Supporting Information

For
The Synthesis of Multi-substituted Pyrrolidinones via a Direct [3+2] Cycloaddition of Azaoxyallyl Cations with Aromatic Ethylenes

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1. General Information

All reactions were carried out in anhydrous solvents under argon atmosphere and monitored by TLC on gel F254 plates. The 300 MHz $^1$H NMR spectra were obtained on Bruker JNM ECS 300 MHz instrument, 400 MHz $^1$H NMR and 100 MHz $^{13}$C NMR spectra data were obtained on Bruker Ax-400 MHz instrument, both in CDCl$_3$ ($\delta = 77.00$ ppm) solution. Unless specified, chemical shifts ($\delta$) are reported in ppm using TMS (tetramethylsilane) as internal standard. High-resolution mass spectral analysis (HRMS) data were measured on the ESI Bruker Apex II. IR spectra data were recorded on a Nicolet FT-170SX spectrometer.

2. Experimental Procedure

2.1 Synthesis of $\alpha$-halo hydroxamates.

$$
\begin{align*}
\text{R}^1\text{R}^2\text{Br} & \quad + \quad \text{R}^2\text{ONH}_2\cdot\text{HCl} & \quad \text{Et}_3\text{N} & \quad \text{DCM, 0 }^\circ\text{C} \\
\text{x} & \quad = \quad \text{Br, Cl} & & \\
\text{R}^1\text{R}^2\text{OH} & \quad \text{NOR}^3
\end{align*}
$$

The substrates of $\alpha$-halo hydroxamates were prepared according to literature procedures.$^1$

![Image 1a](image1a)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.87 (s, 1H), 7.49 - 7.33 (m, 5H), 4.93 (s, 2H), 4.28 (d, $J = 6.4$ Hz, 1H), 1.93 - 1.73 (m, 3H).

![Image 1b](image1b)
\[^1\text{H} \text{NMR} \ (300 \text{ MHz, CDCl}_3) \]: \( \delta \ 9.78 \text{ (s, 1H)}, \ 7.38 - 7.34 \text{ (m, 5H)}, \ 4.94 - 4.90 \text{ (m, 2H)}, \ 4.16 - 4.11 \text{ (m, 1H)}, \ 2.01 \text{ (tdd, } J = 21.7, 14.5, 7.1 \text{ Hz, 2H)}, \ 0.95 \text{ (t, } J = 7.1 \text{ Hz, 3H}).

\( \text{Cl} \)
\( \text{O} \)
\( \text{N} \)
\( \text{OBn} \)

\( 1c \)

\[^1\text{H} \text{NMR} \ (300 \text{ MHz, CDCl}_3) \]: \( \delta \ 10.48 \text{ (s, 1H)}, \ 7.37 - 7.27 \text{ (m, 5H)}, \ 6.02 \text{ (s, 1H)}, \ 4.92 \text{ (s, 2H)}.

\( \text{MeMe} \)
\( \text{O} \)
\( \text{N} \)
\( \text{OBn} \)

\( 1d \)

\[^1\text{H} \text{NMR} \ (300 \text{ MHz, CDCl}_3) \]: \( \delta \ 9.06 \text{ (s, 1H)}, \ 7.44 - 7.38 \text{ (m, 5H)}, \ 4.95 \text{ (s, 2H)}, \ 1.94 \text{ (s, 6H)}.

\( \text{Me} \)
\( \text{O} \)
\( \text{N} \)
\( \text{OBu} \)

\( 1e \)

\[^1\text{H} \text{NMR} \ (300 \text{ MHz, CDCl}_3) \]: \( \delta \ 10.25 \text{ (s, 1H)}, \ 4.57 \text{ (q, } J = 6.8 \text{ Hz, 1H)}, \ 1.73 \text{ (d, } J = 6.8 \text{ Hz, 3H)}, \ 1.22 \text{ (s, 9H)}.

\( \text{Me} \)
\( \text{O} \)
\( \text{N} \)
\( \text{OBn} \)

\( 1f \)

\[^1\text{H} \text{NMR} \ (300 \text{ MHz, CDCl}_3) \]: \( \delta \ 9.87 \text{ (s, 1H)}, \ 7.39 - 7.33 \text{ (m, 5H)}, \ 4.89 \text{ (s, 2H)}, \ 4.33 \text{ (q, } J = 6.9 \text{ Hz, 1H)}, \ 1.62 \text{ (d, } J = 6.9 \text{ Hz, 3H)}.

2.2 General procedure of synthesis of pyrrolidinones.

\[ \begin{align*}
\text{R}_1 \text{R}_2 \text{O} &+ \text{R}_3 \text{R}_4 \text{N} & & \text{Base (2.0 equiv)} \\
\text{X} & & \text{Solvent, temp.} & \rightarrow \\
\text{3} & & \\
\end{align*} \]
To a solution of α-halo hydroxamates (0.2 mmol) in dry HFIP was added Et₃N (0.4 mmol) and styrenes (0.4 mmol) at 50 °C. The reaction was monitored by TLC. After the α-halo hydroxamates consumed completely, the solvent was evaporated under vacuum and flash column chromatography using petrol ether and acetone (v/v = 10 : 1) as eluent provided the desired products.

