**Supporting Information**

# Carboxylative cyclization of propargylamines with supercritical carbon dioxide

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**General Information.** $^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra were recorded on a JEOL Lambda 300 spectrometer; chemical shifts were referenced to residual protio impurities in the deuterated solvent ($^{1}H$), to the deuterated solvent ($^{13}C$) or to external $CF_3COOH$ ($^{19}F$). All spectra were obtained at ambient probe temperature unless stated otherwise. Abbreviations for NMR data are as follows: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, or m = multiplet. HRMS-ESI was performed on a JEOL AccuTOF CS spectrometer.

Liquefied carbon dioxide (99.999%) was purchased from Showa Tansan. *N*-methylpropargylamine (**1a**) and propargylamine (**1i**) were purchased from Aldrich Chemicals and were used after purification by distillation. Other terminal propargylamines (**1b**-**1h**) and *N*-methylbut-2-ylamine (**3a**) were prepared by propargylation of primary amines by treatment of the corresponding propargyl chlorides

and a base. Internal propargylamines (**3b**-**3f**) were prepared by Sonogashira reactions[1] of *N*-methyl-*N*-*tert*-butoxycarbonylpropargylamine[2] with aryl halides. The following deprotection of the *tert*-butoxycarbonyl (Boc) moiety on the amino group was performed by treatment with ethereal HCl or trimethylsilyl iodide.

**Analytical data for new compounds.**

***3-Methyl-5-methyleneoxazolidin-2-one (2a)***

$^{1}$H NMR (300.5 MHz, $CDCl_3$, rt): δ 2.83 (s, 3H, NC$H_3$), 4.10 (s, 2H, C$H_2$), 4.21 (d, $^{4}J$(H-H) = 2.0 Hz, 1H, C=C*H*), 4.63 (d, $^{4}J$(H-H) = 2.0 Hz, 1H, C=C*H*); $^{13}$C NMR (75.5 MHz, $CDCl_3$, rt): δ 30.2, 49.7, 86.2, 148.7, 155.6.

***3-Ethyl-5-methyleneoxazolidin-2-one (2b)***

$^{1}$H NMR (300.5 MHz, $CDCl_3$, rt): δ 1.13 (t, $^{3}J$(H-H) = 7.3 Hz, 3H, $NCH_2CH_3$), 3.31 (q, $^{3}J$(H-H) = 7.3 Hz, 2H, $NCH_2CH_3$), 4.12 (ABX pattern, 2H, C$H_2$), 4.24 (ABX pattern, 1H, C=C*H*), 4.68 (ABX pattern, 1H, C=C*H*) ); $^{13}$C NMR (75.5 MHz, $CDCl_3$, rt): δ 12.5, 19.5, 36.2, 53.4, 85.4, 154.5, 155.7.

***3-Propyl-5-methyleneoxazolidin-2-one (2c)***

$^{1}$H NMR (300.5 MHz, $CDCl_3$, rt): δ 0.87 (t, $^{3}J$(H-H) = 7.3 Hz, 3H, $NCH_2CH_2CH_3$), 1.52 (m, 2H, $NCH_2CH_2CH_3$), 3.20 (t, $^{3}J$(H-H) = 7.3 Hz, 2H, N $CH_2CH_2CH_3$), 4.10 (ABX pattern, 2H, C$H_2$), 4.22 (ABX pattern, 1H, C=C*H*), 4.67 (ABX pattern, 1H, C=C*H*).

***3-(2'-Propyl)-5-methyleneoxazolidin-2-one (2d)***

$^1$H NMR (300.5 MHz, $CDCl_3$, rt): δ 1.19 (d, $^3J$(H-H) = 6.8 Hz, 6H, NCH($CH_3$)$_2$), 4.04 (sept, $^3J$(H-H) = 6.8 Hz, 1H, NC*H*($CH_3$)$_2$), 4.21 (s, 2H, C$H_2$), 4.35 (s, 1H, C=C*H*), 4.67 (s, 1H, C=C*H*).

