Rhodium-Catalyzed Denitrogenative Transannulation of 1,2,3-Triazolyl-Carbamates: Efficient Access to 4-Aminooxazolidinones

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1. Methods:
All reactions were carried out under nitrogen atmosphere in screw cap reaction tubes and the workups were performed under air. All the solvents used for the reactions were dried by following the reported procedures. Unless otherwise noted, all materials were purchased from commercial suppliers and used as received. All sulfonyl azides were prepared in house using conventional procedure. Reactions were monitored using thin-layer chromatography (SiO$_2$). A gradient elution using petroleum ether and ethyl acetate was performed based on Merck aluminium TLC sheets (silica gel 60F$_{254}$). TLC plates were visualized with UV light (254 nm) or KMnO$_4$ stain or Vannilin stain. For column chromatography, silica gel (100–200 mesh) from SRL Co. was used. NMR spectra were recorded at 400 MHz (1H) or 500 MHz (1H) and at 100 MHz (13C) or 125 MHz (13C), respectively. Chemical shifts (d) are reported in ppm, using the residual solvent peak in CDCl$_3$ (dH = 7.26 and d$^13$C = 77.20 ppm), CD$_2$Cl$_2$ (dH = 5.32 and d$^13$C = 54.00 ppm), DMSO-D$_6$ (dH = 2.50 and d$^13$C = 39.51 ppm) as internal standards, and coupling constants (J) are given in Hz. HRMS were recorded using ESI-TOF techniques.

2. Experimental Procedures
(a) Typical Procedure for the Synthesis of (1-tosyl-1H-1,2,3-triazol-4-yl) methyl arylcarbamate$^1$ (5a to 5u):

A solution of prop-2-yn-1-yl tosylcarbamate (1.00 g, 3.95 mmol) in toluene (10 mL) and a solution of TsN$_3$ (0.79 g, 4.0 mmol) in toluene (10 mL) were added to a 50 mL round bottom flask equipped with a stirrer bar under nitrogen. Then Copper(I)-thiophene-2-carboxylate (37.56 mg, 5 mol %) was added to the mixture under nitrogen condition. The resulting mixture was
stirred for 12h at room temperature. After determining the completeness of triazole formation by TLC, the reaction was quenched with a saturated NH$_4$Cl aq. solution, and extracted with EtOAc. The combined organic layer was washed with brine, dried over Na$_2$SO$_4$, and concentrated under reduced pressure. The resulting residue was purified by recrystallization (Hex/DCM 19:1) to give 5a (1.55 g, 86%) as a white powder.

5a:

(1-tosyl-1H-1,2,3-triazol-4-yl)methyl tosylcarbamate

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.12 (s, 1H), 8.11 (s, 1H), 7.98 (d, $J = 8.3$ Hz, 2H), 7.87 (d, $J = 8.2$ Hz, 2H), 7.39 (d, $J = 8.2$ Hz, 2H), 7.32 (d, $J = 8.1$ Hz, 2H), 5.17 (s, 2H), 2.45 (s, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 150.32, 147.90, 145.60, 135.32, 132.74, 130.75, 129.87, 129.03, 128.50, 126.62, 124.01, 58.95, 22.04, 21.87.

HRMS (ESI): C$_{18}$H$_{18}$N$_4$O$_6$S$_2$ [M+Na]$^+$ calculated = 473.0565; found = 473.0585.

5b:

(1-tosyl-1H-1,2,3-triazol-4-yl)methyl phenylcarbamate

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.24 (s, 1H), 7.99 (d, $J = 8.3$ Hz, 2H), 7.41 – 7.33 (m, 4H), 7.30 (t, $J = 7.7$ Hz, 2H), 7.08 (t, $J = 7.2$ Hz, 1H), 6.85 (s, 1H), 5.28 (s, 2H), 2.44 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.07, 147.72, 143.00, 137.53, 132.94, 130.75, 129.28, 128.99, 124.01, 123.89, 118.99, 57.67, 22.02.

HRMS (ESI): C$_{17}$H$_{16}$N$_4$O$_6$S [M+Na]$^+$ calculated = 395.0790; found = 395.0784.
5c:

(1-tosyl-1H-1,2,3-triazol-4-yl)methyl p-tolylcarbamate

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.35 (s, 1H), 8.00 (d, $J$ = 7.9 Hz, 2H), 7.38 (d, $J$ = 7.9 Hz, 2H), 7.25 (d, $J$ = 12.0 Hz, 2H), 7.11 (d, $J$ = 7.6 Hz, 2H), 6.74 (s, 1H), 5.28 (s, 2H), 2.45 (s, 2H), 2.31 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): δ 153.18, 147.70, 143.14, 134.94, 133.63, 132.94, 130.66, 129.74, 128.97, 123.88, 119.15, 57.60, 22.00, 20.91.

HRMS (ESI): C$_{18}$H$_{18}$N$_4$O$_4$S [M+Na]$^+$ calculated = 409.0946; found = 409.0941.

5d:

(1-tosyl-1H-1,2,3-triazol-4-yl)methyl (4-chlorophenyl)carbamate

$^1$H NMR (500 MHz, CDCl$_3$): δ 8.27 (s, 1H), 8.01 (d, $J$ = 8.4 Hz, 2H), 7.40 (d, $J$ = 8.1 Hz, 2H), 7.34 (d, $J$ = 8.0 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.06 (s, 1H), 5.29 (s, 2H), 2.46 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): δ 153.01, 147.80, 142.81, 136.24, 132.85, 130.68, 129.24, 128.99, 123.94, 120.21, 120.20, 57.70, 22.01.

HRMS (ESI): C$_{17}$H$_{15}$ClN$_4$O$_4$S [M+Na]$^+$ calculated = 429.0400; found = 429.0395.

5e:

(1-tosyl-1H-1,2,3-triazol-4-yl)methyl (4-bromophenyl)carbamate

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.24 (s, 1H), 7.99 (d, $J$ = 8.1 Hz, 2H), 7.39 (t, $J$ = 8.8 Hz, 4H), 7.27 (d, $J$ = 5.0 Hz, 2H), 6.98 (s, 1H), 5.27 (s, 2H), 2.44 (s, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 152.93, 147.81, 142.77, 136.73, 132.82, 132.20, 130.70, 129.00, 127.70, 123.97, 120.50, 116.50, 57.72, 22.04.

HRMS (ESI): C$_{17}$H$_{15}$Br$_4$Na$_4$O$_4$S [M+Na]$^+$ calculated = 472.9895; found = 472.9890.

