## Electronic Supporting Information

$\mathrm{KO}^{t}$ Bu Promoted Selective Ring-Opening $N$-alkylation of 2-Oxazolines to Access 2-Aminoethyl Acetates and N -Substituted Thiazolidinones<br>Qiao Lin, ${ }^{1}$ Shiling Zhang, ${ }^{1}$ and Bin $\mathrm{Li}^{1 *}$<br>${ }^{1}$ School of Biotechnology and Health Sciences, Wuyi University, Jiangmen 529020, P. R. China

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## General remarks

All reagents were obtained from commercial sources and used as received. Technical grade petroleum ether ( $40-60^{\circ} \mathrm{C}$ bp.) and ethyl acetate were used for chromatography column.
${ }^{1} \mathrm{H}$ NMR spectra were recorded in $\mathrm{CDCl}_{3}$ at ambient temperature on Bruker AVANCE I 300 or 400 spectrometers at 300.1 or 400.1 MHz , using the solvent as internal standard ( 7.26 ppm ). ${ }^{13} \mathrm{C}$ NMR spectra were obtained at 75 or 100 MHz and referenced to the internal solvent signals (central peak is 77.2 ppm ). Chemical shift ( $\delta$ ) and coupling constants $(J)$ are given in ppm and in Hz, respectively. The peak patterns are indicated as follows: $s$, singlet; d, doublet; t , triplet; q , quartet; m , multiplet, and br. for broad.

GC analyses were performed with GC-14C (Shimadzu) equipped with a $30-\mathrm{m}$ capillary column (Supelco, SPB-5, fused silica capillary column, $30 \mathrm{M}^{*} 0.25 \mathrm{~mm} * 0.25 \mathrm{~mm}$ film thickness), was used with $\mathrm{N}_{2} /$ air as vector gas. GCMS were measured by GCMS-7890A-5975C (Agilent) with GC-7890A equipped with a $30-\mathrm{m}$ capillary column (HP-5ms, fused silica capillary column, $30 \mathrm{M}^{*} 0.25 \mathrm{~mm} * 0.25 \mathrm{~mm}$ film thickness), was used with helium as vector gas. HRMS were measured by MAT 95XP (Termol) (LCMS-IT-TOF).

The following GC conditions were used: initial temperature $80^{\circ} \mathrm{C}$, for 2 minutes, then rate $20^{\circ} \mathrm{C} / \mathrm{min}$. until $260^{\circ} \mathrm{C}$ and $260^{\circ} \mathrm{C}$ for 20 minutes.

## General procedure for $\mathrm{KO}^{t} \mathrm{Bu}$ catalyzed selective ring-opening N -alkylation of 2-oxazolines with benzyl bromides

$\mathrm{KO}^{\prime} \mathrm{Bu}(0.5 \mathrm{mmol}, 56 \mathrm{mg})$, 2-oxazoline ( 0.5 mmol ), benzyl bromide ( 1.0 mmol ) and DMC ( 2 mL ) were introduced in a tube, equipped with magnetic stirring bar and was stirred at $50{ }^{\circ} \mathrm{C}$. After 16 h , the conversion of the reaction was analyzed by gas chromatography. The solvent was then evaporated under vacuum and the desired product was purified by using a silica gel chromatography column and a mixture of petrol ether/ethyl acetate as eluent.

## General procedure for $\mathrm{KO}^{t} \mathrm{Bu}$ catalyzed selective ring-opening N -alkylation of 2-oxazolines with benzyl chlorides

$\mathrm{KO}^{\mathrm{t}} \mathrm{Bu}(0.5 \mathrm{mmol}, 56 \mathrm{mg}), \mathrm{I}_{2}(0.5 \mathrm{mmol}, 127 \mathrm{mg})$, 2-oxazoline ( 0.5 mmol ), benzyl chloride ( 1.0 mmol ) and DMC ( 2 mL ) were introduced in a tube, equipped with magnetic stirring bar and was stirred at $80^{\circ} \mathrm{C}$. After 16 h , the conversion of the reaction was analyzed by gas chromatography. The solvent was then evaporated under vacuum and the desired product was purified by using a silica gel chromatography column and a mixture of petrol ether/ethyl acetate as eluent.

