), 2.05–2.16 (m, 2/5×1 H), 1.64–2.01 (m, 2/5×7 H, 3/5×7 H), 1.47–1.55 (m, 3/5×1 H, 2/5×1 H), 1.18–1.28 (m, 3/5×6 H), 1.10–1.17 (m, 2/5×6 H). 13C NMR (150 MHz, CDCl3) δ 172.88, 172.82, 167.15, 167.06, 133.78, 133.76, 131.87(2×C), 128.66, 128.65, 127.05 (C×2), 64.65, 64.57, 52.68, 52.63, 52.19, 51.83, 44.65, 44.30, 32.08, 31.87, 31.52, 31.33, 30.88, 30.83, 29.40, 29.30, 26.16 (C×2), 26.07 (C×2), 25.95 (C×2) (OCOCF3 is difficult to detect).

1HRMS–ESI (m/z): [M+Na]+ calced. for C21H26F3NNaO5, 452.1655; found, 452.1646.
IR (KBr, cm⁻¹): ν 3415, 1621, 1400, 1120, 617.

7-benzamido-8-methoxy-8-oxo-4-(2,2,2-trifluoroacetoxy)octyl benzoate (3af)

![Structure of 3af]

Colourless oil. 1H NMR (600 MHz, CDCl3) δ 8.02 (d, J = 7.2 Hz, 2 H), 7.80 (d, J = 7.8 Hz, 2 H), 7.56 (t, J = 7.2 Hz, 2H), 7.45 (dd, J = 7.2, 7.8 Hz, 4H), 6.75 (d, J = 7.8 Hz, 1H), 5.23 (br s, 1H), 4.88–4.90 (m, 1H), 4.30–4.38 (m, 2H), 3.80 (s, 3H), 2.28–2.34 (m, 1H), 1.74–2.09 (m, 7H). 13C NMR (100 MHz, CDCl3) δ 172.55, 167.13, 166.46, 157.27 (q, J = 42.0 Hz), 133.59, 133.01, 131.96, 130.04, 129.54, 128.68, 128.38, 127.03, 114.56 (q, J = 285.0 Hz), 78.36, 63.98, 52.79, 51.78, 30.40, 29.55, 28.60, 24.38. HRMS–ESI (m/z): [M+Na]+ calced. for C25H26F3NNaO7, 532.1554; found, 532.1553. IR (KBr, cm⁻¹): ν 3415, 1722, 1534, 1277, 714.

(3R,5R,8R,9S,10S,13R,14S,17R)-17-((2R,4R)-7-benzamido-6,6-dimethyl-4-(2,2,2-trifluoroacetoxy)heptan-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-yl benzoate (3ag)
Colourless oil. \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.05 (d, \(J = 7.2\) Hz, 2H), 7.78 (d, \(J = 7.2\) Hz, 2H), 7.75 (t, \(J = 7.5\) Hz, 1H), 7.52 (t, \(J = 7.5\) Hz, 1H), 7.45 (dd, \(J = 7.2, 7.5\) Hz, 2H), 7.43 (dd, \(J = 7.2, 7.5\) Hz, 2H), 6.35 (t, \(J = 6.4\) Hz, 1H), 5.40 (br s, 1H), 4.92–5.03 (m, 1H), 3.52 (dd, \(J = 13.7, 7.6\) Hz, 1H), 3.14 (dd, \(J = 13.7, 5.6\) Hz, 1H), 1.95–1.98 (m, 2H), 1.79–1.92 (m, 6H), 1.66–1.69 (m, 1H), 1.52–1.57 (m, 4H), 1.36–1.49 (m, 4H), 1.26–1.32 (m, 3H), 1.20–1.22 (m, 2H), 1.14–1.17 (m, 2H), 1.04–1.11 (m, 4H), 0.99 (s, 6H), 0.98 (s, 3H), 0.96 (s, 3H), 0.62 (s, 3H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 167.64, 166.12, 157.47 (q, \(J = 42.0\) Hz), 134.62, 132.66, 131.52, 130.93, 129.50, 128.64, 128.24, 126.81, 114.59 (q, \(J = 285.0\) Hz), 75.48, 74.99, 56.47, 56.30, 49.48, 44.31, 43.15, 42.81, 41.94, 40.45, 40.06, 35.76, 35.06, 34.75, 34.63, 32.50, 32.36, 28.37, 27.02, 26.76, 26.31, 25.50, 25.36, 24.12, 23.35, 20.82, 18.86, 11.80. HRMS–ESI (m/z): [M+Na]\(^+\) calcd. for C\(_{44}\)H\(_{58}\)F\(_3\)NNaO\(_5\), 760.4159; found, 760.4153. IR (KBr, cm\(^{-1}\)): \(\nu\) 3416, 1636, 1400, 1120, 616.

