Electronic Supplementary Information

DABCO-catalyzed ring opening of activated cyclopropanes and recyclization leading to γ-lactams with an all-carbon quaternary center

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I. General information:

All reagents were purchased from commercial sources and used without further treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. $^1$H NMR and $^{13}$C NMR spectra were recorded at 25 ºC on a Varian 500 MHz and 125 MHz, respectively, with TMS as the internal standard. Melting points were obtained with a micro melting point XT4A Beijing Keyi electrooptic apparatus and are uncorrected. High resolution mass spectra were recorded on Bruck microtof. All reactions were monitored by TLC with Taizhou GF254 silica gel coated plates. Flash column chromatography was carried out using 200-300 mesh silica gel at increased pressure.

II. General procedure for the construction of γ-lactams (2a as an example):

To a solution of 1a (203 mg, 1.0 mmol) and DABCO (44 mg, 0.2 mmol) in CH$_3$CN (2.0 mL) was added acrylonitrile (0.08 mL, 1.1 mmol) in a 25 mL flask. The reaction mixture was stirred at 60 ºC for 6 h, cooled down to room temperature, poured into brine and extracted with EtOAc. The combined organic phase was washed with water (3 × 10 mL), dried over anhydrous MgSO$_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether/diethyl ether) to afford the desired product 2a (238 mg, 93%).
III. Characterization of the products

3-(3-acetyl-2-oxo-1-phenylpyrrolidin-3-yl)propanenitrile (2a)

Colorless crystals. m.p. 86-88 °C. ^1H NMR (500 MHz, CDCl_3): \( \delta = 2.00-2.06 \) (m, 1H), 2.34 (s, 3H), 2.35-2.46 (m, 4H), 2.77-2.82 (m, 1H), 3.81-3.89 (m, 2H), 7.20-7.23 (t, \( J = 7.5 \) Hz, 1H), 7.39-7.42 (t, \( J = 7.5 \) Hz, 2H), 7.40-7.61 (d, \( J = 8.0 \) Hz, 2H). ^13C NMR (125 MHz, CDCl_3): \( \delta = 13.0, 26.1, 26.9, 29.6, 45.8, 62.7, 118.8, 120.0, 125.4, 129.0, 138.5, 170.4, 203.5 \). HRMS (ESI-TOF): Calc for C_{15}H_{16}N_2O_2 [M+H]: 257.1290; found: 257.1290.

3-(3-acetyl-2-oxo-1-(p-tolyl)pyrrolidin-3-yl)propanenitrile (2b)

White solid. m.p. 91-93 °C. ^1H NMR (500 MHz, CDCl_3): \( \delta = 1.98-2.04 \) (m, 1H), 2.14 (s, 3H), 2.30-2.46 (m, 10H), 2.74-2.79 (m, 1H), 3.77-3.87 (m, 2H), 7.18-7.20 (d, \( J = 8.5 \) Hz, 2H), 7.46-7.47 (d, \( J = 8.5 \) Hz, 2H). ^13C NMR (125 MHz, CDCl_3): \( \delta = 13.0, 20.9, 26.1, 26.2, 29.8, 30.9, 46.0, 62.6, 118.9, 120.0, 129.5, 135.3, 136.0, 170.2, 203.7 \). HRMS (ESI-TOF): Calc for C_{16}H_{18}N_2O_2 [M+H]: 271.1447; found: 271.1453.

3-(3-acetyl-1-(4-methoxyphenyl)-2-oxopyrrolidin-3-yl)propanenitrile (2c)

Colorless crystals. ^1H NMR (500 MHz, CDCl_3): \( \delta = 2.00-2.04 \) (m, 1H), 2.33 (s, 3H), 2.34-2.39 (m, 2H), 2.42-2.46 (m, 4H), 2.74-2.79 (m, 1H), 3.77-3.84 (m, 5H), 6.91-6.93 (m, 2H), 7.48-7.50 (m, 2H). ^13C NMR (125 MHz, CDCl_3): \( \delta = 13.0, 26.1, 26.2, 29.8, 46.2, 55.4, 62.4, 114.1, 118.9, 121.8, 131.6, 157.1, 170.0, 203.8 \). HRMS (ESI-TOF): Calc for C_{16}H_{18}N_2O_2 [M+H]: 287.1396; found: 287.1391.