## General procedure for $\mathrm{KO}^{t} \mathrm{Bu} / \mathbf{I}_{2}$ promoted selective N -alkylation of 2-oxazolines of thiazolidin-2-one derivatives

$\mathrm{KO}^{t} \mathrm{Bu}(1 \mathrm{mmol}, 112 \mathrm{mg})$, $\mathrm{I}_{2}(1 \mathrm{mmol}, 254 \mathrm{mg}), 2-($ methylthio $)-4,5$-dihydrothiazole ( 0.5 $\mathrm{mmol})$, benzyl halide ( 1.0 mmol ) and DMC $(2 \mathrm{~mL})$ were introduced in a tube, equipped with magnetic stirring bar and was stirred at $80^{\circ} \mathrm{C}$. After 16 h , the conversion of the
reaction was analyzed by gas chromatography. The solvent was then evaporated under vacuum and the desired product was purified by using a silica gel chromatography column and a mixture of petrol ether/ethyl acetate as eluent.

## Gram scale procedure for synthesis of 2-(dibenzylamino)ethyl acetate (3a)

$\mathrm{KO}^{\prime} \mathrm{Bu}(10 \mathrm{mmol}, 1.12 \mathrm{~g}$ ), 2-methyl-2-oxazole ( $10 \mathrm{mmol}, 0.85 \mathrm{~mL}$ ), benzyl bromide ( 20 $\mathrm{mmol}, 2.38 \mathrm{~mL})$ and $\mathrm{DMC}(10 \mathrm{~mL})$ were introduced in a tube, equipped with magnetic stirring bar and was stirred at $50^{\circ} \mathrm{C}$. After 16 h , the conversion of the reaction was analyzed by gas chromatography. The solvent was then evaporated under vacuum and the desired product was purified by using a silica gel chromatography column and a mixture of petrol ether/ethyl acetate as eluent, and was isolated as a light yellow oil in 2.38 g (84\%).

## Procedure for synthesis of 2-(dibenzylamino)ethanol (6)

$\mathrm{K}_{2} \mathrm{CO}_{3}$ ( $1.0 \mathrm{mmol}, 112 \mathrm{mg}$ ), 2-(dibenzylamino)ethyl acetate ( 0.5 mmol , $142 \mu \mathrm{~L}$ ), and methanol ( 2 mL ) were introduced in a tube, equipped with magnetic stirring bar and was stirred at room temperature. After 24 h , the conversion of the reaction was analyzed by gas chromatography. The solvent was then evaporated under vacuum and the desired product was purified by using a silica gel chromatography column and a mixture of petrol ether/ethyl acetate as eluent, and was isolated as a light yellow oil in 106 mg (88\%).

## Characterization data of substrates

2-(dibenzylamino)ethyl acetate (3a)


Light yellow oil, yield $=80 \%, 113 \mathrm{mg},{ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=7.43-7.28(\mathrm{~m}, 10 \mathrm{H})$, $4.21(\mathrm{t}, 2 \mathrm{H}, J=6.0 \mathrm{~Hz}), 3.69(\mathrm{~s}, 4 \mathrm{H}), 2.77(\mathrm{t}, 2 \mathrm{H}, J=6.0 \mathrm{~Hz}), 2.07(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}(75$ $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=171.1,139.5,128.9,128.4,127.1,62.5,58.8,51.8,21.1$. HRMS (EI): $\mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{18} \mathrm{H}_{22} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}]^{+} 284.1645$, found 284.1640.

2-(bis(4-methylbenzyl)amino)ethyl acetate (3b)


Organge oil, yield $=85 \%, 132 \mathrm{mg},{ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=7.32(\mathrm{~d}, 4 \mathrm{H}, J=8.1 \mathrm{~Hz})$, $7.18(\mathrm{~d}, 4 \mathrm{H}, J=7.8 \mathrm{~Hz}), 4.22(\mathrm{t}, 2 \mathrm{H}, J=6.0 \mathrm{~Hz}), 3.67(\mathrm{~s}, 4 \mathrm{H}), 2.77(\mathrm{t}, 2 \mathrm{H}, J=6.0 \mathrm{~Hz}), 2.40(\mathrm{~s}$, $6 \mathrm{H}), 2.09(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=171.1,136.6,136.4,129.0,128.8,62.6$, 58.4, 51.5, 21.2, 21.1. HRMS (EI): $m / z$ calcd for $\mathrm{C}_{20} \mathrm{H}_{26} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}]^{+} 312.1958$, found 312.1966.