3. References


4. X- Ray Ellipsoid Plots of 3a (CCDC 1836255).

5. NMR Spectra Data of the Products

(3S,5S)-1-(benzyloxy)-3-methyl-5-phenylpyrrolidin-2-one
White solid (mᵣ = 37 mg, 66%, d.r. = 7.2 : 1), (mᵣ = 35 mg, 62%, d.r. = 5.5 : 1); m.p.: 74.9 - 76.1 °C; ¹H NMR (400 MHz, ) δ 7.37 (m, 5H), 7.30 - 7.23 (m, 3H), 7.22 - 7.11 (m, 2H), 5.06
(d, J = 10.0 Hz, 1H), 4.58 (d, J = 10.0 Hz, 1H), 4.44 - 4.35 (m, 1H), 2.65 - 2.43 (m, 2H), 1.68 - 1.59 (m, 1H), 1.32 (d, J = 6.8 Hz, 3H).

White solid (m\textsuperscript{b} = 35 mg, 62%, d.r. = 5.5 : 1); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, ppm): δ 7.37 (m, 5H), 7.29 - 7.23 (m, 3H), 7.21 - 7.10 (m, 2H), 5.05 (d, J = 10.0 Hz, 1H), 4.57 (d, J = 10.0 Hz, 1H), 4.40 (dd, J = 9.1, 6.6 Hz, 1H), 2.65 - 2.43 (m, 2H), 1.68 - 1.58 (m, 1H), 1.32 (d, J = 6.8 Hz, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}, ppm): δ 174.7, 139.32, 134.98, 129.39, 128.68, 128.59, 128.46, 128.39, 128.28, 127.44, 126.78, 126.50, 77.39, 61.95, 60.80, 35.28, 34.09, 16.43; IR ν (cm\textsuperscript{-1}): 3033, 2932, 2849, 1713, 1604, 1496, 1456, 1369, 1124, 731, 699; HRMS ESI Calcd for C\textsubscript{18}H\textsubscript{19}NO\textsubscript{2} [M+Na]\textsuperscript{+}: 304.1313, Found: 304.1310.

\textsuperscript{a}The reaction was carried out X = Br. \textsuperscript{b}The reaction was carried out X = Cl.

3b

(3S,5S)-1-(benzyloxy)-5-(4-fluorophenyl)-3-methylpyrrolidin-2-one

White solid (m = 37 mg, 62%, d.r. = 12.5 : 1); m.p.: 61.2 - 62.0 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, ppm): δ 7.30 - 7.25 (m, 5H), 7.15 - 7.13 (m, 2H), 7.06 (dd, J = 14.7, 6.1 Hz, 2H), 5.04 (d, J = 10.5, 1H), 4.59 (d, J = 10.1 Hz, 1H), 4.36 (dd, J = 9.2, 6.5 Hz, 1H), 2.61 - 2.42 (m, 2H), 1.57 (m, 1H), 1.31 (d, J = 6.7 Hz, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}, ppm): δ 174.70, 162.59 (d, J = 246.9 Hz), 163.808, 134.95 (d, J = 3.2 Hz), 134.90, 129.49, 129.38, 129.08 (d, J = 8.3 Hz), 128.69, 128.40, 128.34, 115.62 (d, J = 21.6 Hz), 77.41, 61.26, 35.36, 34.06, 16.38; IR ν (cm\textsuperscript{-1}): 3034, 2932, 2850, 1711, 1607, 1512, 1367, 1124, 836, 732, 698; HRMS ESI Calcd for C\textsubscript{18}H\textsubscript{18}FNO\textsubscript{2} [M+Na]\textsuperscript{+}: 322.1219, Found: 322.1210.
(3S,5S)-1-(benzoyloxy)-5-(4-chlorophenyl)-3-methylpyrrolidin-2-one

White solid (m = 37 mg, 58%, d.r. = 11.1 : 1); m.p.: 96.1 - 97.9 °C; $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 7.36 - 7.25 (m, 5H), 7.23 - 7.19 (m, 2H), 7.16 (dd, $J$ = 7.8, 1.6 Hz, 2H), 5.07 - 5.03 (d, $J$ = 10.3 Hz, 1H), 4.63 (d, $J$ = 10.2 Hz, 1H), 4.33 (dd, $J$ = 9.1, 6.7 Hz, 1H), 2.50 (m, 2H), 1.59 - 1.50 (m, 1H), 1.33 - 1.28 (d, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 174.72, 137.85, 134.90, 134.04, 129.38, 128.92, 128.85, 128.70, 128.68, 128.42, 128.36, 127.82, 61.30, 35.30, 34.02, 16.51; IR ν (cm$^{-1}$): 3033, 2969, 2932, 2876, 1712, 1594, 1489, 1454, 1366, 1124, 827, 732, 699; HRMS ESI Calcd for C$_{18}$H$_{16}$ClNO$_2$ [M+Na]$^+$: 338.0924, Found: 338.0918.

