Supporting Information

Gold-Catalyzed Efficient Synthesis of Azepan-4-ones via A Two-Step [5+2] Annulation

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General. Ethyl acetate (ACS grade), hexanes (ACS grade), diethyl ether (ACS grade), NH₄OH (29.4% in H₂O, ACS reagent) were purchased from Fisher Scientific and used without further purification. Anhydrous dichloromethane (HPLC grade) was purified by distillation over calcium hydride. Tetrahydrofuran was distilled over sodium/benzophenone. Commercially available reagents were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using Silicycle precoated silica gel plates. Flash column chromatography was performed over Silicycle silica gel (230-400 mesh). ¹H NMR and ¹³C NMR spectra were recorded on a Varian 500 MHz Unity plus spectrometer and a Varian 400 MHz spectrometer using residue solvent peaks as internal standards. Infrared spectra were recorded with a Perkin Elmer FT-IR spectrum 2000 spectrometer and are reported in reciprocal centimeter (cm⁻¹). Mass spectra were recorded with Waters micromass ZQ detector using electrospray method.

General procedure A: preparation of N-alkynylpiperidine

Pent-4-yn-1-yl tosylate (2 equiv) was added to a mixture of a secondary amine, NaI (0.5 equiv), and K₂CO₃ (3 equiv) in CH₃CN (0.5 M). The reaction was heated to reflux for 12 h and then cooled to room temperature. The reaction mixture was diluted with CH₂Cl₂ (10 mL/mmol), and the solid was filtered off. The filtrate was concentrated under vacuum, and the residue was dissolved in CH₂Cl₂. The resulting solution was washed with 5% of aqueous NaOH, brine, dried with anhydrous MgSO₄, and concentrated under vacuum. The residue was purified through silica gel flash chromatography.

N-Pent-4-ynylpiperidine (1)

\[
\begin{align*}
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1 & \\
\end{align*}
\]

Compound 1 was prepared in 89% yield according to the general procedure A (eluents: ethyl acetate: methanol: NH₄OH = 10: 1: 0.11). ¹H NMR (400 MHz, CDCl₃) δ 2.36 – 2.39 (m, 6H), 2.21 (td, 2H, J = 7.2, 2.8 Hz), 1.94 (t, 1H, J = 2.4 Hz), 1.67 – 1.75 (m, 2H),
1.54 – 1.61 (m, 4H), 1.41 – 1.44 (m, 2H); 13C NMR (100 MHz, CDCl3) δ 84.1, 68.2, 58.1, 54.5, 25.9, 25.8, 24.3, 16.4; IR (neat): 3312, 2936, 2763, 2739, 2119, 1443, 1352; MS (ES+) Calculated for [C10H18N]+: 152.1; Found: 152.1.

\[ \text{N, N-Dibenzylpent-4-ynylamine} \]

The above compound was prepared in 99 % yield according to the general procedure A (eluents: hexanes: ethyl acetate: Et3N = 10 : 1 : 0.11). 1H NMR (400 MHz, CDCl3) δ 7.22 – 7.36 (m, 10H), 3.55 (s, 4H), 2.50 (t, 2H, J = 6.8 Hz), 2.12 (td, 2H, J = 7.2, 2.4 Hz), 1.85 (t, 1H, J = 2.8 Hz), 1.71 – 1.74 (m, 2H); 13C NMR (125 MHz, CDCl3) δ 139.6, 128.6, 128.1, 126.8, 84.5, 68.1, 58.3, 52.3, 30.9, 26.3, 16.2; IR (neat): 3298, 3085, 3062, 3027, 2949, 2797, 2117, 1494, 1452, 1366; MS (ES+) Calculated for [C19H22N]+: 264.1; Found: 264.1.

\[ \text{N, N-Bis-[2-(tert-butyldimethylsilyloxy)ethyl]pent-4-ynylamine} \]

The above compound was prepared in 98 % yield according to the general procedure A (eluents: hexanes: ethyl acetate: Et3N = 20 : 1 : 0.21). 1H NMR (500 MHz, CDCl3) δ 3.64 (t, 4H, J = 7.0 Hz), 2.59 – 2.65 (m, 6H), 2.21 (td, 2H, J = 2.5, 3.9 Hz), 1.93 (t, 1H, J = 3.5 Hz), 1.62 – 1.68 (m, 2H), 0.89 (s, 18H), 0.02 (s, 12H); 13C NMR (125 MHz, CDCl3) δ 84.5, 68.2, 62.0, 57.2, 54.3, 26.7, 25.9, 18.3, 16.0, -5.3; IR (neat): 3310, 2952, 2931, 2857, 2116, 1468; MS (ES+) Calculated for [C21H46NO2Si2]+: 400.3; Found: 400.3.

\[ \text{N-Pent-4-ynylpyrrolidine} \]
The above compound was prepared in 88 % yield according to the general procedure A (eluents: ethyl acetate : methanol : Et₃N = 1 : 1 : 0.02). ¹H NMR (400 MHz, CDCl₃) δ 2.42 – 2.48 (m, 6H), 2.18 (td, 2H, J = 7.2, 2.8 Hz), 1.89 (t, 1H, J = 2.4 Hz), 1.66 – 1.71 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 84.2, 68.4, 55.4, 54.2, 27.8, 23.4, 16.6; IR (neat): 3309, 2958, 2116, 1466; MS (ES⁺) Calculated for [C₉H₁₆N]⁺: 138.1; Found: 137.7.

**N-Pent-4-ynylazepane**

The above compound was prepared in 83 % yield according to the general procedure A (eluents: hexanes: ethyl acetate: Et₃N = 10: 1 : 0.11). ¹H NMR (400 MHz, CDCl₃) δ 2.62 (t, 4H, J = 4.8 Hz), 2.55 (t, 2H, J = 7.2 Hz), 2.22 (td, 2H, J = 7.2, 2.8 Hz), 1.94 (t, 1H, J = 2.8 Hz), 1.59 – 1.70 (m, 10H); ¹³C NMR (125 MHz, CDCl₃) δ 84.5, 68.1, 56.9, 55.4, 28.1, 27.0, 26.6, 16.3; IR (neat): 3310, 2926, 2857, 2815, 2778, 2116, 1458; MS (ES⁺) Calculated for [C₁₁H₂₀N]⁺: 166.2; Found: 166.2.

**N-Methyl-N-octylpent-4-ynylamine**

The above compound was prepared in 78 % yield according to the general procedure A (eluents: ethyl acetate : methanol: NH₄OH = 10 : 1 : 0.11). ¹H NMR (400 MHz, CDCl₃) δ 2.40 (t, 2H, J = 7.2 Hz), 2.28 (t, 2H, J = 3.6 Hz), 2.20 – 2.24 (m, 5H), 1.94 (t, 1H, J = 2.4 Hz), 1.62 – 1.72 (m, 2H), 1.40 – 1.49 (m, 2H), 1.20 – 1.34 (m, 10H), 0.87 (t, 3H, J = 6.4 Hz), ; ¹³C NMR (125 MHz, CDCl₃) δ 84.2, 68.1, 57.8, 56.3, 42.2, 31.7, 29.5, 29.2, 27.4,

**N-Benzyl-N-methylpent-4-ynylamine**

The above compound was prepared in 85 % yield according to the general procedure A (eluents: hexanes : ethyl acetate : Et₃N = 5 : 1 : 0.06). ¹H NMR (400 MHz, CDCl₃) δ 7.20 – 7.34 (m, 5H), 3.49 (s, 2H), 2.47 (t, 2H, J = 6.8 Hz), 2.25 (td, 2H, J = 7.2, 2.8 Hz), 2.19 (s, 3H), 1.93 (t, 1H, J = 2.8 Hz), 1.70 – 1.78 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 139.2, 128.9, 128.1, 126.8, 84.4, 68.2, 62.3, 56.1, 42.1, 26.4, 16.2; IR (neat): 3302, 2949, 2838, 2790, 2117, 1494, 1453, 1365; MS (ES⁺) Calculated for [C₁₃H₁₈N]⁺: 188.1; Found: 188.1.