2-(bis(2-methylbenzyl)amino)ethyl acetate (3c)


Light yellow oil, yield $=73 \%, 113 \mathrm{mg},{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.40-7.37(\mathrm{~m}, 2 \mathrm{H})$, $7.22-7.18(\mathrm{~m}, 6 \mathrm{H}), 4.18(\mathrm{t}, 2 \mathrm{H}, J=6.0 \mathrm{~Hz}), 3.67(\mathrm{~s}, 4 \mathrm{H}), 2.77(\mathrm{t}, 2 \mathrm{H}, J=5.7 \mathrm{~Hz}), 2.34(\mathrm{~s}, 6 \mathrm{H})$, $2.05(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=171.0,137.5,137.1,130.4,130.2,127.2$, 125.6, 62.5, 57.6, 52.3, 21.1, 19.2. HRMS (EI): $m / z$ calcd for $\mathrm{C}_{20} \mathrm{H}_{26} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}]^{+} 312.1958$, found 312.1952 .

2-(bis(4-(tert-butyl)benzyl)amino)ethyl acetate (3d)


Light yellow oil, yield $=78 \%, 154 \mathrm{mg},{ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=7.42-7.36(\mathrm{~m}, 8 \mathrm{H})$, $4.26(\mathrm{t}, 2 \mathrm{H}, J=6.0 \mathrm{~Hz}), 3.70(\mathrm{~s}, 4 \mathrm{H}), 2.80(\mathrm{t}, 2 \mathrm{H}, J=6.0 \mathrm{~Hz}), 2.10(\mathrm{~s}, 3 \mathrm{H}), 1.39(\mathrm{~s}, 18 \mathrm{H})$. ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=171.1,149.9,136.5,128.5,125.2,62.7,58.3,51.8,34.6$, 31.6, 21.1. HRMS (EI): $m / z$ calcd for $\mathrm{C}_{26} \mathrm{H}_{38} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}]^{+} 396.2897$, found 396.2902.

## 2-(bis(4-fluorobenzyl)amino)ethyl acetate (3e)



Brown oil, yield $=79 \%, 126 \mathrm{mg},{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.35-7.30(\mathrm{~m}, 4 \mathrm{H}), 7.05-6.99$ $(\mathrm{m}, 4 \mathrm{H}), 4.17(\mathrm{t}, 2 \mathrm{H}, J=5.7 \mathrm{~Hz}), 3.60(\mathrm{~s}, 4 \mathrm{H}), 2.72(\mathrm{t}, 2 \mathrm{H}, J=5.7 \mathrm{~Hz}), 2.05(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=171.1,160.5\left(\mathrm{~d}, J_{C F}=243.3 \mathrm{~Hz}\right), 135.0\left(\mathrm{~d}, J_{C F}=3.075 \mathrm{~Hz}^{2}\right), 130.2$ $\left(\mathrm{d}, J_{C F}=7.875 \mathrm{~Hz}\right), 115.1\left(\mathrm{~d}, J_{C F}=21.075 \mathrm{~Hz}^{2}\right), 62.3,57.9,51.7,21.1$. HRMS (EI): $m / z$ calcd for $\mathrm{C}_{18} \mathrm{H}_{20} \mathrm{~F}_{2} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}]^{+} 320.1457$, found 320.1451.

2-(bis(2-fluorobenzyl)amino)ethyl acetate (3f)


Light yellow oil, yield $=72 \%, 115 \mathrm{mg},{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.53-7.48(\mathrm{~m}, 2 \mathrm{H})$, 7.29-7.01 (m, 6H), $4.22(\mathrm{t}, 2 \mathrm{H}, J=6.0 \mathrm{~Hz}), 3.78(\mathrm{~s}, 4 \mathrm{H}), 2.79(\mathrm{t}, 2 \mathrm{H}, J=6.0 \mathrm{~Hz}), 2.05(\mathrm{~s}, 3 \mathrm{H})$. ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=171.1,159.8\left(\mathrm{~d}, J_{C F}=244.4 \mathrm{~Hz}^{2}\right), 131.1\left(\mathrm{~d}, J_{C F}=4.5 \mathrm{H}_{\mathrm{z}}\right)$, $128.7\left(\mathrm{~d}, J_{C F}=8.175 \mathrm{~Hz}\right), 125.8\left(\mathrm{~d}, J_{C F}=13.875 \mathrm{~Hz}\right), 124.0\left(\mathrm{~d}, J_{C F}=3.6 \mathrm{~Hz}\right), 115.2\left(\mathrm{~d}, J_{C F}=\right.$ 22.05 Hz ), 62.4, $51.9,51.3\left(\mathrm{~d}, J_{C F}=2.25 \mathrm{~Hz}\right.$, 21.0. HRMS (EI): $m / z$ calcd for $\mathrm{C}_{18} \mathrm{H}_{19} \mathrm{~F}_{2} \mathrm{NO}_{2} \mathrm{Na}$ $[\mathrm{M}+\mathrm{Na}]^{+} 342.1276$, found 342.1279 .