(3S,5S)-1-(benzoyloxy)-5-(4-bromophenyl)-3-methylpyrrolidin-2-one

Colourless oil (m = 36 mg, 50%, d.r. > 20 : 1); $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 7.49 (d, $J$ = 8.4 Hz, 2H), 7.30 - 7.26 (m, 3H), 7.17 - 7.13 (m, 4H), 5.05 (d, $J$ = 10.2 Hz, 1H), 4.63 (d, $J$ = 10.2 Hz, 1H), 4.31 (dd, $J$ = 9.1, 6.6 Hz, 1H), 2.50 (m, 2H), 1.58 - 1.49 (m, 1H), 1.30 (d, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 174.74, 138.41, 134.92, 131.81, 131.49, 129.40, 129.00, 128.71, 128.38, 122.18, 122.02, 77.40, 61.38, 35.28, 34.02, 16.40; IR ν (cm$^{-1}$): 3033, 2969, 2932, 2876, 1712, 1594, 1489, 1454, 1377, 1124, 837, 823, 732, 699, 553; HRMS ESI Calcd for C$_{18}$H$_{18}$BrNO$_2$ [M+Na]$^+$: 382.0419, Found: 382.0413.
(3S,5S)-1-(benzyloxy)-3-methyl-5-(p-tolyl)pyrrolidin-2-one

White solid (m = 34 mg, 58%, d.r. = 11.4 : 1); m.p.: 87.3 - 90.1 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm): \(\delta\) 7.34 - 7.28 (m, 3H), 7.27 - 7.18 (m, 4H), 7.16 - 7.13 (m, 2H), 5.04 (d, J = 10.0 Hz, 1H), 4.56 (d, J = 10.0 Hz, 1H), 4.35 (dd, J = 9.1, 6.7 Hz, 1H), 2.55 - 2.44 (m, 2H), 2.38 (s, 3H), 1.62 - 1.59 (m, 1H), 1.31 (d, J = 6.7 Hz, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\), ppm): \(\delta\) 174.63, 138.19, 136.19, 135.02, 129.40, 129.34, 128.56, 128.26, 127.38, 77.39, 61.68, 35.25, 34.07, 21.18, 16.42; IR v (cm\(^{-1}\)): 3032, 2968, 2930, 2875, 2850, 1716, 1616, 1498, 1454, 1367, 1124, 844, 731, 698; HRMS ESI Calcd for C\(_{19}\)H\(_{21}\)NO\(_2\) [M+Na]\(^+\): 318.1470, Found: 318.1464.

(3S,5S)-1-(benzyloxy)-5-(4-(tert-butyl)phenyl)-3-methylpyrrolidin-2-one

White solid (m = 43 mg, 64%, d.r. > 20 : 1); m.p.: 93.1 - 97.6 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm): \(\delta\) 7.42 - 7.40 (m, 2H), 7.28 - 7.21 (m, 5H), 7.06 (dd, J = 7.8, 1.5 Hz, 2H), 5.07 (d, J = 10.0 Hz, 1H), 4.54 (d, J = 9.9 Hz, 1H), 4.38 (dd, J = 9.2, 6.6 Hz, 1H), 2.50 (m, 2H), 1.64 (m, 1H), 1.35 (s, 9H), 1.33 - 1.30 (d, J = 7.2 Hz, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\), ppm): \(\delta\) 174.61, 151.47, 136.04, 134.96, 129.45, 128.56, 128.22, 127.24, 125.56, 77.48, 61.63, 35.10, 34.59, 34.10, 31.31, 16.41; IR v (cm\(^{-1}\)): 3032, 2963, 2872, 1719, 1614, 1512, 1454, 1418, 1363, 1127, 835, 699; HRMS ESI Calcd for C\(_{22}\)H\(_{27}\)NO\(_2\) [M+Na]\(^+\): 360.1939, Found: 360.1936.
3g

(3S,5S)-1-(benzxyloxy)-5-(4-methoxyphenyl)-3-methylpyrrolidin-2-one
Colourless oil (m = 40 mg, 64%, d.r. = 8.3 : 1); $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 7.34 - 7.23 (m, 5H), 7.17 - 7.11 (m, 2H), 6.94 - 6.87 (m, 2H), 5.02 (d, J = 9.9 Hz, 1H), 4.54 (d, J = 9.9 Hz, 1H), 4.38 - 4.33 (m, 1H), 3.82 (s, 3H), 2.55 - 2.44 (m, 2H), 1.61 (qdd, J = 10.7, 8.6, 3.5 Hz, 1H), 1.32 - 1.30 (d, J = 6.9Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 174.62, 159.59, 135.00, 131.00, 129.40, 128.72, 128.57, 128.27, 113.98, 113.87, 77.38, 61.40, 55.31, 35.19, 34.09, 16.39; IR ν (cm$^{-1}$): 3032, 1715, 1612, 1514, 1454, 1368, 1248, 1225, 832, 730, 699; HRMS ESI Calcd for C$_{19}$H$_{21}$NO$_3$ [M+Na]$^+$: 334.1419, Found: 334.1424.