3-(3-acetyl-1-(2,4-dimethylphenyl)-2-oxopyrrolidin-3-yl)propanenitrile (2d)

White solid. m.p. 74-76 °C. ^1H NMR (500 MHz, CDCl_3): \( \delta = 2.05-2.11 \) (m, 1H), 2.14 (s, 3H), 2.32 (s, 3H), 2.33-2.45 (m, 5H), 2.46-2.50 (m, 2H), 2.74-2.79 (m, 1H), 3.60-3.65 (m, 1H), 3.68-3.73 (m, 1H), 6.98-6.99 (d, \( J = 8.0 \) Hz, 1H), 7.04-7.05 (d, \( J = 8.5 \) Hz, 1H), 7.09 (s, 1H). ^13C NMR (125 MHz, CDCl_3): ...
MHz, CDCl$_3$): $\delta = 12.9, 17.6, 20.9, 26.1, 27.1, 29.6, 47.7, 61.3, 118.9, 126.0, 127.6, 131.8, 133.7, 134.7, 138.2, 170.4, 204.0$. HRMS (ESI-TOF): Calc for C$_{17}$H$_{20}$N$_2$O$_2$ [M+H]: 285.1603; found: 285.1607.

3-(3-acetyl-1-(2-chlorophenyl)-2-oxopyrrolidin-3-yl)propanenitrile (2e)

![Chemical structure of 2e](image)

White solid. m.p. 77-79 °C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 2.09-2.14$ (m, 1H), 2.33-2.42 (m, 5H), 2.45-2.50 (m, 2H), 2.78-2.83 (m, 1H), 3.68-3.72 (m, 1H), 3.75-3.80 (m, 1H), 7.25-7.27 (m, 1H), 7.30-7.35 (m, 2H), 7.47-7.49 (m, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 12.9, 26.2, 27.3, 29.5, 47.0, 61.0, 119.0, 128.0, 129.1, 129.8, 130.5, 132.0, 135.1, 171.2, 203.7$. HRMS (ESI-TOF): Calc for C$_{17}$H$_{15}$ClN$_2$O$_2$ [M+H]: 291.0909; found: 291.0984.

3-(3-acetyl-1-(4-chlorophenyl)-2-oxopyrrolidin-3-yl)propanenitrile (2f)

![Chemical structure of 2f](image)

White solid. m.p. 119-121 °C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 2.00-2.06$ (m, 1H), 2.33 (s, 3H), 2.34-2.45 (m, 4H), 2.79-2.83 (m, 1H), 3.77-3.85 (m, 2H), 7.35-7.37 (d, $J = 8.5$ Hz, 2H), 7.56-7.58 (t, $J = 9.5$ Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 13.0, 25.9, 26.1, 29.8, 45.8, 62.7, 118.7, 121.0, 129.0, 130.6, 137.1, 170.4, 203.3$. HRMS (ESI-TOF): Calc for C$_{15}$H$_{15}$ClN$_2$O$_2$ [M+H]: 291.0909; found: 291.0905.

3-(3-acetyl-1-(5-chloro-2-methoxyphenyl)-2-oxopyrrolidin-3-yl)propanenitrile (2g)

![Chemical structure of 2g](image)

White solid. m.p. 55-57 °C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 2.05-2.11$ (m, 1H), 2.26-2.38 (m, 5H), 2.43-2.56 (m, 2H), 2.70-2.75 (m, 1H), 3.66-3.74 (m, 2H), 3.82 (s, 3H), 6.90-6.92 (d, $J = 8.5$ Hz, 1H), 7.22-7.22 (d, $J = 2.5$ Hz, 2H), 7.27-7.30 (m, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 12.8, 26.1, 27.4, 29.4, 46.9, 55.9, 60.8, 113.0, 119.1, 125.4, 127.0, 128.4, 129.1, 153.3, 171.6, 203.9$. HRMS (ESI-TOF): Calc for C$_{16}$H$_{17}$ClN$_2$O$_3$ [M+H]: 321.1006; found: 321.1006.

3-(3-acetyl-1-(2-nitrophenyl)-2-oxopyrrolidin-3-yl)propanenitrile (2h)

![Chemical structure of 2h](image)
Colorless oil. 1H NMR (500 MHz, CDCl3): δ = 2.15-2.19 (m, 1H), 2.31-2.45 (m, 7H), 2.86-2.91 (m, 1H), 3.82-3.86 (m, 1H), 3.89-3.94 (m, 1H), 7.35-7.36 (m, 1H), 7.47-7.51 (m, 1H), 7.67-7.71 (m, 1H), 8.00-8.02 (m, 1H). 13C NMR (125 MHz, CDCl3): δ = 12.8, 26.1, 27.0, 29.2, 30.9, 47.2, 61.4, 118.8, 125.6, 127.0, 128.3, 131.1, 134.0, 145.3, 171.0, 203.0. HRMS (ESI-TOF): Calc for C15H12N3O4 [M+H]: 302.1141; found: 302.1147.