2-(bis(2-chlorobenzyl)amino)ethyl acetate (3g)


Light yellow oil, yield $=70 \%, 123 \mathrm{mg},{ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=7.62-7.59(\mathrm{~m}, 2 \mathrm{H})$, 7.37-7.16 (m, 6H), $4.24(\mathrm{t}, 2 \mathrm{H}, J=6.0 \mathrm{~Hz}), 3.86(\mathrm{~s}, 4 \mathrm{H}), 2.84(\mathrm{t}, 2 \mathrm{H}, J=6.0 \mathrm{~Hz}), 2.06(\mathrm{~s}, 3 \mathrm{H})$. ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=171.0,136.8,134.1,130.5,129.5,128.2,126.8,62.5,55.9$, 52.6, 21.1. HRMS (EI): $m / z$ calcd for $\mathrm{C}_{18} \mathrm{H}_{20} \mathrm{Cl}_{2} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}]^{+} 352.0866$, found 352.0861 .

2-(diallylamino)ethyl acetate (3h)


Light yellow oil, yield $=69 \%, 63 \mathrm{mg},{ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=5.95-5.81(\mathrm{~m}, 2 \mathrm{H})$, 5.26-5.19 (m, 4H), 4.19 (t, 2H, $J=6.0 \mathrm{~Hz}$ ), $3.22(\mathrm{~d}, 4 \mathrm{H}, J=6.3 \mathrm{~Hz}), 2.79(\mathrm{t}, 2 \mathrm{H}, J=6.0 \mathrm{~Hz})$, $2.07(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=171.1,134.3,119.0,62.1,57.3,51.2,21.2$. HRMS (EI): $m / z$ calcd for $\mathrm{C}_{10} \mathrm{H}_{18} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}]^{+}$184.1332, found 184.1339.
(2E,2'E)-dimethyl 4,4'-((2-acetoxyethyl)azanediyl)bis(but-2-enoate) (3i)


Light red oil, yield $=71 \%, 106 \mathrm{mg},{ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=6.92-6.83(\mathrm{~m}, 2 \mathrm{H})$, 6.04-5.98 (m, 2H), $4.10(\mathrm{t}, 2 \mathrm{H}, J=5.7 \mathrm{~Hz}), 3.71(\mathrm{~s}, 6 \mathrm{H}), 3.27(\mathrm{~d}, 4 \mathrm{H}, J=5.7 \mathrm{~Hz}), 2.70(\mathrm{t}, 2 \mathrm{H}, J$ $=5.7 \mathrm{~Hz}), 2.05(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=171.0,166.6,145.4,122.9,62.1$, 55.3, 52.5, 51.6, 21.0. HRMS (EI): $m / z$ calcd for $\mathrm{C}_{14} \mathrm{H}_{22} \mathrm{NO}_{6}[\mathrm{M}+\mathrm{H}]^{+} 300.1442$, found 300.1448 .


Brown oil, yield $=58 \%, 95 \mathrm{mg},{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=6.93-6.85(\mathrm{~m}, 2 \mathrm{H}), 6.01(\mathrm{~d}$, $2 \mathrm{H}, J=15.6 \mathrm{~Hz}), 4.22-4.10(\mathrm{~m}, 6 \mathrm{H}), 3.28(\mathrm{~d}, 4 \mathrm{H}, J=5.4 \mathrm{~Hz}), 2.74-2.70(\mathrm{~m}, 2 \mathrm{H}), 2.07(\mathrm{~s}, 3 \mathrm{H})$, 1.31-1.25 (m, 6H). ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=171.0,166.2,145.1,123.3,62.2,60.5$, 55.3, 52.5, 21.0, 14.3. HRMS (EI): $m / z$ calcd for $\mathrm{C}_{16} \mathrm{H}_{26} \mathrm{NO}_{6}[\mathrm{M}+\mathrm{H}]^{+} 328.1755$, found 328.1757.