Late-stage functionalization of steroids compounds:

**Preparation of 4ag:**

**Procedure:** KO\(^{1}\)Bu (13 mg, 0.12 mmol, 3.6 equiv) was added to an oven-dried vial and then THF (0.2 mL) was added under agron atmosphere. The mixture was cooled to \(-78\) °C. Five minutes later, a solution of 3ag (23.9 mg, 0.032 mmol, 1.0 equiv) in THF (0.4 mL) was slowly added and stirred for another 30 min at that temperature. Then, the reaction was allowed to warm to room temperature and stirred for 5 hours. The reaction was diluted with water, extracted with EtOAc and washed with brine.
The combined solvent was dried with Na$_2$SO$_4$ and concentrated under reduce pressure. The desired residue was purified by flash column chromatography on silica gel (PE:EA:DCM = 5:1:0.5 as eluent) to give the title product 4ag.

$$((2R)-2-((2R)-2-((3R,5R,8R,10S,13R,14S,17R)-3-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)propyl)-4,4-dimethylpyrrolidin-1-yl)(phenyl)methanone \textit{(4ag)}$$

![Chemical Structure](image)

Colourless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.80 (d, $J = 7.5$ Hz, 2H), 7.49 (t, $J = 7.2$ Hz, 1H), 7.44 (dd, $J = 7.5$, 7.2 Hz, 2H), 7.30 (t, $J = 6.0$ Hz, 1H), 3.91–3.97 (m, 1H), 3.59–3.67 (m, 1H), 3.51 (dd, $J = 13.5$, 6.3 Hz, 1H), 3.31 (dd, $J = 13.5$, 6.9 Hz, 1H), 2.16 (d, $J = 5.1$ Hz, 1H), 1.99–2.01 (m, 1H), 1.77–1.88 (m, 4H), 1.63–1.70 (m, 1H), 1.48–1.62 (m, 4H), 1.36–1.45 (m, 6H), 1.17–1.30 (m, 6H), 1.04–1.11 (m, 5H), 1.02 (s, 3H), 0.98 (d, $J = 8.7$ Hz, 3H), 0.97 (s, 3H), 0.92 (s, 3H), 0.69 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 167.45, 135.05, 131.17, 128.49, 126.90, 71.86, 66.18, 56.85, 56.56, 48.80, 47.84, 46.10, 42.86, 42.07, 40.42, 40.25, 36.44, 35.83, 35.32, 34.80, 34.56, 32.49, 30.54, 29.69 (grease), 28.61, 28.57, 27.18, 26.40, 24.86, 24.19, 23.36, 20.82, 18.54, 12.13. HRMS–ESI ($m/z$): [M+H]$^+$ calcd. for C$_{35}$H$_{53}$NHO$_2$, 520.4149; found, 520.4149. IR (KBr, cm$^{-1}$): $\nu$ 3752, 3415, 1623, 1400, 1120, 615.

**Preparation of 5ag:**

![Chemical Structure](image)

**Procedure:** 3ag (23.5 mg, 0.032 mmol, 1.0 equiv), NaN$_3$ (4.2 mg, 0.064 mmol, 2.0 equiv), DMF (0.15 mL), were added to an oven-dried vial, and the mixture was heated at 90 ºC for 6 hours. The reaction was diluted with water, extracted with
EtOAc and washed with brine. The combined solvent was dried with anhydrous Na₂SO₄ and concentrated under reduce pressure. The desired residue was purified by flash column chromatography on silica gel (PE:EA:DCM = 10:1:0.5 as eluent) to give the title product 5ag.