3-(3-acetyl-1-(naphthalen-1-yl)-2-oxopyrrolidin-3-yl)propanenitrile (2i)

Colorless oil. 1H NMR (500 MHz, CDCl3): δ = 2.19-2.25 (m, 1H), 2.41-2.60 (m, 7H), 2.87-2.92 (m, 1H), 3.75-3.78 (m, 1H), 3.79-3.91 (m, 1H), 7.33-7.35 (d, J = 7.0 Hz, 1H), 7.49-7.60 (m, 4H), 7.86-7.92 (m, 2H). 13C NMR (125 MHz, CDCl3): δ = 13.1, 26.3, 27.4, 29.8, 48.8, 61.7, 118.9, 121.8, 124.7, 125.6, 126.6, 127.1, 128.7, 129.0, 129.3, 134.3, 134.5, 171.5, 204.2. HRMS (ESI-TOF): Calc for C19H18N2O2 [M+H]: 307.1447; found: 307.1446.

3-(3-acetyl-2-oxo-1-(pyridin-2-yl)pyrrolidin-3-yl)propanenitrile (2j)

White solid. m.p. 83-85 °C. 1H NMR (500 MHz, CDCl3): δ = 1.97-2.02 (m, 1H), 2.32 (s, 3H), 2.33-2.39 (m, 2H), 2.43-2.47 (m, 2H), 2.69-2.74 (m, 1H), 3.99-4.05 (m, 1H), 4.15-4.19 (m, 1H), 7.09-7.12 (m, 1H), 7.72-7.75 (m, 1H), 8.35-8.39 (m, 2H). 13C NMR (125 MHz, CDCl3): δ = 12.9, 25.8, 26.1, 29.6, 44.3, 63.3, 114.6, 118.8, 120.2, 137.7, 147.6, 150.9, 171.3, 203.2. HRMS (ESI-TOF): Calc for C14H15N3O2 [M+H]: 257.1164; found: 257.1171.

3-(2-cyanoethyl)-2-oxo-1-phenylpyrrolidine-3-carbonitrile (3)

Colorless oil. 1H NMR (500 MHz, CDCl3): δ = 2.10-2.27 (m, 1H), 2.28-2.32 (m, 1H), 2.37-2.43 (m, 1H), 2.61-2.73 (m, 2H), 2.81-2.88 (m, 1H), 3.84-3.89 (m, 1H), 3.95-4.00 (m, 1H), 7.22-7.25 (t, J = 7.0 Hz, 1H), 7.38-7.42 (t, J = 7.0 Hz, 2H), 7.55-7.57 (d, J = 7.0 Hz, 2H). 13C NMR (125 MHz, CDCl3): δ = 13.3, 29.8, 30.6, 44.8, 45.3, 117.5, 118.1, 120.2, 125.9, 129.0, 137.7, 166.0. HRMS (ESI-TOF): Calc for C14H13N3O [M+H]: 239.1059; found: 239.1055.

ethyl 3-(3-acetyl-2-oxo-1-phenylpyrrolidin-3-yl)propanoate (4a)
White solid. m.p. 56-58 °C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 1.24-1.27 (t, $J$ = 7.5 Hz, 3H), 1.86-1.92 (m, 1H), 2.22-2.23 (m, 3H), 2.35 (s, 3H), 2.45-2.50 (m, 1H), 2.79-2.83 (m, 1H), 3.71-3.75 (m, 1H), 3.79-3.84 (m, 1H), 4.12-4.16 (m, 2H), 7.16-7.19 (t, $J$ = 7.5 Hz, 1H), 7.36-7.40 (t, $J$ = 8.5 Hz, 2H), 7.59-7.61 (d, $J$ = 8.0 Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 14.1, 25.6, 26.1, 29.7, 45.9, 60.7, 63.4, 119.9, 125.1, 128.9, 138.9, 171.0, 172.4, 204.6. HRMS (ESI-TOF): Calc for C$_{17}$H$_{21}$NO$_4$ [M+H]: 303.1471; found: 303.1477.