***3,4-Dimethyl-5-methyleneoxazolidin-2-one (2e)***

$^1$H NMR (300.5 MHz, $CDCl_3$, rt): δ 1.38 (d, $^3J$(H-H) = 6.3 Hz, 3H, CHC$H_3$), 2.81 (s, 3H, NC$H_3$), 4.31 (m, 1H, C=C*H*), 4.38 (m, 1H, C*H*$CH_3$), 4.57 (m, 1H, C=C*H*).

***3-Ethyl-4-methyl-5-methyleneoxazolidin-2-one (2f)***

$^1$H NMR (300.5 MHz, $CDCl_3$, rt): δ 1.12 (t, $^3J$(H-H) = 7.2 Hz, 3H, $NCH_2CH_3$), 1.37 (d, $^3J$(H-H) = 6.8 Hz, 3H, CHC$H_3$), 3.14 (m, 1H, $NCH_2CH_3$), 3.53 (m, 1H, $NCH_2CH_3$), 4.25 (m, 1H, C=C*H*), 4.42 (m, 1H, C*H*$CH_3$), 4.71 (m, 1H, C=C*H*).

***3-Benzyl-4-methyl-5-methyleneoxazolidin-2-one (2g)***

$^1$H NMR (300.5 MHz, $CDCl_3$, rt): δ 1.22 (d, $^3J$(H-H) = 6.3 Hz, 3H, CHC$H_3$), 4.0–4.1 (m, 3H, C=C*H*, C$H_2C_6H_5$), 4.6–4.7 (m, 2H, C=C*H*, C*H*$CH_3$, C$H_2C_6H_5$), 7.1–7.3 (m, 5H, $NCH_2C_6H_5$).

***3,4,4-Trimethyl-5-methyleneoxazolidin-2-one (2h)***

$^1$H NMR (300.5 MHz, $CDCl_3$, rt): δ 1.34 (s, 6H, C($CH_3$)$_2$), 2.76 (s, 3H, NC$H_3$), 4.19 (d, $^4J$(H-H) = 3.4 Hz, 1H, C=C*H*), 4.59 (d, $^4J$(H-H) = 3.4 Hz, 1H, C=C*H*).

***(Z)-5-Benzylidene-3-methyloxazolidin-2-one (4b)***

$^1$H NMR (300.5 MHz, $CDCl_3$): δ 2.91 (s, 3H, NC$H_3$), 4.22 (s, 2H, C$H_2$), 5.46 (s, 1H, CC*H*), 7.20 (t, $^3J$(H-H) = 7.3 Hz, 1H, *p*-$C_6H_5$), 7.30 (dd, 2H, $^3J$(H-H) = 7.3, 7.6 Hz, *m*-$C_6H_5$), 7.53 (d, $^3J$(H-H) = 7.6 Hz, 2H, *o*-$C_6H_5$); $^{13}$C NMR (75.6 MHz, $CDCl_3$): δ 29.9, 50.3, 102.3, 126.2, 127.7, 127.9, 133.0, 141.2, 155.2. Anal. Calcd for $C_{11}H_{11}NO_2$: C 69.83; H 5.86; N 7.40, Found: C 69.59; H 5.78; N 7.27.

***(Z)-3-Methyl-5-(4'-trifluoromethylbenzylidene)oxazolidin-2-one (4c)***

$^{1}$H NMR (300.5 MHz, $CDCl_3$): δ 2.86 (s, 3H, NC$H_3$), 4.19 (d, $^{4}J$(H-H) = 1.7 Hz, 2H, C$H_2$), 5.43 (t, $^{4}J$(H-H) = 2.0 Hz, 1H, CC$H$), 7.45 (m, 2H, $C_6H_4$), 7.54 (m, 2H, $C_6H_4$); $^{13}$C NMR (75.6 MHz, $CDCl_3$): δ 30.1, 50.6, 101.2, 124.0 (q, $^{1}J_{C\text{-}F}$ = 271.6 Hz), 125.0 (q, $^{2}J_{C\text{-}F}$ = 3.8 Hz), 128.0, 137.0, 144.0, 155.0; $^{19}$F NMR (282.7 MHz, $CDCl_3$): δ -63.4 (s). HRMS(ESI): *m*/*z* Calcd for $C_{12}H_{10}F_3NNaO_2$: 280.0561, Found: 280.0547 $[M+Na]^+$.