(3R,5R,8R,10S,13R,14S,17R)-17-((2R,4R)-4-azido-7-benzamido-6,6-dimethylheptan-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-yl benzoate (5ag)

Colourless oil. ¹H NMR (600 MHz, CDCl₃) δ 8.05 (d, J = 8.1 Hz, 1/2×4H, 1/2×4H), 7.78 (d, J = 7.2 Hz, 1/2×4H, 1/2×4H), 7.55 (t, J = 7.5 Hz, 1/2×2H, 1/2×2H), 7.51 (t, J = 6.6 Hz, 1/2×2H, 1/2×2H), 7.45 (dd, J = 8.1, 7.2 Hz, 1/2×4H, 1/2×4H), 7.43 (dd, J = 7.2, 6.6 Hz, 1/2×4H, 1/2×4H), 6.64 (t, J = 6.0 Hz, 1H), 6.45 (t, J = 6.1 Hz, 1H), 4.94–5.01 (m, 1/2×2H, 1/2×2H), 3.59 (dd, J = 13.7, 7.8 Hz, 1H), 3.52 (dd, J = 13.5, 7.5 Hz, 1H), 3.40–3.54 (m, 1/2×2H, 1/2×2H), 3.23 (dd, J = 13.8, 5.7 Hz, 1H), 3.17 (dd, J = 13.8, 5.1 Hz, 1H), 1.92–2.00 (m, 1/2×4H, 1/2×4H), 1.75–1.93 (m, 1/2×10H, 1/2×10H), 1.61–1.69 (m, 1/2×6H, 1/2×6H), 1.49–1.55 (m, 1/2×4H, 1/2×4H), 1.36–1.47 (m, 1/2×14H, 1/2×14H), 1.25–1.31 (m, 1/2×7H, 1/2×7H), 1.07–1.13 (m, 1/2×11H, 1/2×11H), 1.06 (s, 3H), 1.03 (s, 3H), 1.02 (s, 3H), 1.00 (s, 3H), 0.99 (s, 3H), 0.97 (d, J = 6.6 Hz, 3H), 0.96 (s, 6H), 0.70 (s, 3H), 0.66 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 167.49, 167.37, 166.13, 134.87, 134.81, 132.68, 132.66, 131.42, 131.37, 130.94, 130.92, 129.51, 128.63, 128.61, 128.24, 126.81, 75.00, 74.97, 57.24, 56.76, 56.51, 56.48, 56.46, 49.18, 48.45, 44.84, 43.14, 42.99, 42.86, 41.95, 41.94, 41.59, 40.48, 40.45, 40.19, 40.16, 35.80, 35.79, 35.07, 34.81, 34.73, 34.65, 33.53, 33.30, 32.36, 28.60, 28.45, 27.03, 26.85, 26.77, 26.33, 26.31, 26.16, 25.23, 25.13, 24.19, 24.14, 23.37, 20.86, 18.76, 18.53, 12.05, 12.04. HRMS–ESI (m/z): [M+Na]⁺ calcd. for C₄₂H₅₆N₅O₃, 689.4401; found, 689.4400. IR (KBr, cm⁻¹): ν 3418, 1637, 1400,
Preparation of 6ag and 7ag:

**Procedure:** 3ag (23.5 mg, 0.032 mmol, 1.0 equiv), K$_2$CO$_3$ (28 mg, 0.2 mmol, 4.0 equiv), DMF (0.1 mL) were added to an oven-dried vial, and the mixture was heated at 100 °C for 5 hours. The reaction was diluted with water, extracted with EtOAc and washed with brine. The combined solvent was dried with Na$_2$SO$_4$ and concentrated under reduce pressure. The desired residue was purified by flash column chromatography on silica gel (PE:EA:DCM = 5:1:0.5 as eluent) to give the title product 6ag.

To a solution of 6ag (10.8 mg, 0.02 mmol, 1.0 equiv) in DCM (0.1 mL) was added SOCl$_2$ (0.04 mmol, 2.0 equiv) at room temperature then the vial was sealed with a cap and heated at 100 °C for 1.5 hours. The vial was allowed to cool to room temperature. The solvent was then removed in vacuo and the residue was further purified with flash column chromatography (PE: EtOAc: DCM = 5:1:0.5) to give the titled compound 7ag.