3h

(3S,5S)-1-(benzxyloxy)-5-(3-fluorophenyl)-3-methylpyrrolidin-2-one
Colourless oil (m = 26 mg, 43%, d.r. > 20 : 1); $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 7.37 - 7.25 (m, 4H), 7.17 (dd, J = 7.6, 1.7 Hz, 2H), 7.10 - 6.97 (m, 3H), 5.08 (d, J = 10.1 Hz, 1H), 4.65 (d, J = 10.2 Hz, 1H), 4.35 (dd, J = 9.0, 6.7 Hz, 1H), 2.59 - 2.43 (m, 2H), 1.57 (m, 1H), 1.31 (d, J = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 174.77, 162.89 (d, J = 246.8 Hz), 142.15, 134.90, 130.27 (d, J = 8.2 Hz), 129.41, 128.75, 128.37, 123.01 (d, J = 2.9 Hz), 115.32 (d, J = 21.1 Hz), 114.21 (d, J = 22.0 Hz), 77.33, 61.48, 35.22, 34.02, 16.42; IR ν (cm$^{-1}$): 3033, 2933, 2849, 1713, 1594, 1491, 1455, 1367, 1123, 731, 697; HRMS ESI Calcd for C$_{18}$H$_{18}$FNO$_2$ [M+Na]$^+$: 322.1219, Found: 322.1223.
3i

(3S,5S)-1-(benzyloxy)-5-(3-chlorophenyl)-3-methylpyrrolidin-2-one
White solid (m = 37 mg, 59%, d.r. > 20 : 1); m.p.: 83.8 - 86.1 °C; $^1\text{H}$ NMR (400 MHz, CDCl$_3$, ppm): δ 7.33 - 7.25 (m, 6H), 7.19 - 7.15 (m, 3H), 5.07 (d, $J = 10.1$ Hz, 1H), 4.65 (d, $J = 10.2$ Hz, 1H), 4.32 (dd, $J = 9.0$, 6.7 Hz, 1H), 2.58 - 2.43 (m, 2H), 1.58 - 1.48 (m, 1H), 1.31 (d, $J = 6.8$ Hz, 3H); $^{13}\text{C}$ NMR (100 MHz, CDCl$_3$, ppm): δ 174.69, 141.53, 134.88, 134.54, 130.00, 129.43, 128.77, 128.52, 128.38, 127.50, 125.48, 125.40, 77.36, 61.45, 35.19, 34.02, 16.40; IR ν (cm$^{-1}$): 3032, 2970, 2933, 2875, 1715, 1454, 1124, 733, 698; HRMS ESI Calcd for C$_{18}$H$_{18}$ClNO$_2$ [M+Na]$^+$: 338.0924, Found: 338.0925.

3j

(3S,5S)-1-(benzyloxy)-5-(3-bromophenyl)-3-methylpyrrolidin-2-one
White solid (m = 28 mg, 39%, d.r. > 20 : 1); m.p.: 89.5 - 91.5 °C; $^1\text{H}$ NMR (400 MHz, CDCl$_3$, ppm): δ 7.49 - 7.46 (m, 1H), 7.41 (s, 1H), 7.32 - 7.27 (m, 4H), 7.26 (m, 1H), 7.24 - 7.16 (m, 2H), 5.07 (d, $J = 10.1$ Hz, 1H), 4.64 (d, $J = 10.2$ Hz, 1H), 4.29 (dd, $J = 9.0$, 6.7 Hz, 1H), 2.57 - 2.43 (m, 2H), 1.56 (m, 1H), 1.31 (d, $J = 6.7$ Hz, 3H); $^{13}\text{C}$ NMR (100 MHz, CDCl$_3$, ppm): δ 174.66, 141.76, 134.87, 131.45, 130.44, 130.29, 129.44, 128.78, 128.39, 125.93, 122.68, 77.38, 61.40, 35.19, 34.02, 16.38; IR ν (cm$^{-1}$): 3032, 2967, 2930, 2874, 2850, 1716, 1454, 1123, 788, 733, 697; HRMS ESI Calcd for C$_{18}$H$_{18}$BrNO$_2$ [M+Na]$^+$: 382.0419, Found: 382.0417.
3k

(3S,5S)-1-(benzyloxy)-5-(2-chlorophenyl)-3-methylpyrrolidin-2-one
Colourless oil (m = 31 mg, 48%, d.r. = 11.1 : 1); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.38 - 7.35 (m, 2H), 7.32 - 7.29 (m, 3H), 7.28 - 7.22 (m, 4H), 5.07 (d, $J$ = 10.4 Hz, 1H), 4.88 (dd, $J$ = 16.3, 8.9 Hz, 2H), 2.68 (ddd, $J$ = 12.8, 9.2, 7.5 Hz, 1H), 2.55 - 2.44 (m, 1H), 1.48 - 1.41 (m, 1H), 1.23 (d, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 174.20, 137.36, 134.92, 132.83, 129.75, 129.29, 128.93, 128.75, 128.45, 127.63, 127.24, 76.35, 58.00, 33.73, 30. 16.80; IR $\nu$ (cm$^{-1}$): 3033, 2928, 2850, 1704, 1595, 1497, 1454, 1124, 733, 699; HRMS ESI Calcd for C$_{18}$H$_{18}$ClNO$_2$ [M+Na]$^+$: 338.0924, Found: 338.0923.