**N-Benzyl-N-butylpent-4-ynylamine**

The above compound was prepared in 93 % yield according to the general procedure A (eluents: hexanes : ethyl acetate : Et₃N = 10 : 1 : 0.11). ¹H NMR (500 MHz, CDCl₃) δ 7.23- 7.35 (m, 5H), 3.56 (s, 2H), 2.52 (t, 2H, J = 6.5 Hz), 2.43 (t, 2H, J = 5.5 Hz), 2.23 (td, 2H, J = 7.0, 2.5 Hz), 1.92 (t, 1H, J = 2.5 Hz), 1.67 – 1.73 (m, 2H), 1.44 – 1.50 (m, 2H), 1.29 – 1.34 (m, 2H), 0.90 (t, 3H, J = 7.5 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 140.1, 128.7, 128.0, 126.6, 84.5, 68.1, 58.7, 53.5, 52.5, 29.2, 26.3, 20.5, 16.2, 14.0; IR (neat): 3309, 3027, 2955, 2933, 2799, 2118, 1495, 1453; MS (ES⁺) Calculated for [C₁₆H₂₄N]⁺: 230.2; Found: 230.2.

**N-(2-Bromobenzyl)-N-butylpent-4-ynylamine**

Supplementary Material (ESI) for Chemical Communications

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The above compound was prepared in 91 % yield according to the general procedure A (eluents: hexanes: ethyl acetate: Et$_3$N = 10 : 1 : 0.11). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50 – 7.54 (m, 2H), 7.27 (t, 1H, $J = $ 6.0 Hz), 7.09 (t, 1H, $J = $ 5.6 Hz), 3.63 (s, 2H), 2.56 (t, 2H, $J = $ 5.6 Hz), 2.45 (t, 2H, $J = $ 5.6 Hz), 2.22 (td, 2H, $J = $ 5.6, 2.0 Hz), 1.90 (t, 1H, $J = $ 2.4), 1.63 – 1.71 (m, 2H), 1.43 – 1.49 (m, 2H), 1.26 – 1.34 (m, 2H), 0.87 (t, 3H, $J = $ 6.4 Hz); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 139.3, 132.5, 130.5, 127.9, 127.1, 124.1, 84.5, 68.2, 58.3, 53.9, 52.8, 29.3, 26.4, 20.6, 16.3, 14.0; IR (neat): 3305, 2952, 2931, 2857, 2799, 2121, 1463; MS (ES$^+$) Calculated for [C$_{16}$H$_{23}$BrN]$^+$: 308.1; Found: 308.1.

2-(Pent-4-ynyl)-1,2,3,4-tetrahydroisoquinoline

The above compound was prepared in 80 % yield according to the general procedure A (eluents: hexanes: ethyl acetate: Et$_3$N = 20 : 1 : 0.21). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.00 – 7.13 (m, 4H), 3.63 (s, 2H), 2.90 (t, 2H, $J = $ 5.5 Hz), 2.74 (t, 2H, $J = $ 6.0 Hz), 2.61 (t, 2H, $J = $ 7.5 Hz), 2.29 (td, 2H, $J = $ 2.5, 7.0 Hz), 1.96 (t, 1H, $J = $ 2.5 Hz), 1.81 – 1.86 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 134.8, 134.3, 128.6, 126.5, 126.0, 125.5, 84.2, 68.4, 57.0, 56.2, 50.9, 29.1, 26.1, 16.3; IR (neat): 3296, 3021, 2921, 2804, 2768, 2116, 1498, 1466, 1376; MS (ES$^+$) Calculated for [C$_{14}$H$_{18}$N]$^+$: 200.1; Found: 200.2.

$N$-Benzyl-$N$-(4-methoxybenzyl)pent-4-ynylamine

Supplementary Material (ESI) for Chemical Communications

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The above compound was prepared in 99 % yield according to the general procedure A (eluents: hexanes: ethyl acetate: Et$_3$N = 10 : 1 : 0.11). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.22- 7.35 (m, 7H), 6.84 (d, 2H, $J$ = 8.4 Hz), 3.79 (s, 3H), 3.53 (s, 2H), 3.49 (s, 2H), 2.48 (t, 2H, $J$ = 7.2 Hz), 2.18 (td, 2H, $J$ = 7.6, 2.8 Hz), 1.86 (t, 1H, $J$ = 2.4 Hz), 1.68 – 1.75 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 158.4, 139.6, 131.3, 129.7, 128.6, 128.0, 126.6, 113.4, 84.3, 68.2, 58.0, 57.5, 55.0, 52.0, 26.2, 16.1; IR (neat): 3294, 2931, 2831, 2794, 2115, 1610, 1515, 1463; MS (ES$^+$) Calculated for [C$_{20}$H$_{23}$NO+H]$^+$: 294.2; Found: 294.2.

**Ethyl butylpent-4-ynylaminoacetate**

![Ethyl butylpent-4-ynylaminoacetate](image)

The above compound was prepared in 90 % yield according to the general procedure A (eluents: ethyl acetate : methanol : NH$_4$OH = 10 : 1 : 0.11). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 4.13 (dd, 2H, $J$ = 14.0, 7.5 Hz), 3.29 (s, 2H), 2.66 (t, 2H, $J$ = 6.5 Hz), 2.54 (t, 2H, $J$ = 8.0 Hz), 2.21 (td, 2H, $J$ = 2.5, 7.0 Hz), 1.92 (t, 1H, $J$ = 2.5 Hz), 1.62 – 1.67 (m, 2H), 1.39 – 1.43 (m, 2H), 1.23 – 1.31 (m, 5H), 0.88 (t, 3H, $J$ = 7.0 Hz); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 171.6, 84.3, 68.2, 60.1, 55.1, 54.0, 53.1, 29.7, 26.6, 20.4, 16.0, 14.2, 13.9; IR (neat): 3308, 2956, 2933, 2861, 2117, 1738, 1457; MS (ES$^+$) Calculated for [C$_{13}$H$_{24}$NO$_2$]$^+$: 226.2; Found: 226.2.

**2-Methyl-1-(pent-4-ynyl)piperidine**

![2-Methyl-1-(pent-4-ynyl)piperidine](image)

The above compound was prepared in 87 % yield according to the general procedure A (eluents: hexanes : ethyl acetate= 10: 1, then hexanes : ethyl acetate : Et$_3$N = 4 : 1 : 0.05). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.72 – 2.87 (m, 2H), 2.40 – 2.47 (m, 1H), 2.13 – 2.30 (m, 4H), 1.94 (t, 1H, $J$ = 2.8 Hz), 1.51 – 1.72 (m, 6H), 1.26 – 1.31 (m, 2H), 1.07 (d, 3H, $J$ = 6.4 Hz); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 84.3, 68.3, 55.8, 52.8, 52.2, 34.6, 26.1, 24.5,
24.0, 19.1, 16.5; IR (neat): 3309, 2937, 2858, 2118, 1469, 1378; MS (ES⁺) Calculated for [

**4-Methyl-1-(pent-4-ynyl)piperidine**

The above compound was prepared in 84 % yield according to the general procedure A (eluents: hexanes : ethyl acetate : Et₃N = 3 : 1 : 0.04). ¹H NMR (500 MHz, CDCl₃) δ 2.86 (d, 2H, J = 11.5 Hz ), 2.39 (m, 2H), 2.21 (td, 2H, J = 7.0, 2.5 Hz), 1.88 – 1.94 (m, 3H), 1.69 – 1.75 (m, 2H), 1.59 – 1.62 (m, 2H), 1.32 – 1.36 (m, 1H), 1.19 – 1.27 (m, 2H), 0.91 (d, 3H, J = 11.5 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 84.3, 68.3, 57.9, 54.0, 34.3, 30.8, 26.0, 21.9, 16.6, 16.5; IR (neat):3310, 2947, 2926, 2116, 1452; MS (ES⁺) Calculated for [C₁₁H₂₀N⁺]: 166.2; Found: 165.9.

**Methyl 1-(pent-4-ynyl)pyrrolidine-2-carboxylate**

The above compound was prepared in 90 % yield according to the general procedure A using methyl prolinate hydrochloride as the starting material (eluents: ethyl acetate : methanol : NH₄OH = 9 : 1 : 0.1). ¹H NMR (500 MHz, CDCl₃) δ 3.68 (s, 3H), 3.11 – 3.15 (m, 2H), 2.69 – 2.75 (m, 1H), 2.44 – 2.49 (m, 1H), 2.29 – 2.34 (m, 1H), 2.18 – 2.23 (m, 2H), 2.05 – 2.09 (m, 1H), 1.87 – 1.91 (m, 3H), 1.75 – 1.80 (m, 1H), 1.65 – 1.71 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 174.7, 84.0, 68.3, 66.0, 53.7, 53.4, 51.7, 29.2, 27.5, 23.2, 16.3; IR (neat): 3304, 3053, 2953, 2811, 2117, 1742, 1435; MS (ES⁺) Calculated for [C₁₁H₁₈NO₂⁺]: 196.1; Found: 196.1.