**3ag** (23.5 mg, 0.032 mmol, 1.0 equiv), K$_2$CO$_3$ (28 mg, 0.2 mmol, 4.0 equiv), DMF (0.1 mL) were added to an oven-dried vial, and the mixture was heated at 100 °C for 5 hours. The reaction was diluted with water, extracted with EtOAc and washed with brine. The combined solvent was dried with Na$_2$SO$_4$ and concentrated under reduce pressure. The desired residue was purified by flash column chromatography on silica gel (PE:EA:DCM = 5:1:0.5 as eluent) to give the title product 6ag.

(3R,5R,8R,10S,13R,14S,17R)-17-((2R,4R)-7-benzamido-4-hydroxy-6,6-dimethylheptan-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-yl benzoate (6ag)

Colourless oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 8.05 (d, $J$ = 7.2 Hz, 2H), 7.80 (d, $J$ = 7.2 Hz, 2H), 7.54 (t, $J$ = 7.5 Hz, 1H), 7.49 (t, $J$ = 7.2 Hz, 1H), 7.43 (dd, $J$ = 7.2, 7.5 Hz, 2H), 7.42 (dd, $J$ = 7.2, 7.2 Hz, 2H), 7.29 (t, $J$ = 6.3 Hz, 1H), 4.95–5.00 (m, 1H), 3.93–3.96 (m, 1H), 3.52 (dd, $J$ = 13.5, 6.3 Hz, 1H), 3.31 (dd, $J$ = 13.5, 6.9 Hz, 1H),
2.15 (d, \( J = 4.5 \) Hz, 1H), 2.01–2.03 (m, 1H), 1.97 (q, \( J = 12.0 \) Hz, 1H), 1.79–1.91 (m, 4H), 1.66–1.71 (m, 1H), 1.50–1.60 (m, 6H), 1.39–1.47 (m, 4H), 1.26–1.31 (m, 3H), 1.18–1.23 (m, 3H), 1.06–1.15 (m, 5H), 1.02 (s, 3H), 1.00 (d, \( J = 6.6 \) Hz, 3H), 0.98 (s, 3H), 0.97 (s, 3H), 0.71 (s, 3H). 13C NMR (150 MHz, CDCl3) \( \delta \) 167.45, 166.14, 135.03, 132.67, 131.18, 130.93, 129.51, 128.50, 128.24, 126.90, 75.00, 66.16, 56.90, 56.55, 48.79, 47.83, 46.11, 42.88, 41.95, 40.48, 40.22, 35.80, 35.07, 34.80, 34.65, 32.48, 32.36, 29.69 (grease), 28.61, 28.57, 27.05, 26.76, 26.34, 24.86, 24.18, 23.36, 20.87, 18.56, 12.15. HRMS–ESI (m/z): [M+Na]+ calcd. for C42H59NNaO4, 664.4336; found, 664.4331. IR (KBr, cm\(^{-1}\)): \( \nu \) 3415, 2926, 1622, 1400, 1119, 615.

(3R,5R,8R,10S,13R,14S,17R)-17-((2R,4R)-7-benzamido-4-chloro-6,6-dimethylheptan-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-yl benzoate (7ag)