3l

(3S,5S)-1-(benzyloxy)-5-(2-bromophenyl)-3-methylpyrrolidin-2-one
Colourless oil (m = 29 mg, 40%, d.r. = 3.7 : 1); $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 7.54 (m, 1H), 7.35 (m, 2H), 7.34 - 7.29 (m, 3H), 7.29 - 7.26 (m, 1H), 7.20 - 7.15 (m, 2H), 5.09 (d, $J$ = 10.5 Hz, 1H), 5.03 (d, $J$ = 11.1 Hz, 1H), 4.86 (dd, $J$ = 15.4, 8.9 Hz, 2H), 2.73 - 2.65 (m, 1H), 2.55 - 2.45 (m, 1H), 1.41 (m, 1H), 1.24 (d, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 174.16, 139.45, 134.89, 133.00, 129.29, 129.24, 128.76, 128.47, 127.86, 127.70, 122.67, 76.78, 60.35, 33.85, 33.55, 16.83; IR $\nu$ (cm$^{-1}$): 3033, 2961, 2875, 2850, 1704, 1595, 1497, 1381, 1454, 1124, 732, 699, 541; HRMS ESI Calcd for C$_{18}$H$_{18}$BrNO$_2$ [M+Na]$^+$: 382.0419, Found: 382.0412.
3m

(3S,5S)-1-(benzyloxy)-3-methyl-5-(o-tolyl)pyrrolidin-2-one
White solid (m = 42 mg, 71%, d.r. = 5.9 : 1); m.p.: 90.6 - 92.0 °C; $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 7.34 (m, 2H), 7.31 - 7.24 (m, 4H), 7.22 (dd, $J$ = 7.1, 1.7 Hz, 1H), 7.20 - 7.14 (m, 3H), 5.09 (d, $J$ = 10.4 Hz, 1H), 4.71 (d, $J$ = 10.3 Hz, 1H), 4.63 (t, $J$ = 7.6 Hz, 1H), 2.59 - 2.44 (m, 2H), 2.21 (s, 3H), 1.53 - 1.45 (m, 1H), 1.28 (d, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 174.38, 137.53, 135.65, 134.78, 130.76, 129.45, 129.32, 128.60, 128.37, 127.64, 126.41, 126.25, 125.98, 76.80, 57.86, 34.10, 33.82, 18.98, 16.64; IR ν (cm$^{-1}$): 3030, 2968, 2931, 2874, 1714, 1606, 1494, 1454, HRMS ESI Calcd for C$_{19}$H$_{21}$NO$_2$ [M+Na]$^+$: 318.1470, Found: 318.1477.

3n

(3S,5S)-5-(2-aminophenyl)-1-(benzyloxy)-3,5-dimethylpyrrolidin-2-one
Yellow oil (m = 40 mg, 65%, d.r. > 20 : 1); $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 8.99 (s, 1H), 7.27 (dd, $J$ = 8.4, 5.3 Hz, 5H), 7.13 (t, $J$ = 7.7 Hz, 1H), 7.03 (dd, $J$ = 7.4, 1.2 Hz, 1H), 6.79 (t, $J$ = 7.3 Hz, 1H), 6.54 (d, $J$ = 8.1 Hz, 1H), 5.28 (s, 1H), 4.95 - 4.79 (m, 3H), 4.17 (s, 1H), 3.82 (s, 1H), 1.97 (s, 3H), 1.47 (d, $J$ = 6.9 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 170.92, 142.88, 134.70, 130.14, 129.30, 128.69, 128.49, 128.26, 128.38, 128.02, 127.99, 118.71, 116.17, 111.63, 78.25, 54.30, 34.02, 32.95, 24.13, 19.52; IR ν (cm$^{-1}$): 3032, 2973, 2934, 1663, 1600, 1507, 1452, 1372, 909, 747; HRMS ESI Calcd for C$_{19}$H$_{22}$N$_2$O$_2$ [M+Na]$^+$: 333.1573, Found:333.1578.
(3S,5S)-1-(benzyloxy)-3,5-dimethyl-5-(3-(trifluoromethyl)phenyl)pyrrolidin-2-one

Colourless oil (m = 35 mg, 47%, d.r. > 20 : 1); $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 7.71 (s, 1H), 7.67 (d, $J = 7.9$ Hz, 1H), 7.57 (d, $J = 7.7$ Hz, 1H), 7.48 (t, $J = 7.8$ Hz, 1H), 7.26 (m, 3H), 7.19 (m, 2H), 5.09 (d, $J = 9.7$ Hz, 1H), 4.72 (d, $J = 9.7$ Hz, 1H), 2.67 - 2.57 (m, 1H), 2.39 (dd, $J = 12.8$, 9.3 Hz, 1H), 1.91 (dd, $J = 12.8$, 7.9 Hz, 1H), 1.68 (s, 3H), 1.25 (d, $J = 7.2$ Hz, 3H);

$^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 174.66, 145.39, 134.90, 130.88 (d, $J = 32$ Hz), 129.72, 129.20, 129.03, 128.60, 128.31, 124.44 (d, $J = 4$ Hz), 124.01 (d, $J = 270$ Hz), 123.01 (d, $J = 4$ Hz), 78.30, 64.35, 42.14, 32.65, 22.75, 16.26; IR ν (cm$^{-1}$): 3024, 2969, 2930, 1718, 1618, 1456, 1374, 1333, 1243, 1125, 702; HRMS ESI Calcd for C$_{20}$H$_{20}$FNO$_2$ [M+Na]$^+$: 386.1338, Found: 386.1348.