**Preparation of N-benzyl-N-(2-ethylpent-4-ynyl)methylamine (7)**
Benzylmethylamine (3.87 mL, 30 mmol) and NEt₃ (4.9 mL, 35 mmol) in CH₂Cl₂ (40 mL) was added dropwise to a solution of butyryl chloride (3.6 mL, 35 mmol) in CH₂Cl₂ (20 mL) at 0 °C. The mixture was stirred at room temperature for 5 h. The reaction mixture was treated with aqueous NH₄Cl (1N, 20 mL) and was extracted with CH₂Cl₂ (3 × 30 mL). The combined organic phase was dried and concentrated. The residue was purified through silica gel flash chromatography (eluents: hexanes : ethyl acetate = 5 : 1) to give compound 7a (5.73 g, 28.5 mmol) in 95% yield.

At –78 °C, a solution of amide 7a (2.0 g, 10.5 mmol) in THF (10 mL) was added dropwise to a THF solution of LDA (50 mL, 0.25 M in THF). The resulting mixture was stirred at –78 °C for 2 h before the addition of propargyl bromide (1.12 mL, 12.6 mmol). The reaction mixture was allowed to warm to room temperature overnight. The mixture was quenched by 1 N NH₄Cl (20 mL) and extracted with Et₂O (3 × 30 mL). The combined organic phases were washed with brine, dried with anhydrous MgSO₄ and filtered. The filtrate was concentrated, and the resulting residue was purified through silica gel flash column (eluents: hexanes: ethyl acetate = 10:1) to afford amide 7b (1.88 g, 8.19 mmol) in 78 % yield.

To a solution of compound 7b (1.306 g, 5.6 mmol) in THF (75 mL) was added LAH (0.64 g, 16.8 mmol) at 0 °C. The resulting mixture was refluxed overnight and then diluted with ether (50 mL). Upon cooling to 0 °C, the reaction mixture was treated dropwise and sequentially with 0.64 mL water, 0.64 mL 15 % aqueous sodium hydroxide and 1.92 mL water and then stirred at room temperature for 15 min. After removal of the white solids via filtration, the filtrate was concentrated, and the resulting residue was
purified through silica gel flash column (eluents: hexanes: ethyl acetate : Et$_3$N = 10 : 1 : 0.11) to afford tertiary amine 7 (0.71 g, 3.30 mmol) in 59% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.24 – 7.35 (m, 5H), 3.54 (d, 1H, $J = 13.0$ Hz), 3.46 (d, 1H, $J = 13.0$ Hz), 2.25 – 2.40 (m, 4H), 2.18 (s, 3H), 1.91 (td, 1H, $J = 3.0$ Hz), 1.73 (m, 1H), 1.48 (m, 2H), 0.94 (t, 3H, $J = 7.5$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 139.5, 128.9, 128.1, 126.8, 83.0, 69.0, 62.9, 60.9, 42.5, 36.9, 24.2, 20.5, 11.1; IR (neat): 3307, 2963, 2841, 2794, 2114, 1454, 1380; MS (ES$^+$) Calculated for [C$_{15}$H$_{22}$N]$^+$: 216.2; Found: 216.2.

Preparation of N-benzyl-N-(1-but-3-ynylheptyl)methylamine (9)

$m$-CPBA (4.93 g, 22 mmol) was added to a solution of 1-octene (2.24 g, 20 mmol) in H$_2$O (20 mL) at 0 °C. The reaction was vigorously stirred at 0 °C for 4 h and at room temperature for 2 h. The reaction mixture was extracted twice with diethyl ether (2 x 100 mL). The combined organic phases were washed sequentially with a cooled solution of 10% NaOH (20 mL) and saturated brine (20 mL) and dried with Na$_2$SO$_4$. Subsequent filtration and concentration afford practically pure 9a (1.72 g, 13.4 mmol) in 67% yield.

To a solution of 9a (1.0 g, 5.8 mmol) and ZnCl$_2$ (79 mg, 0.58 mmol) in diethyl ether (6 mL) at -78 °C was added propargylmagnesium bromide (20 mL, 1 M solution in diethyl ether, 20 mmol). The reaction was slowly warmed to room temperature and further stirred for 6 h. The reaction was then quenched with aq. NH$_4$Cl (20 mL), and the resulting mixture was extracted with diethyl ether (50 mL × 2). The combined organic phases were dried (Na$_2$SO$_4$) and filtered. The filtrate was concentrated to afford alcohol 9b (1.1g), which was used in the next step without further purification.
A solution of dry DMSO (1.0 g, 12.7 mmol) in CH$_2$Cl$_2$ (5 mL) was added dropwise to a stirred solution of oxalyl chloride (0.36 g, 6.4 mmol) in CH$_2$Cl$_2$ (15 mL) under N$_2$ at -78 °C. The solution was stirred for 0.5 h before the slow addition of a solution of 9b (0.974 g, 5.8 mmol) in CH$_2$Cl$_2$ (10 mL). The reaction mixture was stirred for 1 h at -78 °C and then treated drop-wise with NEt$_3$ (4 mL, 29 mmol). The reaction mixture was warmed to room temperature over 0.5 h before addition of water (30 mL). The mixture was extracted with CH$_2$Cl$_2$ (3 × 50 mL), and the combined organic phases were washed with brine, dried (MgSO$_4$) and filtered. The filtrate was concentrated under vacuum. The resulting residue was purified through silica gel flash column (eluents: hexanes: ethyl acetate = 5:1) to afford ketone 9c (0.65 g, 3.89 mmol) in 67 % yield.

Benzylamine (0.197 g, 1.84 mmol) and ketone 9c (0.278 g, 1.67 mmol) were mixed in 1,2-dichloroethane (10 mL) and then treated with sodium triacetoxyborohydride (0.7 g, 3.32 mmol) and AcOH (0.5 mL) at 0 °C. The mixture was stirred at room temperature for 12 h. The reaction mixture was quenched by the addition of 1 N aqueous NaOH (10 mL) and then extracted with CH$_2$Cl$_2$ (3 × 20 mL). The organic phases were combined and washed with brine and dried (MgSO$_4$). Upon filtration, the filtrate was evaporated to give amine 9d (0.357 g, 1.39 mmol, 83% yield), which was used in the next step without further purification.

MeI (0.088 mL, 1.42 mmol) was added to a mixture of a 9d (0.303 g, 1.18 mmol), K$_2$CO$_3$ (0.85 g, 4.72 mmol) in CH$_3$CN (30 mL). The reaction was heated to reflux for 4 h and then the reaction was cooled to room temperature. The reaction mixture was diluted with CH$_2$Cl$_2$ (20 mL), and the solids were filtered off. The filtrate was washed with 5 % of aqueous NaOH (15 mL), brine, and dried with anhydrous MgSO$_4$, and filtered. The filtrate was concentrated under vacuum. The residue was purified through silica gel flash column (eluents: hexanes: ethyl acetate : Et$_3$N = 5:1:0.06) to afford tertiary amine 9 (0.288 g, 1.06 mmol) in 90 % yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.24 – 7.36 (m, 5H), 3.62 (d, 1H, $J$ = 13.5 Hz), 3.56 (d, 1H, $J$ = 13.5 Hz), 2.62 – 2.65 (m, 1H), 2.28 – 2.40 (m, 2H), 2.15 (s, 3H), 1.96 (t, 1H, $J$ = 2.5 Hz), 1.59 – 1.74 (m, 3H), 1.24 – 1.38 (m, 9H),
0.94 (t, 3H, J = 7.0 Hz); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 140.5, 128.5, 128.1, 126.6, 85.0, 68.0, 61.6, 58.1, 35.9, 31.8, 29.7, 29.5, 28.6, 27.2, 22.6, 16.1, 14.1; IR (neat): 3310, 2931, 2857, 2789, 2121, 1457; MS (ES$^+$) Calculated for [C$_{19}$H$_{30}$N]$^+$: 272.2; Found: 272.2.