Colourless oil. \(^1\)H NMR (600 MHz, CDCl3) \( \delta \) 8.05 (d, \( J = 7.2 \) Hz, 2H), 7.78 (d, \( J = 7.2 \) Hz, 2H), 7.55 (t, \( J = 7.5 \) Hz, 1H), 7.51 (t, \( J = 7.2 \) Hz, 1H), 7.45 (dd, \( J = 7.2, 7.5 \) Hz, 2H), 7.43 (dd, \( J = 7.2, 7.2 \) Hz, 2H), 6.49–6.51 (m, 1H), 4.95–5.00 (m, 1H), 4.12–4.16 (m, 1H), 3.63 (dd, \( J = 13.8, 8.1 \) Hz, 1H), 3.24 (dd, \( J = 13.8, 5.1 \) Hz, 1H), 1.92–2.03 (m, 4H), 1.77–1.89 (m, 5H), 1.67–1.69 (m, 1H), 1.57–1.63 (m, 2H), 1.39–1.47 (m, 4H), 1.27–1.30 (m, 4H), 1.17–1.22 (m, 3H), 1.08–1.14 (dt, \( J = 16.2, 4.5 \) Hz, 5H), 1.06 (s, 3H), 1.01 (s, 3H), 0.97 (s, 3H), 0.96 (d, \( J = 6.0 \) Hz, 3H), 0.71 (s, 3H). 13C NMR (150 MHz, CDCl3) \( \delta \) 167.43, 166.13, 134.86, 132.66, 131.39, 130.96, 129.51, 128.62, 128.24, 126.82, 75.02, 58.26, 56.56, 56.51, 49.42, 48.41, 47.35, 42.93, 41.97, 40.50, 40.23, 35.81, 35.33, 35.09, 34.67, 33.32, 32.38, 28.25, 27.05, 26.78, 26.70, 26.35, 25.23, 24.18, 23.38, 20.88, 18.03, 12.14. HRMS–ESI (m/z): [M+Na]+ calcd. for C42H58ClINaO3, 682.3997; found, 682.3998. IR (KBr, cm\(^{-1}\)): \( \nu \) 3415, 2927, 1622, 1400, 1118, 616.
Preparation of 8ag:

1. K$_2$CO$_3$ (4.0 equiv) DMF, 100 °C, 16 h
2. PCC (1.2 equiv) DCM, rt, 2 h

Procedure: PCC (5 mg, 0.024 mmol, 1.2 equiv) was added to a solution of 6ag (10.8 mg, 0.02 mmol, 1.0 equiv) in DCM (0.1 mL), then stirred for 2 hours. The vial was allowed to cool to room temperature. The solvent was then removed in vacuo and the residue was further purified with flash column chromatography (PE: EtOAc: DCM = 5:1:0.5) to give the titled compound 8ag.

(3R,5R,8R,10S,13R,14S,17R)-17-((R)-7-benzamido-6,6-dimethyl-4-oxoheptan-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-yl benzoate (8ag)

Colourless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.05 (d, $J = 7.8$ Hz, 2H), 7.86 (d, $J = 7.5$ Hz, 2H), 7.55 (t, $J = 7.2$ Hz, 1H), 7.51 (t, $J = 7.2$ Hz, 1H), 7.46 (dd, $J = 7.8$, 7.2 Hz, 2H), 7.44 (dd, $J = 7.5$, 7.2 Hz, 2H), 7.37 (t, $J = 5.4$ Hz, 1H), 4.94–5.02 (m, 1H), 3.42 (dd, $J = 13.8$, 6.3 Hz, 1H), 3.32 (dd, $J = 13.8$, 6.0 Hz, 1H), 2.51 (dd, $J = 16.5$, 2.1 Hz, 1H), 2.44 (s, 2H), 2.21 (dd, $J = 16.4$, 9.9 Hz, 1H), 1.95–2.00 (m, 3H), 1.76–1.90 (m, 4H), 1.67–1.69 (m, 1H), 1.52–1.62 (m, 5H), 1.40–1.47 (m, 4H), 1.25–1.29 (m, 3H), 1.10–1.15 (m, 4H), 1.08 (s, 3H), 1.07 (s, 3H), 0.96 (s, 3H), 0.92 (d, $J = 6.3$ Hz, 3H), 0.70 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 213.09, 167.31, 166.12, 134.64, 132.68, 131.29, 130.89, 129.49, 128.52, 128.24, 126.94, 74.97, 56.51, 56.04, 52.98, 52.47, 49.50, 42.81, 41.90, 40.41, 40.02, 35.77, 35.41, 35.05, 34.63, 32.57, 32.34, 28.52, 27.00, 26.74, 26.67, 26.43, 26.30, 24.14, 23.34, 20.81, 19.84, 12.07. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{42}$H$_{57}$NNaO$_4$, 662.4180; found, 662.4172. IR (KBr, cm$^{-1}$): v 3415, 1636, 1400, 1119, 616.
Comparative experiments.
Suárez:⁴

Procedure: To an oven-dried 25 mL round bottom flask with a condenser, 2a (23.3 mg, 0.10 mmol, 1.0 equiv), Pb(OAc)₄ (443.38 mg, 1 mmol, 10 equiv), I₂ (127 mg, 0.5 mmol, 5.0 equiv), 7.5 mL cyclohexane were added sequentially under nitrogen atmosphere. The reaction mixture was irradiation with 100 W LED and stirred at 100 °C for 2 hours. After completion, the reaction mixture was cooled down to room temperature and the solvent was removed under reduced pressure. The result was determined by crude ¹H NMR.