5f:

(1-tosyl-1H-1,2,3-triazol-4-yl)methyl quinolin-8-ylcarbamate

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 9.26 (s, 1H), 8.77 (s, 1H), 8.39 (s, 1H), 8.29 (s, 1H), 8.14 (s, 1H), 8.00 (s, 2H), 7.61 – 7.42 (m, 3H), 7.37 (d, $J$ = 5.9 Hz, 2H), 5.34 (s, 2H), 2.42 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 153.04, 148.41, 147.64, 136.42, 134.36, 132.96, 130.65, 129.84, 128.95, 128.17, 127.34, 126.57, 123.75, 121.89, 121.22, 114.90, 57.81, 21.98.

HRMS (ESI): C$_{20}$H$_{18}$N$_5$Na$_4$O$_4$S [M+Na]$^+$ calculated = 446.0899; found = 446.0879.

5g:

(1-tosyl-1H-1,2,3-triazol-4-yl)methyl benzylcarbamate

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.19 (s, 1H), 7.98 (d, $J$ = 8.1 Hz, 2H), 7.42 – 7.35 (m, 3H), 7.34 – 7.25 (m, 5H), 5.20 (s, 2H), 4.35 (d, $J$ = 5.5 Hz, 2H), 2.44 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 156.05, 147.64, 138.18, 133.01, 130.64, 130.43, 128.94, 128.86, 127.76, 127.64, 123.62, 57.67, 45.32, 22.00.

HRMS (ESI): C$_{18}$H$_{19}$N$_4$O$_4$S [M+H]$^+$ calculated = 487.1127; found = 487.1122.

5h:
(1-tosyl-1H-1,2,3-triazol-4-yl)methyl cyclohexylcarbamate

$^1$H NMR (500 MHz, CDCl$_3$): δ 8.17 (s, 1H), 7.98 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 5.15 (s, 2H), 4.69 (d, J = 6.4 Hz, 1H), 3.51 – 3.48 (m, 1H), 2.44 (s, 3H), 1.89 (d, J = 9.9 Hz, 2H), 1.68 (dd, J = 9.8, 3.7 Hz, 2H), 1.31 (dd, J = 16.7, 8.1 Hz, 2H), 1.20 – 1.05 (m, 4H).

$^{13}$C NMR (125 MHz, CDCl$_3$): δ 147.60, 133.09, 130.62, 130.44, 128.95, 127.71, 123.59, 57.30, 50.21, 33.42, 25.56, 24.89, 22.00.

HRMS (ESI): C$_{17}$H$_{22}$N$_4$NaO$_4$S [M+Na]$^+$ calculated = 401.1259; found = 401.1254.

5i:

(1-tosyl-1H-1,2,3-triazol-4-yl)methyl butylcarbamate

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.18 (s, 1H), 7.97 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 5.16 (s, 2H), 4.83 (s, 1H), 3.15 (d, J = 6.0 Hz, 2H), 2.43 (s, 3H), 1.53 – 1.37 (m, 2H), 1.30 (dd, J = 14.3, 7.1 Hz, 2H), 0.89 (t, J = 7.1 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 155.98, 147.61, 133.01, 130.61, 128.91, 123.70, 57.38, 40.99, 32.02, 21.98, 19.97, 13.81.

HRMS (ESI): C$_{15}$H$_{20}$N$_4$NaO$_4$S [M+Na]$^+$ calculated = 375.1103; found = 375.1097.

5j:

(1-(phenylsulfonyl)-1H-1,2,3-triazol-4-yl)methyl tosylcarbamate

$^1$H NMR (500 MHz, CDCl$_3$): δ 8.27 (s, 1H), 8.14 (s, 1H), 8.10 (d, J = 7.8 Hz, 2H), 7.87 (d, J = 7.6 Hz, 2H), 7.74 (t, J = 7.2 Hz, 1H), 7.61 (t, J = 7.6 Hz, 2H), 7.31 (d, J = 7.8 Hz, 2H), 5.18 (s, 2H), 2.43 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): δ 150.35, 145.61, 136.15, 135.85, 135.32, 130.13, 129.88, 128.96, 128.48, 126.61, 124.10, 58.89, 21.88.

HRMS (ESI): C$_{17}$H$_{16}$N$_4$NaO$_6$S$_2$ [M+Na]$^+$ calculated = 459.0409; found = 459.0381.
5k:

\[
\text{(1-((methylsulfonyl)-1H-1,2,3-triazol-4-yl)methyl tosylcarbamate}
\]

\(^1\)H NMR (400 MHz, DMSO-\(\text{D}_6\)): \(\delta\) 7.80 (s, 1H), 7.75 (d, \(J = 8.2\) Hz, 2H), 7.38 (d, \(J = 8.2\) Hz, 2H), 5.10 (s, 2H), 2.44 (s, 3H), 2.37 (s, 3H).

\(^{13}\)C NMR (100 MHz, DMSO-\(\text{D}_6\)): \(\delta\) 151.00, 144.50, 140.58, 136.31, 129.75, 127.57, 125.74, 58.47, 21.18, one methyl peak merge with solvent peak.

HRMS (ESI): C\(_{12}\)H\(_{14}\)N\(_4\)NaO\(_6\)S\(_2\) [M+Na]\(^+\) calculated = 397.0252; found = 397.0225.

5l:

\[
\text{(1-((mesitylsulfonyl)-1H-1,2,3-triazol-4-yl)methyl tosylcarbamate}
\]

\(^1\)H NMR (400 MHz, DMSO-\(\text{D}_6\)): \(\delta\) 7.88 (s, 1H), 7.83 (d, \(J = 8.1\) Hz, 2H), 7.47 (d, \(J = 8.1\) Hz, 2H), 6.84 (s, 2H), 5.18 (s, 2H), 2.56 (s, 6H), 2.43 (s, 3H), 2.23 (s, 3H).

\(^{13}\)C NMR (100 MHz, DMSO-\(\text{D}_6\)): \(\delta\) 151.04, 144.54, 141.88, 140.62, 137.13, 136.31, 136.20, 130.20, 129.79, 127.61, 125.77, 58.49, 22.81, 21.21, 20.42.

HRMS (ESI): C\(_{20}\)H\(_{22}\)N\(_4\)NaO\(_6\)S\(_2\) [M+Na]\(^+\) calculated = 501.0878; found = 501.0869.

5m:

\[
\text{(1-((4-methoxyphenyl)sulfonyl)-1H-1,2,3-triazol-4-yl)methyl tosylcarbamate}
\]
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.11 (s, 1H), 8.01 (d, $J = 8.7$ Hz, 2H), 7.85 (d, $J = 10.7$ Hz, 2H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.01 (d, $J = 10.2$ Hz, 2H), 5.16 (s, 2H), 3.86 (s, 3H), 2.42 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 165.77, 150.51, 145.50, 141.52, 135.39, 131.56, 129.84, 128.44, 126.51, 123.85, 115.38, 58.92, 56.16, 21.84.