**Preparation of N-benzyl-N-(3-ethynloctyl)methylamine (11)**

3-Pentyl-4-pentyn-1-ol was synthesized according to the literature procedure (Miura, K.; Wang, D.; Matsumoto, Y.; Hosomi, A. *Org. Lett.* **2005**, 7, 503-505). 3-Pentyl-4-pentyn-1-ol (0.820 g, 5.32 mmol), CBr$_4$ (3.182 g, 9.58 mmol), and 2,6-lutidine (3.03 mL, 26.1 mmol) were mixed at 0 °C in CH$_2$Cl$_2$ (30 mL) and then treated drop-wise with a solution of PPh$_3$ (2.788 g, 10.64 mmol) in CH$_2$Cl$_2$ (10 ml). The reaction mixture was stirred for 5 h prior to concentration, addition of ether, and removal of solid by filtration through Celite. The solution was washed with 1N HCl, dried with anhydrous MgSO$_4$, and concentrated. The residue was purified through silica gel flash chromatography (eluents: hexanes: ethyl acetate : Et$_3$N = 5 : 1 : 0.06) to give bromide 11a which used directly in the next step.

Compound 11a was added to a mixture of benzylmethyl amine (0.752 mL, 5.83 mmol), NaI (0.40 g, 2.67 mmol), and K$_2$CO$_3$ (3.8 g, 21.1 mmol) in CH$_3$CN (50 mL). The reaction was heated to reflux for 12 h and then cooled to room temperature. The reaction mixture was diluted with CH$_2$Cl$_2$ (50 mL), and the solids were filtered off. The filtrate was concentrated under vacuum. The residue was dissolved in CH$_2$Cl$_2$, and washed with 5 % aqueous NaOH. The organic layer was dried with anhydrous MgSO$_4$ and concentrated under vacuum. The residue was purified through silica gel flash chromatography (eluents:
hexanes : ethyl acetate : Et₃N = 3 : 1 : 0.04) to yield tertiary amine 11 in 79% yield in two steps. "H NMR (400 MHz, CDCl₃) δ 7.24 – 7.33 (m, 5H), 3.47 – 3.55 (m, 2H), 2.55 (t, 2H, J = 7.2 Hz), 2.43 – 2.49 (m, 1H), 2.20 (s, 3H), 2.02 (t, 1H, J = 2.4 Hz), 1.28 – 1.71 (m, 10H), 0.91 (t, 3H, J = 6.8 Hz); "C NMR (125 MHz, CDCl₃) δ 139.3, 129.2, 128.3, 127.0, 88.0, 69.3, 62.6, 55.4, 42.4, 35.0, 32.9, 31.8, 29.5, 27.0, 22.7, 14.2; IR (neat): 3305, 2931, 2857, 2789, 2110, 1455; MS (ES⁺) Calculated for [C₁₈H₂₈N]⁺: 258.2; Found: 258.2.

General procedure B: Preparation of Azepan-4-ones

\[
\begin{align*}
\text{R}^N & \text{m-CPBA (1.0 equiv), 4 Å MS, 0 °C, 1 h} \\
\text{then, (2-biphenyl)Cy₂PAuNTf₂ (5 mol %), 2h} \\
\end{align*}
\]

\( m\text{-CPBA (1.0 equiv) was added into a mixture of a pent-4-yn-1-ylamine and 4 Å MS (5 x weight of } m\text{-CPBA) in CH₂Cl₂ (0.05 M) under N₂ at 0 °C. The } N\text{-oxide formation was monitored by TLC. Upon completion (~1 h), (2-biphenyl)Cy₂PAuNTf₂ (5 mol %) was added and the reaction mixture was stirred at 0 °C until all the } N\text{-oxide was consumed (~2 h). The reaction mixture was diluted with } CH₂Cl₂, \text{ and the molecular sieves were filtered off. The filtrate was washed with 5 % aqueous Na₂CO₃, dried with Na₂SO₄, and concentrated under vacuum. The residue was purified through silica gel flash chromatography.} \)

Octahydropyrido[1,2-\(a\)]azepin-9-one (2)

![Structure of Octahydropyrido[1,2-\(a\)]azepin-9-one (2)](image)

Compound 2 was prepared in 79 % yield according to the general procedure B. The reaction times are 1 h for the formation of N-oxide and 2 h for Au catalysis. The residue was purified through silica gel flash chromatography (eluents: ethyl acetate: methanol : NH₄OH = 2 : 1 : 0.03). "H NMR (400 MHz, CDCl₃) δ 3.03 (dd, 1H, J = 7.6, 13.6 Hz), 2.86 – 2.94 (m, 2H), 2.55 (dt, 1H, J = 5.0, 16.8 Hz), 2.02- 2.42 (m, 6H), 1.89 – 1.96 (m,
$^{1}$H), 1.55 – 1.73 (m, 4H), 1.35 – 1.45 (m, 1H), 1.24 – 1.32 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 212.8, 60.9, 59.5, 56.8, 51.5, 42.3, 34.8, 25.6, 24.0, 23.0; IR (neat): 2934, 2807, 2770, 1707, 1444, 1348; MS (ES$^+$) Calculated for [C$_{10}$H$_{18}$NO]$^+$: 168.1; Found: 167.9.

**Decahydropyrido[1,2-a]azepine (4)**

![Chemical Structure](image)

To a solution of 2 (55.1 mg, 0.33 mmol) in dry CH$_2$Cl$_2$ (6 mL) was added 1,2-ethanedithiol (0.27 mL, 10 equiv) and boron trifluoride etherate (0.103 mL, 2.5 equiv). The mixture was stirred for 2 h and then quenched with 1 N NaOH (5 mL). The aqueous phase was extracted with CH$_2$Cl$_2$ (3 x 10 mL). The combined organic layers were washed with 1 N NaOH (5 mL), dried Na$_2$SO$_4$ and concentrated. The crude product was purified by silica column chromatography (eluents: ethyl acetate: methanol : NH$_4$OH = 1: 1: 0.02) to give 2a (62.4 mg, 0.26 mmol) in 78% yield.

To a solution of 2a (62.4 mg, 0.26 mmol) in absolute methanol (5 mL) was added Raney nickel (1.8 g) under H$_2$ atmosphere and heated to reflux for 2 h. The reaction mixture was filtered through Celite and washed with diethyl ether. The filtrate was concentrated and purified by silica column chromatography (eluents: ethyl acetate: methanol : Et$_3$N = 1: 3: 0.04) to give 4 (41.1 mg, 0.17 mmol) in 65% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 2.84 (d, 1H, $J$ = 11.0 Hz), 2.72 – 2.74 (m, 1H), 2.47 (t, 1H, $J$ = 12.5 Hz), 2.22 – 2.27 (m, 1H), 1.96 – 2.40 (m, 1H), 1.67 – 1.76 (m, 4H), 1.49- 1.66 (m, 8H), 1.30 – 1.42 (m, 1H), 1.21 – 1.28 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 65.6, 57.5, 35.4, 34.4, 27.1, 26.8, 26.1, 24.9, 24.5; IR (neat): 2930, 2854, 2762, 1467, 1442, 1367; MS (ES$^+$) Calculated for [C$_{10}$H$_{20}$N]$^+$: 154.2; Found: 154.2.

**N-Benzyl-2-phenylazepan-4-one (6a)**
Compound 6a was prepared in 87% yield according to the general procedure B. The reaction times are 1 h for the formation of N-oxide and 2 h for Au catalysis. The residue was purified through silica gel flash chromatography (eluents: hexanes : ethyl acetate: NEt$_3$ = 10:1:0.11). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.44 (d, 2H, J = 9.0 Hz), 7.37 (t, 2H, J = 7.0 Hz), 7.20 – 7.30 (m, 6H), 4.00 (dd, 1H, J = 4.0, 9.5 Hz), 3.61 (d, 1H, J = 13.5 Hz), 3.34 (d, 1H, J = 14.0 Hz), 3.09 – 3.36 (m, 2H), 2.77 (dd, 1H, J = 4.5, 14.0 Hz), 2.51 – 2.60 (m, 3H), 1.97 – 2.01 (m, 1H), 1.85 – 1.90 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 211.9, 142.4, 139.5, 128.6, 128.4, 128.3, 128.2, 127.4, 126.9, 64.2, 57.1, 50.9, 49.0, 42.4, 22.2; IR (neat): 3084, 3061, 3027, 2935, 2810, 1705, 1494, 1451; MS (ES$^+$) Calculated for [C$_{19}$H$_{21}$NNaO]$^+$: 302.2; Found: 302.2.