2-(bis((5-chlorothiophen-2-yl)methyl)amino)ethyl acetate (3k)


Brown oil, yield $=66 \%, 120 \mathrm{mg},{ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=6.75-6.69(\mathrm{~m}, 4 \mathrm{H}), 4.20(\mathrm{t}$, $2 \mathrm{H}, J=6.0 \mathrm{~Hz}), 3.81(\mathrm{~s}, 4 \mathrm{H}), 2.80(\mathrm{t}, 2 \mathrm{H}, J=6.0 \mathrm{~Hz}), 2.10(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}(75 \mathrm{MHz}$, $\mathrm{CDCl}_{3}$ ): $\delta=171.0,141.5,129.5,125.6,125.1,62.1,53.1,51.2,21.1$. HRMS (EI): $m / z$ calcd for $\mathrm{C}_{14} \mathrm{H}_{16} \mathrm{Cl}_{2} \mathrm{NO}_{2} \mathrm{~S}_{2}[\mathrm{M}+\mathrm{H}]^{+} 363.9994$, found 363.9997.

## 2-(bis(4-methylbenzyl)amino)-2-methylpropyl acetate (31)



Yellow oil, yield $=72 \%, 122 \mathrm{mg},{ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=7.21(\mathrm{~d}, 4 \mathrm{H}, J=7.8 \mathrm{~Hz})$, $7.06(\mathrm{~d}, 4 \mathrm{H}, J=7.8 \mathrm{~Hz}), 4.11(\mathrm{~s}, 2 \mathrm{H}), 3.79(\mathrm{~s}, 4 \mathrm{H}), 2.31(\mathrm{~s}, 6 \mathrm{H}), 2.11(\mathrm{~s}, 3 \mathrm{H}), 1.19(\mathrm{~s}, 6 \mathrm{H})$. ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=171.2,139.2,135.9,128.7,128.3,70.1,57.8,53.6,23.3$, 21.2, 21.1. HRMS (EI): $m / z$ calcd for $\mathrm{C}_{22} \mathrm{H}_{30} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}]^{+} 340.2271$, found 340.2274.

3-benzylthiazolidin-2-one ${ }^{1}$ (5a)


Light yellow oil, yield $=83 \%, 80 \mathrm{mg},{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=7.37-7.26(\mathrm{~m}, 5 \mathrm{H})$, $4.48(\mathrm{~s}, 2 \mathrm{H}), 3.51(\mathrm{t}, 2 \mathrm{H}, J=7.2 \mathrm{~Hz}), 3.22(\mathrm{t}, 2 \mathrm{H}, J=7.2 \mathrm{~Hz}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}(100 \mathrm{MHz}$, $\mathrm{CDCl}_{3}$ ): $\delta=172.2,136.0,128.8,128.1,127.9,48.6,48.0,25.5$. HRMS (EI): $m / z$ calcd for $\mathrm{C}_{10} \mathrm{H}_{12} \mathrm{ONS}[\mathrm{M}+\mathrm{H}]^{+}$194.0634, found 194.0639.

## 3-(4-methylbenzyl)thiazolidin-2-one (5b)



Yellow oil, yield $=82 \%, 85 \mathrm{mg},{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=7.28-7.17(\mathrm{~m}, 4 \mathrm{H}), 4.45(\mathrm{~s}$, $2 \mathrm{H}), 3.51(\mathrm{t}, 2 \mathrm{H}, J=7.2 \mathrm{~Hz}), 3.22(\mathrm{t}, 2 \mathrm{H}, J=7.6 \mathrm{~Hz}), 2.36(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}(100 \mathrm{MHz}$, $\mathrm{CDCl}_{3}$ ): $\delta=172.2,137.7,133.0,129.5,128.3,128.2,48.5,48.0,25.6,21.2$. HRMS (EI): $\mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{11} \mathrm{H}_{14} \mathrm{ONS}[\mathrm{M}+\mathrm{H}]^{+}$208.0791, found 208.0796.