HRMS (ESI): C$_{18}$H$_{19}$N$_4$O$_7$S$_2$ [M+H]$^+$ calculated = 467.0695; found = 467.0690.

5n:

1-(1-tosyl-1H-1,2,3-triazol-4-yl)ethyl phenylcarbamate

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.14 (s, 1H), 7.98 (d, $J = 8.4$ Hz, 2H), 7.36 (d, $J = 8.3$ Hz, 4H), 7.28 (t, $J = 7.9$ Hz, 2H), 7.06 (t, $J = 7.3$ Hz, 1H), 6.89 (s, 1H), 6.03 (q, $J = 6.6$ Hz, 1H), 2.42 (s, 3H), 1.69 (d, $J = 6.7$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 152.64, 147.63, 137.65, 132.90, 130.63, 129.20, 128.92, 123.82, 121.95, 118.89, 118.87, 65.33, 21.98, 19.85.

HRMS (ESI): C$_{18}$H$_{19}$N$_4$O$_4$S [M+Na]$^+$ calculated = 409.0946; found = 409.0936.

5o:

1-(1-tosyl-1H-1,2,3-triazol-4-yl)hexyl phenylcarbamate

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.12 (s, 1H), 7.98 (d, $J = 8.2$ Hz, 2H), 7.35 (t, $J = 9.3$ Hz, 4H), 7.32 – 7.24 (m, 3H), 7.06 (t, $J = 7.2$ Hz, 1H), 6.82 (s, 1H), 5.91 (t, $J = 6.9$ Hz, 1H), 2.43 (s, 3H), 2.12 – 1.97 (m, 2H), 1.40 – 1.24 (m, 6H), 0.85 (t, $J = 6.5$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 152.85, 147.57, 146.94, 137.70, 133.02, 130.62, 129.22, 128.93, 123.82, 122.22, 118.86, 68.89, 33.83, 31.48, 24.98, 22.56, 21.98, 14.08.

HRMS (ESI): C$_{22}$H$_{26}$KN$_4$O$_4$S [M+K]$^+$ calculated = 481.1312; found = 481.1306.
5p:

![Chemical Structure]

2-(1-tosyl-1H-1,2,3-triazol-4-yl)propan-2-yl phenylcarbamate

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.15 (s, 1H), 7.99 (d, $J = 8.4$ Hz, 2H), 7.36 (d, $J = 8.2$ Hz, 2H), 7.27 (d, $J = 3.9$ Hz, 4H), 7.04 (dt, $J = 8.5, 4.1$ Hz, 1H), 6.66 (s, 1H), 2.43 (s, 3H), 1.89 (s, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 151.95, 147.45, 137.87, 133.15, 130.60, 129.15, 128.93, 123.64, 121.28, 118.96, 118.91, 77.40, 27.62, 22.00.

HRMS (ESI): C$_{19}$H$_{20}$N$_4$NaO$_4$S [M+Na]$^+$ calculated = 423.1103; found = 423.1097.

5q:

![Chemical Structure]

1-(1-tosyl-1H-1,2,3-triazol-4-yl)cyclopentyl phenylcarbamate

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.17 (s, 1H), 7.97 (d, $J = 8.2$ Hz, 2H), 7.34 (d, $J = 8.2$ Hz, 2H), 7.26 (d, $J = 3.4$ Hz, 4H), 7.03 (dt, $J = 8.4, 4.1$ Hz, 1H), 6.66 (s, 1H), 2.60 – 2.49 (m, 2H), 2.41 (s, 3H), 2.28 (dt, $J = 14.0, 7.2$ Hz, 2H), 1.85 (dd, $J = 14.8, 7.9$ Hz, 2H), 1.80 – 1.69 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 152.18, 149.82, 147.38, 137.83, 133.15, 130.56, 129.15, 128.90, 123.62, 122.00, 118.79, 85.71, 38.64, 23.36, 21.99.

HRMS (ESI): C$_{21}$H$_{22}$KN$_4$O$_4$S [M+K]$^+$ calculated = 465.0999; found = 465.0993.

5r:

![Chemical Structure]

1-(1-tosyl-1H-1,2,3-triazol-4-yl)cyclohexyl phenylcarbamate

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.20 (s, 1H), 8.00 (t, $J = 10.5$ Hz, 2H), 7.34 (t, $J = 8.5$ Hz, 2H), 7.31 – 7.24 (m, 4H), 7.05 (dq, $J = 8.7, 4.3$ Hz, 1H), 6.72 (s, 1H), 2.58 (d, $J = 13.5$ Hz, 2H), 2.43
(s, 3H), 2.06 (t, $J = 10.4$ Hz, 2H), 1.70 (ddd, $J = 14.4, 12.8, 7.1$ Hz, 3H), 1.62 – 1.53 (m, 2H), 1.40 (dt, $J = 16.5, 7.1$ Hz, 1H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 151.85, 150.31, 147.35, 137.91, 133.16, 130.55, 129.09, 128.86, 123.53, 122.19, 118.80, 77.77, 35.50, 25.26, 21.97, 21.91. 

HRMS (ESI): C$_{22}$H$_{24}$KN$_4$O$_4$S [M+K]$^+$ calculated = 479.1155; found = 479.1150.

5s:

![Structure of 5s](image)

(4-bromophenyl)(1-tosyl-1H-1,2,3-triazol-4-yl)methyl phenylcarbamate

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.04 (s, 1H), 7.98 (d, $J = 8.3$ Hz, 2H), 7.48 (d, $J = 8.4$ Hz, 2H), 7.38 – 7.27 (m, 8H), 7.07 (t, $J = 7.2$ Hz, 1H), 6.95 (s, 1H), 6.93 (s, 1H), 2.43 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 152.06, 147.82, 146.53, 137.38, 136.61, 132.76, 132.14, 130.69, 129.26, 129.13, 129.03, 124.10, 123.16, 122.38, 118.93, 69.89, 22.04.

HRMS (ESI): C$_{23}$H$_{19}$BrN$_4$NaO$_4$S [M+Na]$^+$ calculated = 549.0208; found = 549.0203.