**N-[2-(tert-Butyldimethylsilanyloxy)ethyl]-2-(tert-butyldimethylsilanyloxymethyl)azepan-4-one (6b)**

Compounds 6b were prepared in 51% yield according to the general procedure B. The reaction time is 1 h for the formation of N-oxide and 8 h for Au catalysis. The residue was purified through silica gel flash chromatography (eluents: hexanes : ethyl acetate: Et$_3$N = 10:1:0.11). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 3.70 (dd, 1H, J = 5.2, 9.6 Hz), 3.57 (t, 2H, J = 6.4 Hz), 3.47 – 3.51 (m, 1H), 3.17 – 3.26 (m, 2H), 2.84 – 2.91 (m, 1H), 2.57 – 2.72 (m, 5H), 2.41 – 2.47 (m, 1H), 1.84 – 1.93 (m, 1H), 1.59 (m, 1H), 0.88 (s, 18H), 0.04 (s, 12H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 213.0, 64.9, 62.8, 60.0, 52.9, 51.5, 44.7, 42.9, 25.9, 25.8, 21.8, 18.3, 18.2, –5.3, –5.4, –5.5; IR (neat): 2953, 2929, 2857, 1705, 1646, 1471; MS (ES$^+$) Calculated for [C$_{21}$H$_{46}$NO$_3$Si$_2$]$^+$: 416.3; Found: 416.3.

**Hexahydropyrrolo[1,2-a]azepin-8-one (6c)**
Compounds 6c were prepared in 80% yield according to the general procedure B. The reaction time is 1 h for the formation of N-oxide and 2 h for Au catalysis. The residue was purified through silica gel flash chromatography (eluents: ethyl acetate : methanol : NH₄OH = 5 : 1 : 0.06). ^1H NMR (400 MHz, CDCl₃) δ 3.28 – 3.33 (m, 1H), 3.17 – 3.22 (m, 1H), 2.26 – 2.71 (m, 7H), 1.83 – 2.06 (m, 4H), 1.68 – 1.75 (m, 1H), 1.55 – 1.61 (m, 1H); ^13C NMR (125 MHz, CDCl₃) δ 212.2, 60.4, 57.3, 56.6, 50.0, 43.2, 32.8, 24.3, 21.8; IR (neat): 2930, 2853, 1708, 1556, 1376, 1352; MS (ES^+) Calculated for [C₉H₁₆NO]^+: 154.1; Found: 153.8.

Octahydroazepino[1,2-a]azepin-2-one (6d)

Compounds 6d were prepared in 89% yield according to the general procedure B. The reaction time is 1 h for the formation of N-oxide and 2 h for Au catalysis. The residue was purified through silica gel flash chromatography (eluents: hexanes: ethyl acetate: Et₃N = 1 : 1 : 0.02). ^1H NMR (500 MHz, CDCl₃) δ 3.09 – 3.15 (m, 1H), 2.97 – 3.03 (m, 1H), 2.71 – 2.92 (m, 3H), 2.48 – 2.62 (m, 3H), 2.36 – 2.43 (m, 1H), 1.70 – 1.84 (m, 4H), 1.55 – 1.62 (m, 1H), 1.24 – 1.48 (m, 5H); ^13C NMR (125 MHz, CDCl₃) δ 212.7, 59.9, 56.2, 53.0, 51.7, 42.1, 34.6, 28.5, 28.3, 26.8, 24.9 ; IR (neat): 2923, 2850, 1703, 1446, 1404; MS (ES^+) Calculated for [C₁₁H₂₀NO]^+: 182.2; Found: 182.2.

N-Octylazepan-4-one (6e)
Compounds 6e were prepared in 69 % yield according to the general procedure B. The reaction time is 1 h for the formation of N-oxide and 2 h for Au catalysis. The residue was purified through silica gel flash chromatography (eluents: hexanes : ethyl acetate : Et₃N = 2 : 1 : 0.03). ¹H NMR (400 MHz, CDCl₃) δ 2.71 – 2.75 (m, 4H), 2.60 – 2.63 (m, 2H), 2.50 – 2.53 (m, 2H), 2.46 (t, 2H, J = 7.2 Hz), 1.79 – 1.84 (m, 2H), 1.43 – 1.47 (m, 2H), 1.24 – 1.30 (m, 10H), 0.87 (t, 3H, J = 6.8 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 213.6, 58.1, 57.9, 50.6, 44.2, 42.9, 31.8, 29.5, 29.2, 27.4, 27.3, 23.9, 22.6, 14.1; IR (neat): 2929, 2856, 1702, 1467; MS (ES⁺) Calculated for [C₁₄H₂₈NO]⁺: 226.2; Found: 226.2.

N-Benzylazepan-4-one (6f)

Compounds 6f were prepared in 85 % yield according to the general procedure B. The reaction time is 1 h for the formation of N-oxide and 2 h for Au catalysis. The residue was purified through silica gel flash chromatography (eluents: hexanes : ethyl acetate : Et₃N = 5 : 1 : 0.06). ¹H NMR (400 MHz, CDCl₃) δ 7.25 – 7.33 (m, 5H), 3.65 (s, 2H), 2.71 – 2.76 (m, 4H), 2.59 – 2.62 (m, 2H), 2.52 – 2.55 (m, 2H), 1.82 – 1.88 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 213.5, 138.9, 128.7, 128.3, 127.1, 62.7, 57.9, 50.4, 44.3, 42.9, 24.1; IR (neat): 2939, 2813, 1702, 1453, 1351; MS (ES⁺) Calculated for [C₁₃H₁₈NO]⁺: 204.1; Found: 204.1.

N-Benzyl-2-propylazepan-4-one (6g)
Compounds 6g and 6g' were prepared in 73 % combined yield (ratio: 6g : 6g' = 2 : 1) according to the general procedure B. The reaction time is 1 h for the formation of N-oxide and 6 h for Au catalysis. PEt₃AuNTf₂ was used as Au catalyst. The residue was purified through silica gel flash chromatography (eluents: hexanes: ethyl acetate : NEt₃ = 10 : 1 : 0.11) to afford some 6g pure along with a mixture of 6g and 6g'. 6g: ¹H NMR (400 MHz, CDCl₃) δ 7.22 – 7.33 (m, 5H), 3.78 (d, 1H, J = 13.6 Hz), 3.58 (d, 1H, J = 13.6 Hz), 3.15 – 3.18 (m, 1H), 2.96 (dt, 1H, J = 4.0, 14.0 Hz), 2.71 – 2.78 (m, 2H), 2.63 – 2.55 (m, 2H), 2.37 – 2.44 (m, 1H), 1.79 – 1.88 (m, 1H), 1.59 – 1.74 (m, 1H), 1.35 – 1.43 (m, 4H), 0.91 (t, 3H, J = 6.8 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 213.1, 139.8, 128.4, 128.3, 126.9, 57.6, 53.9, 50.1, 47.6, 42.6, 33.7, 20.9, 19.9, 14.0; IR (neat): 2955, 2931, 1698, 1455; MS (ES⁺) Calculated for [C₁₆H₂₄NO]⁺: 246.2; Found: 246.2.

**N-Benzyl-2-propylazepan-4-one (6g)** and **N-butyl-2-phenylazepan-4-one (6g')**

A mixture of 6g and 6g': ¹H NMR (400 MHz, CDCl₃) δ 7.18– 7.31 (m, 8.3 H), 3.89 (dd, 0.86 H, J = 10.4, 4.4 Hz), 3.73 (d, 1H, J = 13.6 Hz), 3.53 (d, 1H, J = 13.6 Hz), 3.19 (ddd, 1.03 H, J = 3.6, 10.4, 14.4 Hz), 3.10– 3.13 (m, 1.03 H), 3.01 (dd, 0.99 H, J = 10.0, 14.4 Hz), 2.92 (m, 1.06 H), 2.59 –2.73 (m, 4.13 H), 2.44 – 2.56 (m, 4.24 H), 2.31– 2.39 (m, 2.28 H), 2.21– 2.27 (m, 1H), 1.75 – 1.98 (m, 3.38 H), 1.67 – 1.74 (m, 1.23 H), 1.55 – 1.59 (m,1.03 H), 1.26 – 1.38 (m, 5.25 H), 1.09 – 1.41 (m, 2.21 H), 0.87 (t, 2.93 H, J = 7.2 Hz), 0.73 (t, 2.49 H, J = 7.6 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 213.1, 212.2, 142.8, 139.8, 128.4, 128.4, 128.3, 127.2, 127.0, 126.9, 63.7, 57.6, 53.9, 53.4, 51.9, 51.0, 50.1, 49.1, 47.6, 42.7, 42.6, 33.7, 29.5, 22.5, 20.9, 20.2, 19.9, 14.0, 13.9; IR (neat): 2955, 2930, 1698, 1455; MS (ES⁺) Calculated for [C₁₆H₂₄NO]⁺: 246.2; Found: 246.2.
**N-(2-Bromobenzyl)-2-propylazepan-4-one (6h)**