(3S,5S)-1-(benzyloxy)-3,5-dimethyl-5-(4-(trifluoromethyl)phenyl)pyrrolidin-2-one

Colourless oil (m = 40 mg, 54%, d.r. > 20 : 1); $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 7.57 (dd, $J = 21.7$, 8.4 Hz, 4H), 7.28 - 7.20 (m, 5H), 5.06 (d, $J = 9.8$ Hz, 1H), 4.85 (d, $J = 9.8$ Hz, 1H), 2.61 (dp, $J = 9.2$, 7.2 Hz, 1H), 2.38 (dd, $J = 12.8$, 9.3 Hz, 1H), 1.91 (dd, $J = 12.9$, 7.3 Hz, 1H), 1.67 (s, 3H), 1.21 (d, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 174.60, 148.53, 135.00, 129.74 (d, $J = 32$ Hz), 129.24, 128.64, 128.34, 126.57, 125.42 (d, $J = 4$ Hz), 124.00 (d, $J = 274$ Hz), 122.62, 78.25, 64.59, 42.25, 32.65, 23.25, 16.79; IR ν (cm$^{-1}$): 3024, 2974, 2930, 1718, 1618, 1456, 1374, 1333, 1243, 1125, 702; HRMS ESI Calcd for C$_{20}$H$_{20}$FNO$_2$ [M+Na]$^+$:
(3S,5S)-1-(benzyloxy)-3,5-dimethyl-5-phenylpyrrolidin-2-one

Colourless oil (m = 28 mg, 47%, d.r. > 20 : 1); $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 7.53 - 7.47 (m, 2H), 7.38 (dd, J = 10.2, 4.9 Hz, 2H), 7.32 (dd, J = 5.9, 3.7 Hz, 1H), 7.27 (dd, J = 6.4, 3.4 Hz, 3H), 7.19 (m, 2H), 5.05 (d, J = 9.5 Hz, 1H), 4.67 (d, J = 9.5 Hz, 1H), 2.67 - 2.55 (m, 1H), 2.37 (dd, J = 12.8, 9.3 Hz, 1H), 1.98 (dd, J = 12.8, 7.9 Hz, 1H), 1.67 (s, 3H), 1.25 (d, J = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 174.42, 143.98, 135.02, 129.30, 128.53, 128.48, 128.40, 128.23, 127.55, 126.32, 78.27, 64.43, 42.20, 32.65, 22.70, 16.73; IR ν (cm$^{-1}$): 3032, 2974, 2934, 2876, 1708, 1602, 1497, 1380, 1115, 732, 700; HRMS ESI Calcd for C$_{19}$H$_{21}$NO$_2$ [M+Na]$^+$: 318.1470, Found: 318.1469.

(3S,5S)-1-(benzyloxy)-3-methyl-5-(naphthalen-2-yl)pyrrolidin-2-one

Colourless oil (m = 32 mg, 48%, d.r. > 20 : 1); $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 7.91 (m, 1H), 7.83 (d, J = 8.1 Hz, 2H), 7.56 - 7.46 (m, 4H), 7.29 - 7.15 (m, 5H), 5.17 (d, J = 6.9 Hz, 1H), 5.12 (d, J = 10.4 Hz, 1H), 4.83 (dd, J = 10.4, 7.3Hz, 1H), 2.78 - 2.68 (m, 1H), 2.64 - 2.53 (m, 1H), 1.69 (m, 1H), 1.26 (d, J = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 174.34, 135.05, 133.89, 130.64, 129.38, 129.11, 128.65, 128.34, 126.23, 125.69, 125.50, 122.31, 76.52, 34.34, 33.79, 30.96, 17.01; IR ν (cm$^{-1}$): 3034, 2968, 2931, 2875, 2850, 1708, 1454, 1374, 1122, 732, 699; HRMS ESI Calcd for C$_{22}$H$_{21}$NO$_2$ [M+Na]$^+$: 354.1470, Found: 354.1462.
(3S,5S)-1-(benzyloxy)-3-methyl-5-(thiophen-2-yl)pyrrolidin-2-one

Colourless oil (m = 25 mg, 44%, d.r. > 20 : 1); \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm): \(\delta 7.37 - 7.34\) (m, 1H), \(7.33\) (s, 1H), \(7.29\) (m, 2H), \(7.21\) (m, 2H), \(7.10\) (m, 1H), \(7.02\) (m, 1H), \(5.03\) (d, \(J = 9.8\) Hz, 1H), \(4.77 - 4.69\) (m, 1H), \(4.50\) (d, \(J = 9.7\) Hz, 1H), \(2.72 - 2.59\) (m, 1H), \(2.53 - 2.41\) (m, 1H), \(1.79\) (dt, \(J = 12.6, 9.6\) Hz, 1H), \(1.33\) (d, \(J = 7.0\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm): \(\delta 174.41, 142.62, 134.92, 129.48, 129.44, 128.59, 128.39, 128.29, 127.42, 127.36, 125.90, 78.07, 57.19, 35.39, 34.20, 16.26; IR \(\nu\) (cm\(^{-1}\)): 3033, 2966, 2930, 1716, 1608, 1498, 1454, 1375, 1247, 1003, 910, 731; HRMS ESI Calcd for C\(_{16}\)H\(_{17}\)NO\(_2\)S [M+Na]\(^+\): 310.0872, Found: 310.0881.