Muñiz:⁵
**Procedure:** A Schlenk tube equipped with a stirrer bar is charged with PhI(mcba)$_2$ (113 mg, 0.22 mmol, 1.0 equiv), and the amide 2a (23.3 mg, 0.10 mmol, 1.0 equiv), evacuated, and backfilled with argon, before 1.5 mL of absolute dichloroethane are added. The solution is stirred at 25 °C for 12 h under visible light. After completion, the reaction mixture was cooled down to room temperature and the solvent was removed under reduced pressure. The result was determined by crude $^1$H NMR. 90 % of SM was recovered. (We have successfully reproduced the Muñiz reaction with sulphoamide under this condition).

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**Nagib:**

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Procedure: To an oven-dried vial with a PTFE septa cap, was added a magnetic stir bar, amide 2a (46.7 mg, 0.20 mmol, 1.0 equiv), iodobenzene diacetate (256 mg, 0.8 mmol, 4.0 equiv), and dry sodium iodide (148.7 mg, 0.8 mmol, 4.0 equiv).* This vial was sealed and sequentially evacuated and backfilled with nitrogen three times. Separately, acetonitrile was degassed using a freeze-pump-thaw technique three times. Acetonitrile (2 mL) was added to the vial and the vial was stirred at 25 °C in oil bath and irradiation with blue LED light for 10 hours. After completion, the reaction mixture was cooled down to room temperature and the solvent was removed under reduced pressure. The result was determined by crude \(^1\)H NMR. 85% of SM was recovered. (We have successfully reproduced the Nagib reaction with sulphoamide under this condition).

Yu:[7]

![Diagram of the Nagib reaction](image-url)
Procedure: A Schlenk tube equipped with a stirrer bar is charged with Cu(TFA)$_2$ (3.1 mg, 0.01 mmol, 10 mol%), 1,10-Phenanthroline (1.8 mg, 0.01 mmol, 10 mol%), NBS (53.4 mg, 0.3 mmol, 3.0 equiv), TMSN$_3$ (37 μL, 0.3 mmol, 3.0 equiv), amide 2a (23.3 mg, 0.10 mmol, 1.0 equiv) and DCE (1.0 mL) was added sequentially under air. And then tube was sealed with rubber cap. The mixture was stirred at 60 ºC for 18 h. After completion, the reaction mixture was cooled down to room temperature and the solvent was removed under reduced pressure. The result was determined by crude $^1$H NMR. 55 % of SM was recovered.

Mechanism Studies:

Preparation of 4a:

3a (138 mg, 0.4 mmol, 1.0 equiv), K$_2$CO$_3$ (221 mg, 1.6 mmol, 4.0 equiv), DMF (0.5 M) were added to an oven-dried vial, and the mixture was heated at 100 ºC for 5 hours. The reaction was diluted with water, extracted with EtOAc and washed with
brine. The combined solvent was dried with Na$_2$SO$_4$ and concentrated under reduce pressure. The desired residue was purified by flash column chromatography on silica gel (PE:EA:DCM = 5:1:0.5 as eluent) to give the alcohol.

PPh$_3$ (122 mg, 0.466 mmol, 1.33 equiv) was dissolved in DCM (0.7 M), then cooled to 0 °C, then Br$_2$ (74 mg, 0.466 mmol, 1.33 equiv) was added slowly until the solvent turned to yellow solution, the alcohol was added at one time, the desired mixture was stirring 2 hours at that temperature (Detected by TLC). The reaction was diluted with water and sat. Na$_2$S$_2$O$_3$ solution, extracted with DCM. The combined organic solvent was dried with Na$_2$SO$_4$, and concentrated under reduce pressure. The desired residue was purified by flash column chromatography on silica gel (PE:EA:DCM = 8:1:0.5 as eluent) to give the 4a.