## 3-(2-methylbenzyl)thiazolidin-2-one (5c) <br> 

Colorless solid, yield $=86 \%, 89 \mathrm{mg},{ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.22-7.17(\mathrm{~m}, 4 \mathrm{H})$, $4.49(\mathrm{~s}, 2 \mathrm{H}), 3.44(\mathrm{t}, 2 \mathrm{H}, J=7.2 \mathrm{~Hz}), 3.21(\mathrm{t}, 2 \mathrm{H}, J=7.2 \mathrm{~Hz}), 2.31(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}(150$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=171.9,136.9,133.9,130.8,129.0,128.1,126.3,48.0,46.9,25.6,19.2$. HRMS (EI): $m / z$ calcd for $\mathrm{C}_{11} \mathrm{H}_{14} \mathrm{ONS}[\mathrm{M}+\mathrm{H}]^{+}$208.0791, found 208.0792.

## 3-(4-(tert-butyl)benzyl)thiazolidin-2-one (5d)



Colorless solid, yield $=90 \%, 112 \mathrm{mg},{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.37(\mathrm{~d}, 2 \mathrm{H}, J=8.0 \mathrm{~Hz})$, $7.21(\mathrm{~d}, 2 \mathrm{H}, J=8.4 \mathrm{~Hz}), 4.47(\mathrm{~s}, 2 \mathrm{H}), 3.53(\mathrm{t}, 2 \mathrm{H}, J=7.2 \mathrm{~Hz}), 3.23(\mathrm{t}, 2 \mathrm{H}, J=7.6 \mathrm{~Hz}), 1.33(\mathrm{~s}$, 9H). ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR (100 MHz, $\mathrm{CDCl}_{3}$ ): $\delta=172.2,150.9,133.0,128.0,125.8,48.4,48.1,34.6$, 31.4, 25.5. HRMS (EI): $m / z$ calcd for $\mathrm{C}_{14} \mathrm{H}_{20} \mathrm{ONS}[\mathrm{M}+\mathrm{H}]^{+} 250.1260$, found 250.1262.

## 3-(4-bromobenzyl)thiazolidin-2-one (5e)



Colorless oil, yield $=71 \%, 96 \mathrm{mg},{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.57(\mathrm{~d}, 2 \mathrm{H}, J=8.4 \mathrm{~Hz}$ ), $7.15(\mathrm{~d}, 2 \mathrm{H}, J=8.4 \mathrm{~Hz}), 4.43(\mathrm{~s}, 2 \mathrm{H}), 3.50(\mathrm{t}, 2 \mathrm{H}, J=7.2 \mathrm{~Hz}), 3.24(\mathrm{t}, 2 \mathrm{H}, J=7.2 \mathrm{~Hz}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=172.4,135.2,132.0,129.9,121.9,48.1,48.0,25.6$. HRMS (EI): $m / z$ calcd for $\mathrm{C}_{10} \mathrm{H}_{11} \mathrm{ONBrS}[\mathrm{M}+\mathrm{H}]^{+} 271.9739$, found 271.9742.

3-(2-chlorobenzyl)thiazolidin-2-one (5f)


Yellow oil, yield $=63 \%, 72 \mathrm{mg},{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=7.38-7.24(\mathrm{~m}, 4 \mathrm{H}), 4.62(\mathrm{~s}$, 2 H ), $3.57(\mathrm{t}, 2 \mathrm{H}, J=7.2 \mathrm{~Hz}), 3.26(\mathrm{t}, 2 \mathrm{H}, J=7.6 \mathrm{~Hz}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=$ 172.4, 133.7, 133.6, 130.0, 129.8, 129.3, 127.4, 48.3, 45.9, 25.7. HRMS (EI): m/z calcd for $\mathrm{C}_{10} \mathrm{H}_{11} \mathrm{ONClS}[\mathrm{M}+\mathrm{H}]^{+}$228.0244, found 228.0246.