(3S,7aS)-1-(benzyloxy)-3-methyl-7a-phenyloctahydro-2H-indol-2-one

Colourless oil (m = 32 mg, 48%, d.r. > 20 : 1); \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm): \(\delta 7.66 - 7.61\) (m, 2H), \(7.43\) (dd, \(J = 10.1, 4.8\) Hz, 2H), \(7.39 - 7.34\) (m, 1H), \(7.27 - 7.22\) (m, 3H), \(7.06\) (dd, \(J = 7.1, 2.4\) Hz, 2H), \(4.90\) (d, \(J = 9.3\) Hz, 1H), \(4.26\) (d, \(J = 9.3\) Hz, 1H), \(2.76\) (d, \(J = 14.5\) Hz, 1H), \(2.46\) (m, 1H), \(2.36\) (m, 1H), \(1.70\) (m, 2H), \(1.62 - 1.53\) (m, 3H), \(1.48\) (ddd, \(J = 10.2, 7.4, 3.7\) Hz, 1H), \(1.38\) (m, 1H), \(1.29\) (d, \(J = 6.8\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm): \(\delta 175.06, 140.30, 134.97, 129.27, 129.48, 129.44, 128.59, 128.39, 128.29, 127.42, 127.36, 125.90, 78.47, 65.27, 44.81, 36.26, 30.66, 23.18, 22.04, 20.80, 14.64; IR \(\nu\) (cm\(^{-1}\)): 3031, 2966, 2932, 1717, 1602, 1497, 1452, 1373, 1123, 744, 699; HRMS ESI Calcd for C\(_{22}\)H\(_{25}\)NO\(_2\) [M+Na]\(^+\): 358.1783, Found:
(S)-1-(benzyloxy)-3-methyl-5,5-diphenylpyrrolidin-2-one

Colourless oil (m = 28 mg, 38%); \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm): \(\delta 7.48 - 7.44\) (m, 2H), \(7.40 - 36\) (m, 3H), \(7.33 - 7.21\) (m, 8H), \(7.11\) (m, 2H), \(4.81\) (d, \(J = 8.9\) Hz, 1H), \(4.09\) (d, \(J = 8.9\) Hz, 1H), \(2.73 - 2.67\) (dd, \(J = 8.5, 9.2\) Hz, 1H), \(2.60\) (dd, \(J = 12.0, 10.0\) Hz, 1H), \(2.43 - 2.36\) (m, 1H), \(1.29\) (d, \(J = 7.0\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm): \(\delta 173.46, 142.51, 134.43, 129.54, 128.85, 128.48, 128.23, 128.19, 128.15, 127.51, 127.31, 78.20, 70.92, 49.95, 32.11, 15.58\); IR \(\nu\) (cm\(^{-1}\)): 3033, 2965, 2931, 2875, 2850, 1711, 1600, 1495, 1448, 1375, 1113, 731,699; HRMS ESI Calcd for C\(_{24}\)H\(_{23}\)NO\(_2\) [M+Na]\(^{+}\): 380.1626, Found: 380.1630.

(3S,4R,5S)-1-(benzyloxy)-3-methyl-4,5-diphenylpyrrolidin-2-one

Colourless oil (m = 11 mg, 15%, \(d.r. > 20 : 1\)); \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm): \(\delta 7.27 - 7.25\) (m, 6H), \(7.24 - 7.21\) (m, 4H), \(7.19 - 7.15\) (m, 4H), \(6.99 - 6.97\) (m, 2H), \(5.17\) (d, \(J = 10.1\) Hz, 1H), \(4.68\) (d, \(J = 10.1\) Hz, 1H), \(4.34\) (d, \(J = 8.9\) Hz, 1H), \(2.88 - 2.85\) (t, \(J = 6.0\) Hz, 1H), \(2.61\) (dq, \(J = 10.0, 7.0\) Hz, 1H), \(1.28\) (d, \(J = 7.0\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm): \(\delta 173.2, 129.52, 128.71, 128.66, 128.54, 128.37, 128.33, 127.75, 127.52, 127.43, 77.00, 69.36, 54.93, 42.21, 14.71\); IR \(\nu\) (cm\(^{-1}\)): 3032, 2961, 2919, 1708, 1601, 1497, 1455, 1374, 909, 732; HRMS ESI Calcd for C\(_{24}\)H\(_{23}\)NO\(_2\) [M+Na]\(^{+}\): 380.1621, Found:380.1624.
(3S,5S)-1-(benzyloxy)-3-ethyl-5-phenylpyrrolidin-2-one
Colourless oil (m = 38 mg, 64%, d.r. = 11.1 : 1); \( ^1H \) NMR (400 MHz, CDCl₃, ppm): \( \delta \) 7.43 - 7.35 (m, 3H), 7.33 (dd, \( J = 7.7, 1.7 \) Hz, 2H), 7.29 - 7.23 (m, 3H), 7.13 (dd, \( J = 7.6, 1.7 \) Hz, 2H), 5.05 (d, \( J = 10.0 \) Hz, 1H), 4.57 (d, \( J = 9.9 \) Hz, 1H), 4.40 (dd, \( J = 9.2, 6.9 \) Hz, 1H), 2.50 (ddd, \( J = 12.4, 9.1, 6.9 \) Hz, 1H), 2.39 (ddd, \( J = 18.3, 9.1, 4.1 \) Hz, 1H), 1.99 (qdd, \( J = 10.9, 6.8, 3.7 \) Hz, 1H), 1.66 (m, 1H), 1.60 - 1.50 (m, 1H), 0.99 (t, \( J = 7.5 \) Hz, 3H); \( ^{13}C \) NMR (100 MHz, CDCl₃, ppm): \( \delta \) 174.25, 139.48, 134.95, 129.50, 129.40, 129.76, 128.69, 128.59, 128.38, 128.28, 127.41, 61.93, 40.34, 32.51, 30.96, 24.12, 10.97; IR \( \nu \) (cm\(^{-1}\)): 3034, 2964, 2934, 2877, 1708, 1604, 1497, 1458, 1367, 1129, 732, 699; HRMS ESI Calcd for C\(_{19}\)H\(_{21}\)NO\(_2\) [M+Na]\(^+\): 318.1470, Found: 318.1471.