**N-(4-bromo-2,2-dimethylhexyl)benzamide (4a)**

![Chemical structure](image)

Colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.79 (d, $J = 7.2$ Hz, 2H), 7.51 (t, $J = 7.2$ Hz, 1H), 7.45 (dd, $J = 7.2$, 7.2 Hz, 2H), 6.54 (br s, 1H), 4.08–4.14 (m, 1H), 3.62 (dd, $J = 13.8$, 8.1 Hz, 1H), 3.25 (dd, $J = 13.8$, 5.4 Hz, 1H), 2.16 (dd, $J = 15.9$, 8.1 Hz, 1H), 1.83–1.94 (m, 2H), 1.80 (dd, $J = 15.9$, 2.1 Hz, 1H), 1.05 (t, $J = 7.2$ Hz, 3H), 1.04 (s, 3H), 1.01 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.45, 134.81, 131.42, 128.63, 126.82, 55.11, 48.53, 47.99, 35.44, 34.77, 26.60, 25.08, 12.01. **HRMS–ESI (m/z):** [M+Na]$^+$ calcd. for C$_{15}$H$_{22}$BrNNaO, 334.0777; found, 334.0778. IR (KBr, cm$^{-1}$): ν 3550, 3476, 3414, 1619, 1400, 1117.

**Preparation of 5a:**

The 5a was prepared as reference 8.

![Chemical structure](image)
To a 25 mL flame dried, foil wrapped flask under N\textsubscript{2}, amide 2a (233 mg, 1.0 equiv, 1.0 mmol) was added followed by acetyl hypobromite solution (7.5 mL, 1.47 mmol, 0.20 M) in CCl\textsubscript{4}. The reaction was stirred at room temperature for 1.5 hours. When the reaction was complete as judged by \textsuperscript{1}H NMR analysis (1.5 hours usually sufficient) the reaction was concentrated under reduced pressure to give a yellow solid. The desired residue was purified by flash column chromatography on silica gel (PE:Et\textsubscript{2}O = 5:1 as eluent) quickly to give the 5a.

General storage: All N-Bromo reagents were stored in foil-wrapped vials in the freezer when not in use.

\textit{N-bromo-N-(2,2-dimethylhexyl)benzamide (5a)}

Yellow oil. \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) \(\delta\) 7.49 (d, \(J = 6.9\) Hz, 2H), 7.38–7.43 (m, 3H), 3.76 (s, 2H), 1.25–1.28 (m, 4H), 1.19–1.23 (m, 2H), 0.96 (s, 6H), 0.88 (t, \(J = 7.1\) Hz, 3H). \textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}) \(\delta\) 173.75, 134.97, 130.20, 128.04, 127.66, 65.07, 40.27, 36.79, 25.92, 25.52, 23.45, 14.05. HRMS–ESI (m/z): [M+Na]\textsuperscript{+} calcd. for C\textsubscript{15}H\textsubscript{22}BrNNaO, 334.0777; found, 334.0767. IR (KBr, cm\textsuperscript{-1}): \(\nu\) 3476, 3414, 1639, 1618, 1121, 1094, 713, 616, 479.
1. TEMPO Control Experiments

\[
\begin{align*}
    &\text{Ph} - \text{N} - \text{H} - \text{H} \quad 2a, 0.1 \text{ mmol} \\
    &\text{Cul (20 mol\%)} \\
    &\text{PhI(OTFA)}_2 (2.2 \text{ equiv}) \\
    &\text{TBAB (50 mol\%)} \\
    &\text{Br}_2 (1.2 \text{ equiv}) \\
    &\text{DCM (1.0 mL)} \\
    &100 ^\circ \text{C}, 5 \text{ h} \\
    &\text{TEMPO (2.0 eq.)} \\
    &\rightarrow \text{Ph} - \text{N} - \text{OTFA} + \text{Recovery 2a (93\%)} \\
    &\text{3a, ND}
\end{align*}
\]