## 3-(4-fluorobenzyl)thiazolidin-2-one (5g)



Yellow oil, yield $=74 \%, 78 \mathrm{mg},{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.25-7.22(\mathrm{~m}, 2 \mathrm{H}), 7.03-6.99$ $(\mathrm{m}, 2 \mathrm{H}), 4.43(\mathrm{~s}, 2 \mathrm{H}), 3.49(\mathrm{t}, 2 \mathrm{H}, J=7.2 \mathrm{~Hz}), 3.22(\mathrm{t}, 2 \mathrm{H}, J=6.8 \mathrm{~Hz}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $(100$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=172.3,161.2\left(\mathrm{~d}, J_{C F}=244.8 \mathrm{~Hz}_{\mathrm{z}}\right), 131.9\left(\mathrm{~d}, J_{C F}=3.1 \mathrm{~Hz}_{\mathrm{z}}\right), 129.9\left(\mathrm{~d}, J_{C F}=8.1\right.$ $\left.\mathrm{H}_{\mathrm{z}}\right), 115.6\left(\mathrm{~d}, J_{C F}=21.4 \mathrm{~Hz}_{\mathrm{z}}\right), 48.0,47.9,25.5 . \mathrm{HRMS}(\mathrm{EI}): \mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{10} \mathrm{H}_{11} \mathrm{ONFS}[\mathrm{M}+\mathrm{H}]^{+}$ 212.0540 , found 212.0538 .

3-(2-fluorobenzyl)thiazolidin-2-one (5h)


Yellow oil, yield $=83 \%, 87 \mathrm{mg},{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.36-7.27(\mathrm{~m}, 2 \mathrm{H}), 7.16-7.04$ $(\mathrm{m}, 2 \mathrm{H}), 4.55(\mathrm{~s}, 2 \mathrm{H}), 3.58(\mathrm{t}, 2 \mathrm{H}, J=7.2 \mathrm{~Hz}), 3.25(\mathrm{t}, 2 \mathrm{H}, J=7.6 \mathrm{~Hz}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR (100 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=172.4,159.8\left(\mathrm{~d}, J_{C F}=246.5 \mathrm{H}_{\mathrm{z}}\right), 130.8\left(\mathrm{~d}, J_{C F}=3.7 \mathrm{~Hz}^{2}\right), 129.8\left(\mathrm{~d}, J_{C F}=8.1\right.$ $\left.\mathrm{H}_{\mathrm{z}}\right), 124.7\left(\mathrm{~d}, J_{C F}=3.5 \mathrm{~Hz}^{2}\right), 122.9\left(\mathrm{~d}, J_{C F}=15.0 \mathrm{~Hz}_{\mathrm{Z}}\right), 115.5\left(\mathrm{~d}, J_{C F}=21.6 \mathrm{H}_{\mathrm{z}}\right), 48.2,41.9\left(\mathrm{~d}, J_{C F}\right.$ $=3.9 \mathrm{~Hz}$ ), 25.6. $\mathrm{HRMS}(\mathrm{EI}): \mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{10} \mathrm{H}_{11} \mathrm{ONFS}[\mathrm{M}+\mathrm{H}]^{+} 212.0540$, found 212.0539 .

4-((2-oxothiazolidin-3-yl)methyl)benzonitrile (5i)


Light yellow solid, yield $=80 \%, 87 \mathrm{mg},{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.61(\mathrm{~d}, 2 \mathrm{H}, J=8.0$ $\mathrm{Hz}), 7.36(\mathrm{~d}, 2 \mathrm{H}, J=8.0 \mathrm{~Hz}), 4.51(\mathrm{~s}, 2 \mathrm{H}), 3.52(\mathrm{t}, 2 \mathrm{H}, J=7.2 \mathrm{~Hz}), 3.27(\mathrm{t}, 2 \mathrm{H}, J=7.2 \mathrm{~Hz})$. ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=172.6,141.6,132.6,128.6,118.5,111.7,48.2,48.1,25.5$. HRMS (EI): $m / z$ calcd for $\mathrm{C}_{11} \mathrm{H}_{11} \mathrm{ON} 2 \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+}$219.0587, found 219.0589.

## 3-((6-methylpyridin-2-yl)methyl)thiazolidin-2-one (5j)



Yellow oil, yield $=77 \%, 80 \mathrm{mg},{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.56(\mathrm{t}, 1 \mathrm{H}, J=7.6 \mathrm{~Hz}$ ), $7.10-7.06(\mathrm{~m}, 2 \mathrm{H}), 4.57(\mathrm{~s}, 2 \mathrm{H}), 3.67(\mathrm{t}, 2 \mathrm{H}, J=7.2 \mathrm{~Hz}), 3.27(\mathrm{t}, 2 \mathrm{H}, J=7.6 \mathrm{~Hz}), 2.53(\mathrm{~s}, 3 \mathrm{H})$. ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=172.5,158.3,155.5,137.4,122.4,119.1,50.5,48.7,25.8$, 24.5. HRMS (EI): $m / z$ calcd for $\mathrm{C}_{10} \mathrm{H}_{13} \mathrm{ON}_{2} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+}$209.0743, found 209.0742 .