***(Z)-5-[3',5'-Bis(trifluoromethyl)benzylidene]-3-methyloxazolidin-2-one (4d)***

$^{1}$H NMR (300.5 MHz, $CDCl_3$): δ 3.00 (s, 3H, NC$H_3$), 4.35 (d, $^{4}J$(H-H) = 2.2 Hz, 2H, C$H_2$), 5.56 (t, $^{4}J$(H-H) = 2.2 Hz, 1H, CC$H$), 7.67 (s, 1H, $C_6H_4$), 7.94 (s, 2H, $C_6H_4$); $^{13}$C NMR (75.6 MHz, $CDCl_3$): δ 30.6, 50.8, 100.2, 120.1, 123.3 (q, $^{1}J_{C\text{-}F}$ = 271.6 Hz), 127.7, 131.7 (q, $^{2}J_{C\text{-}F}$ = 33.6 Hz), 135.5, 145.2, 154.8; $^{19}$F NMR (282.7 MHz, $CDCl_3$): δ -63.7 (s). HRMS(ESI): *m*/*z* Calcd for $C_{13}H_9F_6NNaO_2$: 348.0435, Found: 348.0425 $[M+Na]^+$.

***(Z)-4-(3'-Methyl-2'-oxo-oxazolidin-5'-ylidenemethyl)benzonitrile (4e)***

$^{1}$H NMR (300.5 MHz, $CDCl_3$): δ 3.16 (s, 3H, NC$H_3$), 3.75 (s, 2H, C$H_2$), 6.12 (t, $^{4}J$(H-H) = 1.0 Hz,1H, CC$H$), 7.33 (m, 2H, $C_6H_4$), 7.60 (m, 2H, $C_6H_4$); $^{13}$C NMR (75.6 MHz, $CDCl_3$): δ 30.1, 32.0, 110.5, 112.7, 118.3, 129.2, 132.1, 137.1, 141.1, 155.4. HRMS(ESI): *m*/*z* Calcd for $C_{12}H_{10}N_2NaO_2$: 237.0640, Found: 237.0656 $[M+Na]^+$.

***(Z)-5-(4'-Acetylbenzylidene)-3-methyloxazolidin-2-one (4f)***

$^{1}$H NMR (300.5 MHz, $CDCl_3$): δ 2.58 (s, 3H, COC$H_3$), 3.15 (s, 3H, NC$H_3$), 3.75 (s, 2H, C$H_2$), 6.06 (t, $^{4}J$(H-H) = 1.2 Hz, 1H, CC$H$), 7.32 (m, 2H, $C_6H_4$), 7.91 (m, 2H, $C_6H_4$) ); $^{13}$C NMR (75.6 MHz, $CDCl_3$): δ 26.3, 30.1, 32.0, 112.3, 128.4, 128.7, 135.7, 137.9, 141.0, 155.5, 197.4. HRMS(ESI): *m*/*z* Calcd for $C_{13}H_{13}NNaO_3$: 254.0793, Found: 254.0786 $[M+Na]^+$.

**References**

1 K. M. Miller, C. Molinaro and T. F. Jamison, *Tetrahedron Asymmetry*, 2003, **14**, 3619-

3625.

2 S. I. Kahn and M. W. Grinstaff, *J. Am. Chem. Soc.*, 1999, **121**, 4704-4705.