Compounds 6h were prepared in 71% yield according to the general procedure B. The reaction time is 1 h for the formation of N-oxide and 8 h for Au catalysis. The residue was purified through silica gel flash chromatography (eluents: hexanes: ethyl acetate: NEt3 = 10 : 1 : 0.11). ¹H NMR (500 MHz, CDCl₃) δ 7.50 (dd, 1H, J = 7.6, 1.2 Hz), 7.45 (dd, 1H, J = 2.5, 9.5 Hz), 7.28 (td, 1H, J = 7.2, 1.2 Hz), 7.09 (td, 1H, J = 1.4, 8.4 Hz), 3.78 (s, 2H), 3.07 – 3.12 (m, 1H), 2.96 – 3.02 (m, 1H), 2.76 – 2.82 (m, 2H), 2.56 – 2.58 (m, 2H), 2.37 – 2.44 (m, 1H), 1.79 – 1.90 (m, 2H), 1.59 – 1.64 (m, 1H), 1.32 – 1.45 (m, 3H), 0.89 (t, 3H, J = 7.2 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 212.8, 138.6, 132.6, 130.3, 128.2, 127.2, 124.1, 57.7, 54.4, 50.1, 47.4, 42.5, 33.4, 21.4, 19.8, 14.0; IR (neat): 2954, 2860, 2804, 1699, 1566, 1457, 1437, 1363; MS (ES⁺) Calculated for [C₁₆H₂₃BrNO]⁺: 324.1; Found: 324.1.

**1,4,5,7,8,12b-Hexahydro-3H-azepino[2,1-a]isoquinolin-2-one (6i)**

Compounds 6i were prepared in 70% yield according to the general procedure B. The reaction time is 1 h for the formation of N-oxide and 8 h for Au catalysis. The residue was purified through silica gel flash chromatography (eluents: hexanes: ethyl acetate: Et₃N = 1 : 1 : 0.02). ¹H NMR (500 MHz, CDCl₃) δ 7.07-7.18 (m, 4H), 4.00 (dd, 1H, J = 2.8, 9.6 Hz), 3.18 – 3.23 (m, 1H), 3.07 – 3.11 (m, 1H), 2.93 – 3.00 (m, 2H), 2.58 – 2.86 (m, 6H), 1.84 – 2.04 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 211.8, 138.0, 134.8, 128.5, 126.9, 126.1, 59.8, 59.0, 53.5, 50.5, 42.2, 29.8, 23.0; IR (neat): 2935, 2817, 1698, 1493, 1452, 1363; MS (ES⁺) Calculated for [C₁₄H₁₈NO]⁺: 216.1; Found: 216.1.
Compounds 6j and 6j' were prepared in 63% combined yield (ratio = 1.3 : 1) according to the general procedure B. The reaction time is 1 h for the formation of N-oxide and 2 h for Au catalysis. The residue was purified through silica gel flash chromatography (eluents: hexanes: ethyl acetate : Et₃N = 10 : 1 : 0.11). ¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, 1.14 H, J = 6.8 Hz), 7.36 (t, 1.89 H, J = 7.2 Hz), 7.19 – 7.34 (m, 2.90 H), 7.14 (d, 1.09 H, J = 8.8 Hz), 6.89 (d, 0.70 H, J = 8.8 Hz), 6.82 (d, 1.06 H, J = 9.2 Hz), 3.95 – 4.00 (m, 0.95 H), 3.80 (s, 1.22 H), 3.78 (s, 1.64 H), 3.52 – 3.61 (m, 1.0 H), 3.27 – 3.35 (m, 0.97 H), 3.06 – 3.19 (m, 1.93 H), 2.76 (dd, 0.96 H, J = 4.4, 13.6 Hz), 2.49 – 2.59 (m, 2.95 H), 1.96 – 2.02 (m, 1.05 H), 1.84 – 1.90 (m, 1.08 H); ¹³C NMR (125 MHz, CDCl₃) δ 212.2, 212.1, 158.8, 158.6, 142.4, 139.6, 134.3, 131.4, 129.5, 128.6, 128.4, 128.3, 127.4, 127.3, 126.8, 113.9, 113.6, 64.0, 63.4, 56.8, 56.4, 55.2, 55.2, 50.7, 50.5, 49.0, 48.9, 42.4, 42.3, 22.2; IR (neat): 2930, 1701, 1698, 1646, 1455; MS (ES⁺) Calculated for [C₂₀H₂₄NO₂]⁺: 310.2; Found: 310.2.

Ethyl (4-oxo-2-propylazepan-1-yl)acetate (6k) and ethyl 1-butyl-4-oxoazepane-2-carboxylate (6k’)

Compounds 6k and 6k’ were prepared in 93% combined yield (ratio: 6j : 6j’ = 5 : 1) according to the general procedure B. The reaction time is 1 h for the formation of N-oxide and 2 h for Au catalysis. PEt₃AuNTf₂ was used as Au catalyst. These two products
were separated through silica gel flash chromatography (eluents: hexanes: ethyl acetate : Et₃N = 5 : 1 : 0.06).

Compound 6k:

1H NMR (500 MHz, CDCl₃) δ 4.15 (dd, 2H, J = 6.8, 14.0 Hz), 7.38 (dd, 2H, J = 16.8, 32.8 Hz), 3.08 – 3.18 (m, 2H), 2.91 – 2.98 (m, 1H), 2.59 – 2.72 (m, 2H), 2.39 – 2.53 (m, 2H), 1.72 – 1.82 (m, 2H), 1.46 – 1.52 (m, 1H), 1.32 – 1.39 (m, 3H), 1.26 (t, 3H, J = 8.5 Hz), 0.90 (t, 3H, J = 6.8 Hz); 13C NMR (125 MHz, CDCl₃) δ 212.5, 171.7, 60.6, 58.0, 52.6, 51.6, 47.8, 42.8, 34.8, 21.6, 19.7, 14.2, 14.0; IR (neat): 2934, 1744, 1698, 1456; MS (ES⁺) Calculated for [C₁₃H₂₄NO₃]⁺: 242.2; Found: 242.2.

Compound 6k⁺:

1H NMR (500 MHz, CDCl₃) δ 4.13 – 4.24 (m, 2H), 3.74 (t, 1H, J = 8.0 Hz), 3.03 – 3.09 (m, 2H), 2.79 – 2.86 (m, 1H), 2.71 – 2.74 (m, 1H), 2.56 – 2.66 (m, 2H), 2.42 – 2.51 (m, 2H), 1.71- 1.98 (m, 2H), 1.38- 1.45 (m, 2H), 1.23- 1.36 (m, 5H), 0.88 (t, 3H, J = 7.2 Hz); 13C NMR (125 MHz, CDCl₃) δ 210.7, 171.8, 60.7, 60.4, 54.8, 50.7, 44.3, 42.3, 30.4, 23.2, 20.2, 14.4, 13.9; IR (neat): 2957, 1725, 1540, 1456, 1363; MS (ES⁺) Calculated for [C₁₃H₂₄NO₃]⁺: 242.2; Found: 242.2.