5t:

![Structure of 5t](image)

1-benzyl-3-phenyl-1-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)urea

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.96 (d, $J = 7.7$ Hz, 2H), 7.63 (s, 1H), 7.40 (d, $J = 7.7$ Hz, 3H), 7.35 – 7.20 (m, 9H), 7.01 (t, $J = 6.7$ Hz, 1H), 4.63 (s, 2H), 4.59 (s, 2H), 2.46 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 155.96, 147.76, 144.38, 139.18, 137.18, 132.84, 130.68, 129.14, 128.97, 128.96, 128.18, 127.88, 123.25, 122.53, 120.01, 51.55, 42.24, 22.04.

HRMS (ESI): C$_{24}$H$_{23}$N$_5$NaO$_3$S [M+Na]$^+$ calculated = 484.1419; found = 484.1414.
5u:

2-(1-tosyl-1H-1,2,3-triazol-4-yl)ethyl phenylcarbamate

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.99 (s, 1H), 7.96 (d, $J = 8.3$ Hz, 2H), 7.43 – 7.27 (m, 7H), 7.07 (t, $J = 7.3$ Hz, 1H), 6.84 (s, 1H), 4.42 (t, $J = 6.2$ Hz, 2H), 3.10 (t, $J = 6.2$ Hz, 2H), 2.42 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 147.48, 144.34, 137.80, 133.09, 130.59, 130.44, 129.20, 128.77, 123.73, 121.63, 118.89, 63.28, 25.71, 21.97.

HRMS (ESI): C$_{18}$H$_{18}$KN$_4$O$_4$S [M+K]$^+$ calculated = 425.0686; found = 425.0680.

(b) Optimization Details $^a$: 

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<th>Entry</th>
<th>Rh(II)-cat.</th>
<th>temp ($^\circ$C)</th>
<th>Solvent</th>
<th>yield (%)$^{[b]}$</th>
</tr>
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<td>Rh$_2$(OAc)$_4$</td>
<td>rt</td>
<td>DCE</td>
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<tr>
<td>2</td>
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<td>DCE</td>
<td>78</td>
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<tr>
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<td>DCE</td>
<td>85</td>
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<td>DCM</td>
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</tr>
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<td>8</td>
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<td>toluene</td>
<td>83</td>
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<td>Rh$_2$(OAc)$_4$</td>
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<td>toluene</td>
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<td>Rh$_2$(oct)$_4$</td>
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<td>DCM</td>
<td>81</td>
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</tbody>
</table>
Reaction conditions: [a] 0.1 mmol of 5a, 2 mol % Rh-catalyst and 1 mL solvent. [b] NMR yield was taken by using 0.1 mmol of 1,3,5-trimethoxybenzene as an internal standard. [c] Yield of the isolated product in parenthesis for 0.2 mmol 5a.

(c) Typical Procedure for the Synthesis of Oxazolidinone (9a to 9t): Preparation of 4-methyl-N-(5 methylene-2-oxo-3-tosyloxazolidin-4-yl) benzenesulfonamide:

(1-tosyl-1H-1,2,3-triazol-4-yl)methyl tosylcarbamate (5a, 90.1 mg, 0.2 mmol), Rh2(OAc)4 (1.8 mg, 2 mol %) were added to an oven-dried screw cap reaction tube equipped with a stir bar. The tube was evacuated and refilled with nitrogen three times. Then, dichloromethane (2 mL) was added via syringe. The reaction mixture was heated to 60 °C for 3 h. After the resulting mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (Hex/ EtOAc = 4:1) to give the product 9a (78.5 mg, 0.18 mmol, 93%).

9a:

4-methyl-N-(5-methylene-2-oxo-3-tosyloxazolidin-4-yl)benzenesulfonamide

1H NMR (500 MHz, CDCl3): δ 7.80 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 6.20 (d, J = 7.7 Hz, 1H), 5.77 (d, J = 7.7 Hz, 1H), 4.84 (dd, J = 3.8, 1.6 Hz, 1H), 4.39 (dd, J = 3.8, 1.1 Hz, 1H), 2.44 (s, 3H), 2.43 (s, 3H).
$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 148.21, 147.80, 146.43, 144.57, 138.17, 134.30, 130.01, 129.81, 128.92, 127.43, 93.39, 77.45, 77.20, 76.95, 67.49, 21.95, 21.81.

HRMS (ESI): $^{13}$C$_{18}$H$_{18}$N$_2$NaO$_6$S$_2$ [M+Na]$^+$ calculated = 445.0504; found = 445.0498.

9b:

4-methyl-N-(5-methylene-2-oxo-3-phenyloxazolidin-4-yl)benzenesulfonamide

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.50 (d, $J = 7.8$ Hz, 2H), 7.25 – 7.17 (m, 5H), 7.13 (d, $J = 7.8$ Hz, 2H), 6.18 (d, $J = 9.5$ Hz, 1H), 5.69 (d, $J = 9.5$ Hz, 1H), 4.90 (s, 1H), 4.43 (s, 1H), 2.39 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 150.84, 144.17, 141.66, 137.63, 134.04, 129.93, 129.37, 127.17, 126.88, 124.41, 91.48, 68.24, 21.70.

HRMS (ESI): $^{13}$C$_{17}$H$_{16}$N$_2$NaO$_4$S [M+Na]$^+$ calculated = 367.0728; found = 367.0723.

9c:

4-methyl-N-(5-methylene-2-oxo-3-(p-tolyl)oxazolidin-4-yl)benzenesulfonamide

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.47 (d, $J = 7.5$ Hz, 2H), 7.10 (d, $J = 6.4$ Hz, 2H), 7.06 (d, $J = 7.6$ Hz, 2H), 6.99 (d, $J = 7.9$ Hz, 2H), 6.11 (d, $J = 9.6$ Hz, 1H), 5.85 (d, $J = 9.6$ Hz, 1H), 4.91 – 4.84 (m, 1H), 4.47 – 4.38 (m, 1H), 2.39 (s, 3H), 2.31 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 152.14, 150.94, 143.87, 137.81, 137.37, 131.29, 129.90, 129.74, 126.78, 124.83, 91.27, 68.59, 21.69, 21.20.

HRMS (ESI): $^{13}$C$_{18}$H$_{18}$N$_2$NaO$_4$S [M+Na]$^+$ calculated = 381.0885; found = 381.0879.

9d:

N-(3-(4-chlorophenyl)-5-methylene-2-oxooxazolidin-4-yl)-4-methylbenzenesulfonamide
$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.49 (d, $J$ = 8.1 Hz, 2H), 7.17 (d, $J$ = 8.1 Hz, 2H), 7.15 – 7.12 (m, 4H), 6.14 (d, $J$ = 9.7 Hz, 1H), 5.68 (d, $J$ = 9.7 Hz, 1H), 4.93 (dd, $J$ = 3.6, 2.0 Hz, 1H), 4.48 (dd, $J$ = 3.6, 1.5 Hz, 1H), 2.44 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 151.84, 150.55, 144.43, 137.64, 133.11, 132.51, 129.90, 129.40, 126.69, 125.92, 91.73, 68.35, 21.74.