**butyl 3-(3-acetyl-2-oxo-1-phenylpyrrolidin-3-yl)propanoate (4b)**

White solid. m.p. 36-38 °C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 0.92-0.94 (t, $J$ = 7.5 Hz, 3H), 1.33-1.41 (m, 2H), 1.57-1.63 (m, 2H), 1.86-1.92 (m, 1H), 2.21-2.36 (m, 6H), 2.43-2.48 (m, 1H), 2.76-2.81 (m, 1H), 3.70-3.83 (m, 2H), 4.06-4.09 (t, $J$ = 6.5 Hz, 2H), 7.15-7.18 (t, $J$ = 7.5 Hz, 1H), 7.35-7.38 (t, $J$ = 8.0 Hz, 2H), 7.60-7.61 (d, $J$ = 8.0 Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 13.5, 18.8, 25.3, 25.8, 29.4, 30.3, 45.6, 63.1, 64.4, 119.6, 124.8, 128.6, 138.8, 170.8, 172.2, 204.3. HRMS (ESI-TOF): Calc for C$_{19}$H$_{25}$NO$_4$ [M+H]: 332.1862; found: 332.1867.

**tert-butyl 3-(3-acetyl-2-oxo-1-phenylpyrrolidin-3-yl)propanoate (4c)**

White solid. m.p. 74-76 °C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 1.44 (s, 9H), 1.86-1.92 (m, 1H), 2.16-2.62 (m, 3H), 2.34 (s, 3H), 2.39-2.46 (m, 1H), 2.77-2.81 (m, 1H), 2.70-3.83 (m, 2H), 7.15-7.18 (t, $J$ = 7.5 Hz, 1H), 7.35-7.39 (t, $J$ = 7.5 Hz, 2H), 7.59-7.61 (d, $J$ = 8.5 Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 13.5, 18.5, 25.3, 25.8, 29.4, 30.3, 45.6, 63.1, 64.4, 119.6, 124.8, 128.6, 138.8, 170.8, 172.2, 204.3. HRMS (ESI-TOF): Calc for C$_{19}$H$_{25}$NO$_4$ [M+H]: 332.1862; found: 332.1867.

**3-acetyl-1-phenyl-3-(2-(phenylsulfonyl)ethyl)pyrrolidin-2-one (5)**

White solid. m.p. 121-123 °C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 1.86-1.88 (m, 1H), 2.19 (s, 3H), 2.26-2.30 (t, $J$ = 8.0 Hz, 1H), 2.36-2.40 (m, 1H), 2.63-2.66 (m, 1H), 3.10-3.13 (m, 2H), 3.74-3.80 (m, 2H), 7.14-7.17 (t, $J$ = 7.0 Hz, 1H), 7.33-7.36 (t, $J$ = 8.0 Hz, 2H), 7.53-7.57 (t, $J$ = 8.5 Hz, 4H),
7.63-7.66 (t, J = 8.0 Hz, 1H), 7.88-7.90 (d, J = 8.5 Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 25.8, 26.1, 26.9, 45.6, 51.5, 61.9, 119.8, 125.2, 127.8, 128.8, 129.3, 133.8, 138.3, 138.4, 170.3, 203.7$. HRMS (ESI-TOF): Calc for C$_{20}$H$_{21}$NO$_4$S [M+H]: 372.1270; found: 372.1267.

3-(3-acetyl-2-oxo-1-phenylpyrrolidin-3-yl)-N,N-dimethylpropanamide (6)

White solid. m.p. 61-63 °C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 1.93-1.98$ (m, 1H), 2.22-2.45 (m, 7H), 2.73-2.78 (m, 1H), 2.94 (s, 3H), 3.00 (s, 3H), 3.75-3.82 (m, 2H), 7.16-7.19 (d, J = 7.0 Hz, 1H), 7.36-7.39 (t, J = 7.5 Hz, 2H), 7.60-7.61 (t, J = 7.5 Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 25.9, 26.2, 28.4, 29.5, 35.5, 37.2, 45.9, 63.4, 119.9, 125.0, 128.9, 139.0, 171.4, 171.5, 205.2$. HRMS (ESI-TOF): Calc for C$_{17}$H$_{22}$N$_2$O$_3$ [M+H]: 303.1709; found: 303.1712.