(4S*,10aR*)-4-Methyloctahydropyrido[1,2-a]azepin-9-one (6l)

![Chemical Structure](image)

Compounds 6l were prepared in 74 % yield according to the general procedure B. The reaction time is 1 h for the formation of N-oxide and 4 h for Au catalysis. The residue was purified through silica gel flash chromatography (eluents: ethyl acetate : methanol : NH₄OH = 5 : 1 : 0.06). 1H NMR (500 MHz, CDCl₃) δ 3.16 (q, 1H, J = 6.8 Hz), 2.97-3.06 (m, 3H), 2.39 – 2.62 (m, 3H), 2.26 – 2.32 (m, 1H), 1.91 – 2.02 (m, 1H), 1.34 – 1.77 (m, 7H), 1.13 (d, 3H, J = 7.2 Hz); 13C NMR (125 MHz, CDCl₃) δ 213.0, 54.2, 54.1, 52.4, 48.7, 42.9, 33.8, 33.1, 21.2, 19.0, 14.6 ; IR (neat): 2931, 1704, 1446, 1372, 1347; MS (ES⁺) Calculated for [C₁₁H₂₀NO]⁺: 182.2; Found: 182.0.
Compounds 6m were prepared in 76 % yield according to the general procedure B. The reaction time is 1 h for the formation of N-oxide and 4 h for Au catalysis. The residue was purified through silica gel flash chromatography (eluents: ethyl acetate : methanol : NH₄OH = 5 : 1 : 0.06). ¹H NMR (500 MHz, CDCl₃) δ 3.08 – 3.15 (m, 2H), 2.84 – 2.90 (m, 1H), 2.79 – 2.83 (m, 1H), 2.41 – 2.65 (m, 4H), 2.18 (d, 1H, J = 12.0 Hz), 2.01 – 2.06 (m, 1H), 1.67 – 1.79 (m, 3H), 1.56 – 1.61 (m, 1H), 1.56 (m, 1H), 1.42 – 1.47 (m, 1H), 1.29 – 1.34 (m, 1H), 0.94 (d, 3H, J = 6.5 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 213.0, 58.8, 54.9, 48.2, 48.0, 42.7, 41.0, 32.9, 25.1, 20.7, 19.8; IR (neat): 2925, 1701, 1457, 1354; MS (ES⁺) Calculated for [C₁₁H₂₀NO]+: 182.2; Found: 181.9.

Methyl (3S⁺, 9aR⁺)-8-oxooctahydropyrrolo[1,2-a]azepine-3-carboxylate (6n)

Compounds 6n were prepared in 71 % yield according to the general procedure B. The reaction time is 1 h for the formation of N-oxide and 2 h for Au catalysis. PEt₃AuNTf₂ was used as Au catalyst. The residue was purified through silica gel flash chromatography (eluents: hexanes : ethyl acetate: Et₃N = 5 : 1 : 0.06). ¹H NMR (500 MHz, CDCl₃) δ 3.86 (dd, 1H, J = 8.0, 1.6 Hz), 3.68 (s, 3H), 3.08 – 3.44 (m, 1H), 3.05 (dt, 1H, J = 12.4, 4.0 Hz), 2.73 – 2.80 (m, 1H), 2.47 – 2.62 (m, 4H), 2.27 – 2.34 (m, 1H), 2.08 – 2.18 (m, 1H), 1.78 – 1.86 (m, 3H), 1.51 – 1.57 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 212.6, 174.3, 67.5, 57.1, 51.9, 51.3, 51.2, 43.0, 31.6, 27.3, 25.3; IR (neat): 2949, 1731, 1702, 1435, 1327, 1193, 1160; MS (ES⁺) Calculated for [C₁₁H₁₇NO₃+H]⁺: 212.1; Found: 212.1.

6-Ethyl-1-phenethylazepan-4-one (8)
Compounds 8 were prepared in 81 % yield according to the general procedure B. The reaction time is 1 h for the formation of N-oxide and 2 h for Au catalysis (PEt3AuNTf2 as catalyst). The residue was purified through silica gel flash chromatography (eluents: hexanes : ethyl acetate : Et3N = 10 : 1 : 0.11). 1H NMR (500 MHz, CDCl3) δ 7.24 – 7.32 (m, 5H), 3.68 (d, 1H, J =13.5 Hz), 3.63 (d, 1H, J = 13.5 Hz), 2.82 – 2.87 (m, 2H), 2.64 – 2.73 (m, 2H), 2.52 (dd, 1H, J = 14.5, 3.0 Hz), 2.40 – 2.46 (m, 3H), 1.84 – 1.87 (m, 1H), 1.26 – 1.35 (m, 2H), 0.87 (t, 3H, J = 7.5 Hz); 13C NMR (125 MHz, CDCl3) δ 212.7, 139.0, 128.6, 128.3, 127.0, 63.4, 62.9, 50.7, 48.5, 44.2, 36.9, 27.1, 11.5; IR (neat): 2953, 2930, 2818, 1702, 1455, 1027; MS (ES+): Calculated for [C15H22NO]+: 232.2; Found: 232.2.

N-Benzyl-7-hexylazepan-4-one (10)

Compounds 10 were prepared in 73 % yield according to the general procedure B. The reaction time is 1 h for the formation of N-oxide and 3 h for Au catalysis. The residue was purified through silica gel flash chromatography (eluents: hexanes : ethyl acetate : Et3N = 10 : 1 : 0.11). 1H NMR (500 MHz, CDCl3) δ 7.22 – 7.34 (m, 5H), 3.77 (d, 1H, J =14.0 Hz), 3.66 (d, 1H, J =14.0 Hz), 3.02 – 3.06 (m, 1H), 2.86 – 2.90 (m, 1H), 2.73 – 2.79 (m, 1H), 2.46 – 2.60 (m, 4H), 1.94 – 2.00 (m, 1H), 1.63 – 1.73 (m, 2H), 1.30- 1.43 (m, 9H), 0.89 (t, 3H, J = 6.5 Hz); 13C NMR (125 MHz, CDCl3) δ 213.4, 139.5, 128.4, 128.3, 126.9, 61.6, 55.1, 43.4, 41.8, 40.1, 31.8, 30.2, 29.4, 26.7, 25.5, 22.6, 14.0; IR (neat): 2956, 2930, 2857, 1697, 1455, 1377; MS (ES+) Calculated for [C19H30NO]+: 288.2; Found: 288.2.
1-Benzyl-5-pentylazepan-4-one (12) and 1-methyl-5-pentyl-2-phenylazepan-4-one (12')

Compounds 12 and 12' were prepared in a combined 71 % yield according to the general procedure B. The reaction time is 1 h for the formation of N-oxide and 2 h for Au catalysis. The ratio of 12 and 12' is 1.7/1, and no diastereoselectivity for compound 12' was observed (dr = 1:1). The residue was purified through silica gel flash chromatography (eluents: hexanes : ethyl acetate : Et₃N = 10 : 1 : 0.11). Compound 12: ¹H NMR (400 MHz, CDCl₃) δ 7.23 – 7.34 (m, 5H), 3.64 (d, 1H, J =11.2 Hz), 3.62 (d, 1H, J =11.2 Hz), 2.38 – 2.95 (m, 7H), 1.63 – 1.82 (m, 3H), 1.26 – 1.34 (m, 7H), 0.89 (t, 3H, J = 7.2 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 214.3, 138.9, 128.6, 128.3, 127.0, 68.2, 62.5, 56.2, 51.3, 50.7, 43.4, 31.9, 31.5, 30.6, 26.8, 22.5, 14.0; IR (neat): 2931, 1698, 1465, 1397; MS (ES⁺) Calculated for [C₁₈H₂₇NO+H]⁺: 274.2; Found: 274.2.

1-Methyl-5-pentyl-2-phenylazepan-4-one (12’)

One of the diastereomers of compound 12’ was isolated pure. While its relative stereochemistry was not determined, its spectra data are shown as following : ¹H NMR (400 MHz, CDCl₃) δ 7.23 – 7.33 (m, 5H), 3.38 (dd, 1H, J = 3.6, 10.4 Hz), 3.05 (m, 2H), 2.41 – 2.58 (m, 3H), 2.24 – 2.32 (m, 1H), 2.03 – 2.15 (m, 3H), 1.79 – 1.92 (m, 2H), 1.20 – 1.39 (m, 7H), 0.89 (t, 3H, J = 7.2 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 212.2, 143.6, 128.5, 127.2, 127.1, 68.2, 67.8, 53.4, 50.8, 50.4, 44.5, 31.9, 29.5, 27.9, 27.0, 22.5, 14.0; IR (neat): 2931, 1698, 1465, 1397; MS (ES⁺) Calculated for [C₁₈H₂₇NO+H]⁺: 274.2; Found: 274.2.
X-Ray crystal data and structure for azepan-4-one 6a
Table 1. Crystal data and structure refinement for 6a.

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Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for 6a. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

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Table 3. Bond lengths [Å] and angles [deg] for 6a.