HRMS (ESI): C$_{17}$H$_{15}$ClN$_2$NaO$_4$S [M+Na]$^+$ calculated = 401.0339; found = 401.0333.

9e:

$\text{N-(3-(4-bromophenyl)-5-methylene-2-oxooxazolidin-4-yl)-4-methylbenzenesulfonamide}$

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.46 (d, $J$ = 8.3 Hz, 2H), 7.27 (d, $J$ = 8.7 Hz, 2H), 7.15 (d, $J$ = 8.3 Hz, 2H), 7.06 (d, $J$ = 8.7 Hz, 2H), 6.13 (d, $J$ = 9.6 Hz, 1H), 5.97 (d, $J$ = 9.6 Hz, 1H), 4.90 (dd, $J$ = 3.6, 1.8 Hz, 1H), 4.46 (dd, $J$ = 3.6, 1.4 Hz, 1H), 2.44 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 151.71, 150.54, 144.49, 137.60, 133.06, 132.37, 129.93, 126.70, 126.09, 121.01, 91.78, 77.45, 77.20, 76.95, 68.24, 21.82.

HRMS (ESI): C$_{17}$H$_{15}$BrN$_2$NaO$_4$S [M+Na]$^+$ calculated = 444.9834; found = 444.9828.

Crystal structure is also reported for this compound. (CCDC 1495707)

9f:

$\text{4-methyl-N-(5-methylene-2-oxo-3-(quinolin-8-yl)oxazolidin-4-yl)benzenesulfonamide}$

$^{1}$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.85 (dd, $J$ = 4.2, 1.7 Hz, 1H), 8.10 (dd, $J$ = 8.3, 1.6 Hz, 1H), 7.72 (dd, $J$ = 8.2, 1.2 Hz, 1H), 7.55 (dd, $J$ = 7.3, 1.3 Hz, 1H), 7.43 (ddd, $J$ = 15.6, 8.1, 5.8 Hz, 2H), 7.02 (d, $J$ = 8.3 Hz, 2H), 6.68 (d, $J$ = 12.5 Hz, 1H), 6.65 (d, $J$ = 8.0 Hz, 2H), 6.48 (s, 1H), 5.05 (dd, $J$ = 3.3, 2.0 Hz, 1H), 4.80 (dd, $J$ = 3.3, 1.7 Hz, 1H), 2.20 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 153.31, 152.25, 150.81, 144.31, 143.01, 136.98, 136.54, 131.23, 130.88, 129.43, 129.22, 129.03, 126.58, 125.92, 122.18, 91.10, 70.28, 21.50.

HRMS (ESI): C$_{20}$H$_{17}$N$_3$NaO$_4$S [M+Na]$^+$ calculated = 418.0837; found = 418.0832.
**9g:**

![Structure](attachment:structure.png)

*1H NMR (400 MHz, CDCl₃):* δ 7.73 (d, J = 8.2 Hz, 2H), 7.31 (t, J = 8.1 Hz, 6H), 7.27 (d, J = 2.7 Hz, 1H), 5.88 (d, J = 9.6 Hz, 1H), 5.44 (d, J = 9.6 Hz, 1H), 4.72 – 4.60 (m, 2H), 4.17 (d, J = 15.2 Hz, 1H), 3.91 (dd, J = 3.3, 1.4 Hz, 1H), 2.44 (s, 3H).

*13C NMR (100 MHz, CDCl₃):* δ 153.87, 151.32, 144.59, 137.91, 135.25, 130.26, 128.97, 128.73, 128.32, 127.06, 90.91, 66.34, 44.47, 21.76.

*HRMS (ESI):* C₁₈H₁₈N₂NaO₄S [M+Na]⁺ calculated = 381.0885; found = 381.0879.

**9h:**

![Structure](attachment:structure.png)

*1H NMR (400 MHz, CDCl₃):* δ 7.80 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 5.60 (s, 1H), 5.40 (s, 1H), 4.72 – 4.62 (m, 1H), 4.01 – 3.89 (m, 1H), 3.30 (dt, J = 19.8, 7.9 Hz, 1H), 2.46 (s, 3H), 1.78 – 1.70 (m, 4H), 1.64 (d, J = 10.7 Hz, 2H), 1.57 (d, J = 12.7 Hz, 1H), 1.23 – 1.08 (m, 2H), 1.09 – 0.94 (m, 1H).

*13C NMR (100 MHz, CDCl₃):* δ 152.68, 151.90, 144.69, 138.30, 130.32, 127.10, 90.05, 66.96, 54.07, 30.29, 29.84, 25.91, 25.86, 25.03, 21.75.

*HRMS (ESI):* C₁₇H₂₂KN₂O₄S [M+K]⁺ calculated = 389.0937; found = 389.0932.

**9i:**

![Structure](attachment:structure.png)

*1H NMR (400 MHz, CDCl₃):* δ 7.78 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 6.16 (d, J = 9.7 Hz, 1H), 5.59 – 5.49 (m, 1H), 4.71 – 4.67 (m, 1H), 3.99 (dd, J = 3.5, 1.7 Hz, 1H), 3.36 – 3.25
(m, 1H), 3.10 – 2.92 (m, 1H), 2.43 (s, 3H), 1.48 – 1.37 (m, 2H), 1.25 – 1.11 (m, 2H), 0.87 (t, J = 7.3 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.72, 151.33, 144.44, 138.12, 130.16, 126.92, 90.47, 66.59, 40.77, 29.17, 21.69, 19.87, 13.72.

HRMS (ESI): C$_{15}$H$_{20}$N$_2$NaO$_4$S $[M+Na]^+$ calculated = 347.1041; found = 347.1036.

9j:

\[
\begin{align*}
\text{O} & \quad \text{N-Ts} \\
\text{HN-S-O} & \quad \text{O} \\
\end{align*}
\]

$N$-(5-methylene-2-oxo-3-tosyloxazolidin-4-yl)benzenesulfonamide

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.90 (d, $J = 7.4$ Hz, 2H), 7.79 (d, $J = 7.7$ Hz, 2H), 7.68 – 7.59 (m, 1H), 7.53 (t, $J = 7.5$ Hz, 2H), 7.29 (d, $J = 7.6$ Hz, 2H), 6.19 (dd, $J = 20.6$, 7.2 Hz, 1H), 5.05 (d, $J = 24.2$ Hz, 1H), 4.81 (s, 1H), 4.35 (d, $J = 2.3$ Hz, 1H), 2.41 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 147.73, 146.42, 141.12, 133.50, 130.00, 129.87, 129.21, 128.85, 127.30, 126.57, 93.35, 67.44, 21.92.