1,3-zwitterion (7)

White solid. m.p. 173-175 °C. $^1$H NMR (500 MHz, D$_2$O): $\delta = 1.75-1.76$ (d, J = 7.5 Hz, 3H), 2.32-2.35 (t, J = 8.0 Hz, 2H), 2.72-2.75 (t, J = 8.5 Hz, 2H), 2.79-2.80 (d, J = 6.5 Hz, 6H), 3.01-3.02 (d, J = 6.5 Hz, 6H), 6.83-6.86 (t, J = 7.0 Hz, 1H), 7.11-7.14 (t, J = 8.0 Hz, 2H), 7.25-7.26 (d, J = 8.0 Hz, 2H). $^{13}$C NMR (125 MHz, D$_2$O): $\delta = 20.4, 24.1, 44.2, 51.8, 63.7, 93.2, 119.9, 123.1, 129.5, 139.6, 170.0, 181.4$. HRMS (ESI-TOF): Calc for C$_{18}$H$_{25}$N$_3$O$_2$ [M+H]: 316.2025; found: 316.2021.

2-acetyl-4-(3-acetyl-2-oxo-1-phenylpyrrolidin-3-yl)-N-phenylbutanamide (9a)

Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 1.88-2.00$ (m, 4H), 2.14-2.19 (m, 1H), 2.29 (s, 3H), 2.32-2.33 (d, J = 4.0 Hz, 3H), 2.79-2.82 (m, 1H), 3.46-3.54 (m, 1H), 3.73-3.85 (m, 2H), 7.11-7.20 (m, 2H), 7.30-7.39 (m, 4H), 7.52-7.58 (m, 4H), 8.30-8.35 (d, J = 25.0 Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 24.5, 24.6, 25.4, 25.6, 26.0, 28.8, 29.2, 32.0, 32.3, 46.2, 46.3, 61.5, 61.6, 63.9, 63.9, 120.0, 120.0, 120.2, 120.0, 124.7, 125.3, 125.3, 128.9, 137.4, 137.4, 138.7, 166.3, 166.3, 171.3, 171.4, 204.6, 204.6, 205.5, 205.6$. HRMS (ESI-TOF): Calc for C$_{24}$H$_{26}$N$_2$O$_4$ [M+H]: 407.1971; found: 407.1976.
2-acetyl-4-(3-acetyl-2-oxo-1-(p-tolyl)pyrrolidin-3-yl)-N-(p-tolyl)butanamide (9b)

Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 1.85-2.00$ (m, 4H), 2.13-2.17 (m, 1H), 2.25-2.38 (m, 12H), 2.76-2.83 (m, 1H), 3.43-3.51 (m, 1H), 3.68-3.83 (m, 2H), 7.07-7.17 (m, 4H), 7.38-7.44 (m, 4H), 8.21-8.26 (d, $J = 27.5$ Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 20.8$, 24.5, 24.7, 25.4, 25.7, 26.0, 26.0, 28.8, 29.2, 32.0, 32.3, 46.3, 46.4, 61.5, 61.6, 63.8, 63.8, 120.0, 120.0, 120.3, 120.3, 129.4, 129.4, 129.4, 134.3, 134.3, 134.8, 134.9, 135.1, 135.2, 136.2, 166.1, 166.2, 171.1, 171.2, 204.7, 204.8, 205.6, 205.7. HRMS (ESI-TOF): Calc for C$_{26}$H$_{30}$N$_2$O$_4$ [M+H]: 435.2284; found: 435.2288.

2-acetyl-4-(3-acetyl-1-(2-chlorophenyl)-2-oxopyrrolidin-3-yl)-N-(2-chlorophenyl)butanamide (9c)

Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 1.94-2.18$ (m, 5H), 2.33-2.40 (m, 6H), 2.85-2.88 (m, 1H), 3.56-3.74 (m, 3H), 7.07-7.10 (t, $J = 7.0$ Hz, 1H), 7.22-7.47 (m, 6H), 8.23-8.25 (m, 1H), 8.54-8.63 (d, $J = 41.5$ Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 25.2$, 25.4, 26.0, 26.0, 26.5, 26.8, 29.3, 29.4, 29.8, 31.8, 31.9, 47.2, 47.3, 61.2, 61.6, 62.3, 62.4, 122.3, 122.3, 123.8, 123.9, 125.4, 127.5, 127.5, 127.9, 129.1, 129.1, 129.5, 129.5, 130.4, 132.0, 132.0, 134.0, 135.5, 135.6, 166.2, 166.2, 171.8, 171.8, 204.5, 204.6, 205.7, 206.0. HRMS (ESI-TOF): Calc for C$_{28}$H$_{34}$Cl$_2$N$_2$O$_4$ [M+H]: 475.1191; found: 475.1187.

ESI8
IV. $^1$H and $^{13}$C NMR spectra of compounds 2-7.
ESI12