2. Radical capture experiments

\[
\begin{align*}
    &\text{Ph} - \text{N} - \text{H} - \text{H} \quad 2a, 0.1 \text{ mmol} \\
    &\text{1.0 equiv} \\
    &\text{standard condition} \\
    &\rightarrow \text{Ph} - \text{N} - \text{OTFA} + \text{Recovery 2a (95\%)} \\
    &\text{3a, ND}
\end{align*}
\]

\[
\begin{align*}
    &\text{Ph} - \text{N} - \text{H} - \text{H} \quad 2a, 0.1 \text{ mmol} \\
    &\text{1.0 equiv} \\
    &\text{standard condition} \\
    &\rightarrow \text{Ph} - \text{N} - \text{OTFA} + \text{Recovery 2a (99\%)} \\
    &\text{3a, ND}
\end{align*}
\]

3. Competition experiments

\[
\begin{align*}
    &\text{Ph} - \text{N} - \text{H} - \text{H} \quad 2a, 0.05 \text{ mmol} \\
    &\text{standard condition} \\
    &\rightarrow \text{Ph} - \text{N} - \text{OTFA} + \text{Recovery (2a+2b) total yield, 60\%}
\end{align*}
\]

\[
\begin{align*}
    &\text{Ph} - \text{N} - \text{Br} \quad 2a, 0.1 \text{ mmol} \\
    &\text{Cul (20 mol\%)} \\
    &\text{PhI(OTFA)}_2 (2.2 \text{ equiv}) \\
    &\text{DCM (1.0 mL)} \\
    &100 ^\circ \text{C}, 5 \text{ h} \\
    &\rightarrow \text{Ph} - \text{N} - \text{OTFA} + \text{Recovery 2a (72\%)} \\
    &\text{3a, 70\% (without Cul)}
\end{align*}
\]

\[
\begin{align*}
    &\text{Ph} - \text{N} - \text{Br} \quad 5a, 0.1 \text{ mmol} \\
    &\text{Cul (20 mmol\%)} \\
    &\text{PhI(OTFA)}_2 (2.2 \text{ equiv}) \\
    &\text{DCM (1.0 mL)} \\
    &100 ^\circ \text{C}, 5 \text{ h} \\
    &\rightarrow \text{Ph} - \text{N} - \text{OTFA} + \text{Ph} - \text{N} - \text{H} - \text{H} \quad 2a, 40\%
\end{align*}
\]

Results:

1. By adding TEMPO and 2,6-di-tert-butylphenol to the reaction mixture independently, the reaction was completely inhibited.
2. The intermolecular competition experiment showed that this reaction gave the excellent selectivity on the secondary C–H bond than the tertiary one.

3. The compound 4a can be transferred to the final product, so it may be the possible intermediate in this reaction.

4. The compound 5a was subjected to the reaction condition of CuI (20 mol%) and PIFA (2.2 equiv) in DCE (1.0 mL) at 100 °C, 60% trifluoroacetoxylation product 3a was observed and 40% of protonation product 2a was observed.

Proposed Mechanism:

We propose that this transformation is preferred to a single-electron-oxidation process (Scheme 3). With the assistance of PhI(OTFA)2 and copper catalyst, the N-Br intermediate I (path a) or Cu(III)-amidine intermediate III (path b) can be generated.17 Subsequent homolysis of the N-Br or N-Cu bond afforded amidinyl radical II. This was followed by a 1,5-H radical shift to give the corresponding C-radical V, which resulted in the selective C–H bond trifluoroacetoxylation at δ position. For the next step, two possible pathways could be followed: one is the oxidative addition of a carbon radical by a Cu(II) catalyst to generate Cu(III)-amide intermediate IV, and after ligand exchange and reductive elimination to afford the trifluoroacetoxylation product 3a (path c). The other is the oxidation of carbon radical to carbocation (VI) which is captured by OTFA-, to directly give product (path d). Although we didn’t detect any δ-brominated product (VII) even with decreased PIFA
or shorter reaction time, the possibility that the product is formed through a substitution reaction of intermediate VII cannot be ruled out.
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NMR Spectra
$2\alpha$
Spectra of product:

![Spectra Image]

3a