HRMS (ESI): C$_{17}$H$_{16}$N$_2$NaO$_6$S$_2$ $[M+Na]^+$ calculated = 431.0347; found = 431.0362.

9k:

\[
\begin{align*}
\text{O} & \quad \text{N-Ts} \\
\text{HN-S-O} & \quad \text{O} \\
\end{align*}
\]

$N$-(5-methylene-2-oxo-3-tosyloxazolidin-4-yl)methanesulfonamide

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.96 (d, $J = 8.3$ Hz, 2H), 7.39 (d, $J = 8.1$ Hz, 2H), 6.23 (d, $J = 8.6$ Hz, 1H), 5.88 (d, $J = 8.5$ Hz, 1H), 5.06 (d, $J = 2.0$ Hz, 1H), 4.89 (d, $J = 2.5$ Hz, 1H), 3.26 (s, 3H), 2.45 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 149.56, 148.31, 146.87, 133.74, 130.24, 128.96, 93.27, 67.58, 43.42, 21.99.

HRMS (ESI): C$_{12}$H$_{14}$N$_2$NaO$_6$S$_2$ $[M+Na]^+$ calculated = 369.0191; found = 369.0185.
2,4,6-trimethyl-N-(5-methylene-2-oxo-3-tosyloxazolidin-4-yl)benzenesulfonamide

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.83 (d, $J = 8.0$ Hz, 2H), 7.32 (d, $J = 7.9$ Hz, 2H), 6.95 (s, 2H), 6.18 (d, $J = 6.5$ Hz, 1H), 6.15 – 6.04 (m, 1H), 4.75 (s, 1H), 4.22 (s, 1H), 2.57 (s, 6H), 2.44 (s, 3H), 2.30 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 148.41, 147.23, 146.37, 142.86, 138.73, 136.17, 134.17, 132.02, 129.94, 128.97, 126.57, 93.21, 67.57, 22.95, 21.96, 21.14.

HRMS (ESI): C$_{20}$H$_{22}$N$_2$NaO$_6$S$_2$ [M+Na]$^+$ calculated = 473.0817; found = 473.0811.

4-methoxy-N-(5-methylene-2-oxo-3-tosyloxazolidin-4-yl)benzenesulfonamide

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.80 (m, 4H), 7.29 (d, $J = 7.9$ Hz, 2H), 6.96 (d, $J = 7.9$ Hz, 2H), 6.18 (s, 1H), 5.09 (s, 1H), 4.79 (dd, $J = 13.7$, 2.6 Hz, 1H), 4.37 (d, $J = 3.1$ Hz, 1H), 3.86 (s, 3H), 2.41 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 163.52, 147.86, 146.35, 132.75, 129.98, 129.84, 129.55, 128.88, 126.55, 114.28, 93.23, 67.48, 55.85, 21.90.

HRMS (ESI): C$_{18}$H$_{18}$N$_2$NaO$_7$S$_2$ [M+Na]$^+$ calculated = 461.0453; found = 461.0448.
(E)-N-(5-ethylidene-2-oxo-3-phenyloxazolidin-4-yl)-4-methylbenzenesulfonamide  (dr 2:1, spectral data of the major compound is given)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.96 (d, 2H), 7.41 – 7.26 (m, 7H), 7.14 – 7.02 (m, 1H), 6.73 (d, $J = 6.5$ Hz, 1H), 6.08 – 6.00 (m, 1H), 2.41 (s, 3H), 1.66 (d, $J = 6.7$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 152.70, 147.03, 137.03, 132.93, 130.65, 130.41, 129.28, 128.95, 123.99, 121.95, 118.90, 65.75, 29.86, 20.06.

HRMS (ESI): C$_{18}$H$_{18}$N$_2$NaO$_4$S [M+Na]$^+$ calculated = 381.0885; found = 381.0878

9o:

(E)-N-(5-hexylidene-2-oxo-3-phenyloxazolidin-4-yl)-4-methylbenzenesulfonamide

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.31 (d, $J = 8.2$ Hz, 2H), 7.24 – 7.14 (m, 5H), 6.98 (d, $J = 8.1$ Hz, 2H), 6.37 (d, $J = 8.2$ Hz, 1H), 5.81 (d, $J = 8.6$ Hz, 1H), 5.40 (dd, $J = 8.1$, 7.1 Hz, 1H), 2.33 (s, 3H), 2.12 – 2.02 (m, 2H), 1.45 – 1.23 (m, 6H), 0.90 (t, $J = 6.8$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 152.58, 143.35, 142.11, 138.27, 134.38, 129.55, 129.34, 127.13, 126.44, 125.06, 109.57, 67.26, 31.46, 29.17, 24.96, 22.65, 21.57, 14.19.

HRMS (ESI): C$_{22}$H$_{26}$KN$_2$O$_4$S [M+K]$^+$ calculated = 453.1250; found = 453.1244.

9p:

4-methyl-N-(2-oxo-3-phenyl-5-(propan-2-ylidene)oxazolidin-4-yl)benzenesulfonamide

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 7.38 (d, $J = 8.1$ Hz, 2H), 7.34 – 7.15 (m, 5H), 7.08 (d, $J = 8.1$ Hz, 2H), 6.23 (d, $J = 6.1$ Hz, 1H), 5.65 (d, $J = 6.1$ Hz, 1H), 2.36 (s, 3H), 1.71 (s, 3H), 1.52 (s, 3H).

$^{13}$C NMR (125 MHz, CD$_2$Cl$_2$): $\delta$ 153.09, 144.13, 138.83, 136.09, 135.28, 129.96, 129.79, 127.46, 126.98, 125.33, 113.52, 68.08, 21.74, 17.46, 17.29.