(3S,5S)-1-(benzyloxy)-3-chloro-5-phenylpyrrolidin-2-one
Colourless oil (m = 22 mg, 36%, d.r. > 20 : 1); \( ^1H \) NMR (400 MHz, CDCl₃, ppm): \( \delta \) 7.43 (m, 3H), 7.38 - 7.34 (m, 2H), 7.33 - 7.26 (m, 3H), 7.13 (d, \( J = 6.5 \) Hz, 2H), 5.12 (d, \( J = 10.0 \) Hz, 1H), 4.57 (d, \( J = 10.0 \) Hz, 1H), 4.43 (m, 2H), 3.01 (ddd, \( J = 13.9, 9.0, 7.3 \) Hz, 1H), 2.33 - 2.23 (m, 1H); \( ^{13}C \) NMR (100 MHz, CDCl₃, ppm): \( \delta \) 166.54, 137.67, 134.38, 129.51, 129.36, 129.10, 128.98, 128.93, 128.75, 128.43, 127.90, 127.60, 77.70, 77.20, 61.05, 50.81, 37.03; IR \( \nu \) (cm\(^{-1}\)): 3033, 1728, 1604, 1497, 1457, 1368, 1124, 699; HRMS ESI Calcd for C\(_{17}\)H\(_{16}\)ClNO\(_2\) [M+Na]\(^+\): 324.0762, Found: 324.0766.
(S)-1-(benzyloxy)-3,3-dimethyl-5-phenylpyrrolidin-2-one
White solid (m = 28 mg, 47%); m.p.: 96.2 - 98.6 °C; $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 7.39 (m, 3H), 7.32 - 7.26 (m, 5H), 7.17 (dd, $J = 7.7$, 1.7 Hz, 2H), 5.07 (d, $J = 10.2$ Hz, 1H), 4.62 (d, $J = 10.2$ Hz, 1H), 4.40 (dd, $J = 8.5$, 7.3 Hz, 1H), 2.17 (dd, $J = 12.9$, 7.1 Hz, 1H), 1.82 (dd, $J = 12.8$, 8.7 Hz, 1H), 1.27 (s, 3H), 1.19 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 176.52, 139.40, 134.97, 129.54, 128.70, 128.69, 128.31, 128.27, 127.28, 77.06, 60.48, 42.31, 37.83, 25.58; IR ν (cm$^{-1}$): 3033, 2964, 2929, 2871, 1710, 1604, 1497, 1457, 1388, 1366, 1120, 732, 699; HRMS ESI Calcd for C$_{19}$H$_{21}$NO$_2$ [M+Na]$^+$: 318.1470, Found: 318.1474.

(3S,5S)-1-(tert-butoxy)-3-methyl-5-phenylpyrrolidin-2-one
Colourless oil (m = 18 mg, 36%, d.r. > 20:1); $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 7.35 (d, $J = 7.5$ Hz, 2H), 7.31 (dd, $J = 5.3$, 1.8 Hz, 1H), 7.26 (dd, $J = 5.6$, 4.2 Hz, 2H), 4.75 (t, $J = 7.0$ Hz, 1H), 2.70 (m, 1H), 2.60 - 2.50 (m, 1H), 1.67 (m, 1H), 1.23 (d, $J = 7.2$ Hz, 3H), 1.15 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 176.35, 140.56, 128.47, 127.82, 127.34, 83.55, 63.20, 34.95, 32.68, 27.58, 17.24; IR ν (cm$^{-1}$): 3033, 2976, 2931, 1714, 1604, 1495, 1457, 1388, 1366, 1162, 700; HRMS ESI Calcd for C$_{15}$H$_{21}$NO$_2$ [M+Na]$^+$: 270.1470, Found: 270.1476.
zhang-100

\[ \text{Me} \overset{\text{O}}{\text{N-OBn}} \]

3a\(^{a}\)
$^{3}$g

![Chemical structure image](image_url)
[Image of a chemical structure labeled as 3l with ppm values listed nearby]
Me\textsubscript{3}C\textsuperscript{N-O}Bn

3r

ppm

8 7 6 5 4 3 2 1 0...
Me\(\text{N-OBn}\)\(\text{S}\)

3s


The diagram shows an NMR spectrum for a compound labeled as "Me₅N-Ot-Bu 3z." The spectrum includes peaks at various ppm values, with some peaks being more prominent than others. The ppm scale ranges from 0.000 to 8.000.

- Peaks at 7.372, 7.362, 7.342, and 7.316 ppm
- Peaks at 4.763 and 4.746 ppm
- Peaks at 2.733, 2.713, 2.709, and 2.690 ppm
- Peaks at 1.153 and 1.00 ppm
- Peaks at 7.379, 7.362, 7.342, and 7.316 ppm

The compound structure is also depicted with methyl groups indicated by "Me₅."