## 3-((5-chlorothiophen-2-yl)methyl)thiazolidin-2-one (5k)



Light yellow solid, yield $=50 \%, 58 \mathrm{mg}$, ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=6.87-6.62(\mathrm{~m}, 2 \mathrm{H})$, $4.53(\mathrm{~s}, 2 \mathrm{H}), 3.59(\mathrm{t}, 2 \mathrm{H}, J=7.2 \mathrm{~Hz}), 3.26(\mathrm{t}, 2 \mathrm{H}, J=7.6 \mathrm{~Hz}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}(100 \mathrm{MHz}$, $\mathrm{CDCl}_{3}$ ): $\delta=172.4,137.2,130.3,126.6,126.0,47.9,43.5,25.6 . \operatorname{HRMS}$ (EI): $m / z$ calcd for $\mathrm{C}_{8} \mathrm{H}_{9} \mathrm{ONClS}_{2}[\mathrm{M}+\mathrm{H}]^{+}$233.9814, found 233.9825 .

2-(dibenzylamino)ethanol (6)


Light yellow oil, yield $=88 \%, 106 \mathrm{mg},{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.39-7.29(\mathrm{~m}, 10 \mathrm{H})$, $3.67(\mathrm{~s}, 4 \mathrm{H}), 3.62(\mathrm{t}, 2 \mathrm{H}, J=5.5 \mathrm{~Hz}), 2.70(\mathrm{t}, 2 \mathrm{H}, J=5.5 \mathrm{~Hz}), 2.47($ brs, 1 H$) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=138.9,129.1,128.6,127.4,58.6,58.3,54.8$. HRMS (EI): $m / z$ calcd for $\mathrm{C}_{16} \mathrm{H}_{20} \mathrm{NO}[\mathrm{M}+\mathrm{H}]^{+} 242.1539$, found 242.1531.

References

1. Mahy, W.; Plucinski, P.; Jover, J.; Frost, C. G. Angew. Chem. Int. Ed. 2015, 54, 10944.

## 2-(dibenzylamino)ethyl acetate (3a)





2-(bis(4-methylbenzyl)amino)ethyl acetate (3b)


2-(bis(2-methylbenzyl)amino)ethyl acetate (3c)



2-(bis(4-(tert-butyl)benzyl)amino)ethyl acetate (3d)



## 2-(bis(4-fluorobenzyl)amino)ethyl acetate (3e)



2-(bis(2-fluorobenzyl)amino)ethyl acetate (3f)


## 2-(bis(2-chlorobenzyl)amino)ethyl acetate (3g)




## 2-(diallylamino)ethyl acetate (3h)



(2E,2'E)-dimethyl 4,4'-((2-acetoxyethyl)azanediyl)bis(but-2-enoate) (3i)




2-(bis((5-chlorothiophen-2-yl)methyl)amino)ethyl acetate (3k)




2-(bis(4-methylbenzyl)amino)-2-methylpropyl acetate (3I)

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## 3-benzylthiazolidin-2-one (5a)





## 3-(4-methylbenzyl)thiazolidin-2-one (5b)



## 3-(2-methylbenzyl)thiazolidin-2-one (5c)



## 3-(4-(tert-butyl)benzyl)thiazolidin-2-one (5d)





## 3-(4-bromobenzyl)thiazolidin-2-one (5e)





## 3-(2-chlorobenzyl)thiazolidin-2-one (5f)




## 3-(4-fluorobenzyl)thiazolidin-2-one (5g)



## 3-(2-fluorobenzyl)thiazolidin-2-one (5h)




$\begin{array}{lllllllllllllllllllllllll}210 & 200 & 190 & 180 & 170 & 160 & 150 & 140 & 130 & 120 & 110 & 100 & 90 & 80 & 70 & 60 & 50 & 40 & 30 & 20 & 10 & 0 & -10 \\ \mathrm{f} 1 & (\mathrm{ppm})\end{array}$

## 4-((2-oxothiazolidin-3-yl)methyl)benzonitrile (5i)



## 3-((6-methylpyridin-2-yl)methyl)thiazolidin-2-one (5j)





3-((5-chlorothiophen-2-yl)methyl)thiazolidin-2-one (5k)




2-(dibenzylamino)ethanol (6)