HRMS (ESI): C$_{19}$H$_{28}$KN$_2$O$_4$S [M+K]$^+$ calculated = 411.0781; found = 411.0775.
\[ N-(5\text{-cyclopentylidene-2-oxo-3-phenyloxazolidin-4-yl})-4\text{-methylbenzenesulfonamide} \]

\[ ^1H\text{NMR (400 MHz, CD}_2\text{Cl}_2): \delta 7.29 (d, J = 7.5 \text{ Hz}, 2H), 7.17 (s, 5H), 6.98 (d, J = 7.4 \text{ Hz}, 2H), 6.05 (d, J = 5.1 \text{ Hz}, 1H), 5.56 (d, J = 6.2 \text{ Hz}, 1H), 2.40 – 2.15 (m, 5H), 2.10 (d, J = 16.6 \text{ Hz}, 1H), 2.00 – 1.83 (m, 1H), 1.61 – 1.42 (m, 4H). \]

\[ ^{13}C\text{NMR (100 MHz, CD}_2\text{Cl}_2): \delta 153.20, 144.08, 138.74, 135.26, 133.24, 129.93, 129.72, 127.38, 126.95, 125.35, 123.65, 68.54, 29.60, 28.62, 27.29, 26.55, 21.70. \]

\[ \text{HRMS (ESI): C}_{21}\text{H}_{22}\text{N}_2\text{O}_4\text{S [M+Na}^+] \text{calculated} = 421.1198; \text{found} = 421.1192. \]

\[ N-(5\text{-cyclohexylidene-2-oxo-3-phenyloxazolidin-4-yl})-4\text{-methylbenzenesulfonamide} \]

\[ ^1H\text{NMR (400 MHz, CD}_2\text{Cl}_2): \delta 7.37 (d, J = 8.2 \text{ Hz}, 2H), 7.31 – 7.19 (m, 5H), 7.08 (d, J = 8.2 \text{ Hz}, 2H), 6.32 (d, J = 7.8 \text{ Hz}, 1H), 5.77 (d, J = 7.8 \text{ Hz}, 1H), 2.41 (dd, J = 14.5, 11.6 \text{ Hz}, 1H), 2.37 (s, 3H), 2.20 – 2.05 (m, 2H), 1.95 – 1.82 (m, 1H), 1.52 (ddd, J = 19.4, 19.0, 6.7 \text{ Hz}, 6H). \]

\[ ^{13}C\text{NMR (100 MHz, CD}_2\text{Cl}_2): \delta 153.28, 143.98, 138.89, 135.25, 134.10, 129.99, 129.70, 127.40, 126.85, 125.32, 120.90, 67.79, 27.78, 27.60, 27.36, 27.17, 26.53, 21.72. \]

\[ \text{HRMS (ESI): C}_{22}\text{H}_{24}\text{N}_2\text{O}_4\text{S [M+Na}^+] \text{calculated} = 435.1354; \text{found} = 435.1359. \]
\((E)\)-N-(5-(4-bromobenzylidene)-2-oxo-3-phenyloxazolidin-4-yl)-4-methylbenzenesulfonylamide

\(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)): δ 7.56 (d, \(J = 8.3 \text{ Hz}, 2\)H), 7.50 (d, \(J = 8.5 \text{ Hz}, 2\)H), 7.36 (d, \(J = 8.4 \text{ Hz}, 2\)H), 7.33 – 7.26 (m, 5H), 7.19 (d, \(J = 8.1 \text{ Hz}, 2\)H), 6.26 (d, \(J = 8.5 \text{ Hz}, 1\)H), 5.64 (d, \(J = 9.0 \text{ Hz}, 1\)H), 5.45 (d, \(J = 1.0 \text{ Hz}, 1\)H), 2.43 (s, 3H).

\(^{13}\)C NMR (100 MHz, CD\(_2\)Cl\(_2\)): δ 151.83, 144.91, 143.96, 138.19, 134.39, 132.29, 132.05, 130.85, 130.47, 129.83, 127.84, 127.27, 125.18, 122.22, 106.13, 69.81, 21.82.

HRMS (ESI): C\(_{23}\)H\(_{19}\)BrN\(_2\)NaO\(_4\)S [M+Na]\(^+\) calculated = 521.0147; found = 521.0141

(d) Typical Procedure for the All-in-One-Pot Synthesis of Oxazolidinone from Terminal Alkynes [Entry 1]:

Prop-2-yn-1-yl tosylcarbamate (50.7 mg, 0.2 mmol), TsN\(_3\) (39.4 mg, 0.2 mmol), CuTc (3.8 mg, 10 mol %), Rh\(_2\)(OAc)\(_4\) (1.8 mg, 2 mol %) and dichloromethane (2 mL) were added to an oven-dried culture tube equipped with a stir bar. The reaction mixture was stirred at room temperature for 5-6 h, and then heated at 60 °C for 3 h. After the resulting mixture was cooled to room temperature, filtered through cotton wool, washed with ethyl acetate and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (Hex/EtOAc = 4:1) to give the product 9a (59.1 mg, 0.14 mmol, 70%).

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(e) Procedure for the Gram-scale Synthesis of Oxazolidinone:

```
5a, 1.02 g \rightarrow \text{Rh}_2(\text{OAc})_4 (0.5 \text{ mol }%) \\
\text{DCM, 60 }^\circ\text{C, 24 h} \rightarrow 9a, 0.87 g, 91% 
```

(1-tosyl-1H-1,2,3-triazol-4-yl)methyl tosylcarbamate (5a, 1.02 g, 2.26 mmol), Rh$_2$(OAc)$_4$ (5.0 mg, 0.5 mol %) were added to an oven-dried 100 mL Schlenk tube equipped with a stir bar. The tube was evacuated and refilled with nitrogen three times. Then, dichloromethane (22 mL) was added via syringe. The reaction mixture was heated to 60 °C for 24 h. After the resulting mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. The
residue was purified by column chromatography (Hex/ EtOAc = 4:1) to give the product 9a (0.87 g, 2.06 mmol, 91%).

(f) Procedure for the Hydrogenation of Oxazolidinone 9a:

To a solution of 9a (100 mg, 0.24 mmol) in ethyl acetate (5 mL) was added Pd/C (10 wt.%, 50 mg, 0.0048 mmol) and H\textsubscript{2} gas was bubbled from a balloon at room temperature. After 5 h, the reaction mixture was filtered through a pad of celite and washed with EtOAc (10 mL) and diethyl ether (10 mL). The combined organic phase was dried with Na\textsubscript{2}SO\textsubscript{4}. After removal of the solvent in vacuo, the resulting mixture was purified by silica gel chromatography (EtOAc/hexane, 1:4) to provide 88 mg (87% yield; syn/anti, 5:2) of 12 as a white solid.

12:

4-methyl-N-((4R,5R)-5-methyl-2-oxo-3-tosyloxazolidin-4-yl)benzenesulfonamide

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.79 (d, \(J = 6.6\) Hz, 2H), 7.68 (d, \(J = 8.3\) Hz, 2H), 7.36 (d, \(J = 7.9\) Hz, 2H), 7.23 (d, \(J = 8.2\) Hz, 2H), 5.97 (d, \(J = 35.4\) Hz, 1H), 5.32 (s, 1H), 4.41 (dt, \(J = 11.9, 6.0\) Hz, 1H), 2.46 (s, 3H), 2.39 (s, 3H), 1.28 (d, \(J = 6.5\) Hz, 3H).