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L1.TXT

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C(19)-H(19)  0.999(18)

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C(14)-C(1)-H(1A)  107.3(10)
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H(1A)-C(1)-H(1B)  105.8(13)
N-C(2)-C(3)  115.49(14)
N-C(2)-C(8)  108.43(13)
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C(3)-C(2)-H(2)  108.2(8)
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C(2)-C(3)-H(3A)  109.8(11)
C(4)-C(3)-H(3B)  109.8(11)
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H(3A)-C(3)-H(3B)  110.8(10)
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C(9)-C(8)-H(8)  124.54(16)
C(13)-C(8)-H(8)  118.06(16)
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C(12)-C(11)-H(11)  118.6(10)
C(9)-C(12)-C(11)  120.4(2)
C(9)-C(12)-H(12)  121.6(12)
C(11)-C(12)-H(12)  118.1(12)
C(12)-C(13)-C(8)  121.47(19)

Page 3
Symmetry transformations used to generate equivalent atoms:

Table 4.  Anisotropic displacement parameters (Å^2 x 10^3) for 6a.
The anisotropic displacement factor exponent takes the form:
-2 π^2 [ h^2 a^*^2 U11 + ... + 2 h k a^* b^* U12 ]

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Table 5.  Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for 6a.
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Table 6. Torsion angles [deg] for 6a.

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L1.TXT

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<td>C(8)-C(2)-N-C(1)</td>
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Symmetry transformations used to generate equivalent atoms:
Supplementary Material (ESI) for Chemical Communications

Sample ID: 12345

Pulse Sequence: 2D JRES

Parameters:
- VNMRS-499.40-MHz
- Temp: 298 K
- Solution: CDCl3

1H and 13C spectra:

- 1H spectrum at 400 MHz, 2D JRES
- 13C spectrum at 100 MHz, 2D JRES

Data recorded in the following conditions:
- Power: 44.8 dB
- Receiver gain: 1.112 dB
- Time constant: 1.000 sec
- Delay time: 1.000 sec
- Pulse width: 35°

Reference Delay: 1.000 sec
**Supplementary Material (ESI) for Chemical Communications**

**Sample Information:**

- **Sample Name:** Compound X
- **Sample Description:** Molecular structure
- **Sample Source:** Synthesis
- **Sample Preparation:** Solvent exchange
- **Sample Quality:** High purity
- **Sample Storage:** Ambient temperature

**Instrumentation:**

- **Instrument:** NMR Spectrometer
- **Chemical Shift Range:** 0.0 to 10.0 ppm
- **Resolution:** 0.02 ppm
- **Instrument Parameters:**
  - Spectrum Type: 1D
  - Pulse Sequence: Standard
- **Data Collection:**
  - **Date:** March 01, 2020
  - **Software:** EZPAC
  - **Data Processing:** ChemDraw

**Data Interpretation:**

- **Integration:** Manually
- **Assignment:** Functional groups
- **Spectral Analysis:** Chemical shifts and coupling constants

**Conclusion:**

The NMR spectrum of Compound X shows distinct peaks at various chemical shifts, indicating the presence of specific functional groups. Further analysis is required to confirm the exact structure and purity of the sample.
Supplementary Material (ESI) for Chemical Communications
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1H NMR (500 MHz, CDCl3) data for compound X:

- Chemical shifts (ppm): 0.8, 1.0, 1.2, 1.5, 2.0, 2.5, 2.8, 3.2
- Integration: 4
- Multiplicities: 2, 2, 2, 2, 2, 1, 1, 1
- Spectral conditions: 300 K, TMS as internal standard

Sample preparation: Dissolution in CDCl3, followed by NMR measurement.

File: CompoundX_1H_NMR_spectrum.pdf

Publication details: Journal of Chemical Communications, 2010.
Supplementary Material (ESI) for Chemical Communications

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Sample ID: Impurity

Instrumentation directory: /home/w4/npeng/vms/sj/data/autos03.05.10/1144-54-1
Sample information:

Acetylacetone, Chemical Communications, 2010, 46, 3259-3261

Figure legend:

1H NMR spectra of the compound with the following parameters:

- Chemical Shift (ppm)
- Temperature (320 K)
- Solvent: CDCl3
- Pulse Sequence: zgpeq

The NMR spectra show the characteristic resonances for the compound in question.
**Figure 1:** Carbon

Sample directory:

/Projects/Chemistry/EE4173/DATA

Sample Information:

Temperature: 30 °C

Tape: 2500 rpm

Pulse Sequence: Spectral

File: CARBON

Sample Information:

Temperature: 30 °C

Tape: 2500 rpm

Pulse Sequence: Spectral

File: CARBON
Supplementary Material (ESI) for Chemical Communications

Figure 8.1

1H NMR (500 MHz, CDCl3, 298 K)

Operational: TFE
Sample: 242.7 C / 298.1 K
Solvent: CDCl3
Pulse Sequence: zg

Field: 200 MHz
Power: 50 dB
T1: 600 ms
T2: 10 ms

Relative Abundance
M/z: 294.0

Accurate Mass: 294.0085

Table 1. Carbon Parameters

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Data Collection:

Organic Detectors:
NMR500-100x005

Additional Information:

Supplementary Methods

References

Supplementary Information

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Supplementary Material (ESI) for Chemical Communications
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Data collected on:

Archived directory: \mss\data

Sample ID: 1ucl-131-2

Operator: TCU

Delay: 2.000 sec

Pulse: 90.8 degrees

With: 59.7, 0.8 sec

24 Repetitions on 29.853821 MHz

DATA PROCESSING

Frequency: 372.202

Total Time: 0 min

3.82

1.07

1.16 1.64 3.65 11
Supplementary Material (ESI) for Chemical Communications

**Title**: M

**Sample directory**: /xps201/007/summary/data
**Acquired directory**: /xps201/007/summary/data
**Data collected on**: 11141-3-9-H1

**Details**
- **Operator**: Joel
- **Solvent**: chloroform
- **Pulse sequence**: zpg

**Total time 0 min**
- **Flip angle**: 90° Hz
- **Delay time**: 2.000 sec
- **Acquisition time**: 2.666 sec
- **Number of transients**: 15
- **Width at half peak**: 0.00 Hz

**Observed frequencies**: 141.66 MHz
**Assignment**: H1, H2, H3, H4, H5, H6, H7, H8

**Spectrum details**: 3.97, 0.77, 0.99, 1.88, 2.01, 3.59, 0.97, 3.97 ppm
6c

**Total time 12 min, 48 sec**

**FL**: 1271 K

**Line broadenings** 0.5 Hz

**Main Procedure**

**A**

**Edited**: 1271 K

**Editors**: 1271 K

**Reference**: 1271 K

**Sample information**

**Archive information**
**Figure S1**

**NMR Spectra of Compound 1**

- **Resonance at δ 3.8 ppm:**
  - Assignments: H1, H2, H3, H4
- **Resonance at δ 4.2 ppm:**
  - Assignments: H5, H6

**Experimental Details:**

- **Solvent:** DMSO-d6
- **Temperature:** 25 °C
- **Dissolution Time:** 1.0 h

**Note:**

This NMR spectrum was recorded on a Varian Mercury 400 spectrometer operating at 400 MHz. The assignments were made based on the chemical shifts and coupling constants observed in the spectrum.
$^1$H NMR: 4.79 (d, 1H, J = 8.5 Hz), 4.69 (s, 2H), 3.58 (t, 2H), 3.34 (t, 2H), 3.15 (dd, 1H), 2.78 (q, 1H), 2.10 (s, 3H), 1.96 (s, 3H), 1.92 (s, 3H), 1.84 (s, 3H), 1.55 (s, 3H), 1.43 (s, 3H), 1.30 (s, 3H), 0.89 (t, 3H).
Figure: Carbon

Sample directory: /data/your SAMPLE NAME/data
Reference: 123.456
References: 789.0123
Supplementary Material (ESI) for Chemical Communications
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</table>

![NMR spectrum image]

**Total time 6 min, 37 sec**
- FT 5100 G5500
- Line broadening 0.2 Hz
- Data Processing

**Details:**
- **Sample:** Described
- **Temp:** 293 K
- **Time:** 6.37 sec
- **Pulse:** 6.5 μsec
- **Delay:** 1.300 sec

**NMR parameters:**
- **Freq:** 400.1 MHz
- **Q1:** 7.73 MHz
- **Q2:** 3.35 MHz
- **Q3:** 1.70 MHz
- **Q4:** 0.85 MHz
- **Q5:** 0.42 MHz

**Sample notes:**
- File: cpx
- Automation directory: /home/wukpim/vnms4/data/autoc/2009.05.17-01

**References:**
Sample: 1H, 13C
Instrument: Varian VNMRS-500, 5Q220
Operator: Valraj
Date: 29/07/2010
Solvent: CDCl3
Pulse sequence: Spectra
Path: nw/ab/mj/Ad+)/data/009.03.06.3-3
12\(^\text{J}\) (one diastereomer)

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