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 150.64, 146.09, 144.60, 137.48, 134.52, 130.04, 129.90, 128.72, 127.35, 79.35, 71.59, 21.86, 21.81, 19.29.

HRMS (ESI): C\textsubscript{18}H\textsubscript{20}N\textsubscript{2}O\textsubscript{6}S\textsubscript{2} [M+Na]\textsuperscript{+} calculated = 447.0660; found = 447.0655.
3. Control Experiments:

(a) 2-(1-tosyl-1H-1,2,3-triazol-4-yl)ethyl phenylcarbamate (5u, 77.2 mg, 0.2 mmol), Rh$_2$(OAc)$_4$ (1.8 mg, 2 mol %) were added to an oven-dried screw cap reaction tube equipped with a stir bar. The tube was evacuated and refilled with nitrogen three times. Then, dichloromethane (2 mL) was added via syringe. The reaction mixture was heated to 60 °C for 3 h. But after 3h there was no indication of the formation of product. Then the reaction was continued for 24 h, still no product formation was observed, only starting material was recovered.

(b) (1-tosyl-1H-1,2,3-triazol-4-yl)methyl cyclohexylcarbamate (5h, 75.7 mg, 0.2 mmol), Rh$_2$(OAc)$_4$ (1.8 mg, 2 mol %) were added to an oven-dried screw cap reaction tube equipped with a stir bar. The tube was evacuated and refilled with nitrogen three times. Then, dichloromethane (2 mL) was added via syringe. The reaction mixture was heated to 40 °C for 2 h. After the resulting mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (Hex/ EtOAc = 4:1) to give the product 13 (52.6 mg, 0.15 mmol, 75%).

13: (E)-3-(tosylimino)prop-1-en-2-yl cyclohexylcarbamate
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.48 (s, 1H), 7.81 (d, $J$ = 7.8 Hz, 2H), 7.33 (d, $J$ = 7.8 Hz, 2H), 6.02 (s, 1H), 5.88 (s, 1H), 5.12 (s, 1H), 3.38-3.35 (m, 1H), 2.44 (s, 3H), 1.82 (d, $J$ = 10.6 Hz, 2H), 1.68 (d, $J$ = 12.6 Hz, 2H), 1.33 – 1.25 (m, 2H), 1.22 – 1.08 (m, 4H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 165.53, 149.49, 145.00, 129.92, 129.77, 128.28, 126.52, 122.87, 50.40, 32.90, 25.47, 24.77, 21.79.

HRMS (ESI): C$_{17}$H$_{22}$N$_2$NaO$_4$S [M+Na]$^+$ calculated = 373.1198; found = 373.1192.

(c)

\[
\begin{array}{c}
\text{(E)-3-(tosylimino)prop-1-en-2-yl cyclohexylcarbamate (13, 52 mg, 0.15 mmol) was added to an oven-dried screw cap reaction tube equipped with a stir bar. The tube was evacuated and refilled with nitrogen three times. Then, dichloromethane (1.5 mL) was added via syringe. The reaction mixture was heated to 60 °C for 3 h. After the resulting mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (Hex/ EtOAc = 4:1) to give the product 9h (42 mg, 0.12 mmol, 81%).}
\end{array}
\]

4) References:


(1-tosyl-1H-1,2,3-triazol-4-yl)methyl tosylcarbamate (5a)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
(1-tosyl-1H-1,2,3-triazol-4-yl)methyl phenylcarbamate (5b)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
(1-tosyl-1H-1,2,3-triazol-4-yl)methyl p-tolylcarbamate (5c)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
(1-tosyl-1H-1,2,3-triazol-4-yl)methyl (4-chlorophenyl)carbamate (5d)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
(1-tosyl-1H-1,2,3-triazol-4-yl)methyl (4-bromophenyl)carbamate (5e)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
(1-tosyl-1H-1,2,3-triazol-4-yl)methyl quinolin-8-ylcarbamate (5f)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
(1-tosyl-1H-1,2,3-triazol-4-yl)methyl benzylcarbamate (5g)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
(1-tosyl-1H-1,2,3-triazol-4-yl)methyl cyclohexylcarbamate (5h)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
(1-tosyl-1H-1,2,3-triazol-4-yl)methyl butylcarbamate (5i)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
(1-(phenylsulfonyl)-1H-1,2,3-triazol-4-yl)methyl tosylcarbamate (5j)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
(1-(methylsulfonyl)-1H-1,2,3-triazol-4-yl)methyl tosylcarbamate (5k)

$^1$H NMR (400 MHz, DMSO-$d_6$)

$^{13}$C NMR (100 MHz, DMSO-$d_6$)
(1-(mesitylsulfonyl)-1H-1,2,3-triazol-4-yl)methyl tosylcarbamate (5l)

$^1$H NMR (400 MHz, DMSO-$d_6$)

$^{13}$C NMR (100 MHz, DMSO-$d_6$)
(1-(((4-methoxyphenyl)sulfonyl)-1H-1,2,3-triazol-4-yl)methyl tosylcarbamate (5m)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
1-(1-tosyl-1H-1,2,3-triazol-4-yl)ethyl phenylcarbamate (5n)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
1-(1-tosyl-1H-1,2,3-triazol-4-yl)hexyl phenylcarbamate (5o)

${^1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100 MHz, CDCl$_3$)
2-(1-tosyl-1H-1,2,3-triazol-4-yl)propan-2-yl phenylcarbamate (5p)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
1-(1-tosyl-1H-1,2,3-triazol-4-yl)cyclopentyl
phenylcarbamate (5q)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
1-(1-tosyl-1H-1,2,3-triazol-4-yl)cyclohexyl phenylcarbamate (5r)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
(4-bromophenyl)(1-tosyl-1H-1,2,3-triazol-4-yl)methyl phenylcarbamate

$^{13}$C NMR (100 MHz, CDCl$_3$)
1-benzyl-3-phenyl-1-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)urea (5t)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2-(1-tosyl-1H-1,2,3-triazol-4-yl)ethyl phenylcarbamate (5u)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
4-methyl-N-(5-methylene-2-oxo-3-tosyloxazolidin-4-yl)benzenesulfonamide (9a)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
4-methyl-N-(5-methylene-2-oxo-3-phenyloxazolidin-4-yl)benzenesulfonamide (9b)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
4-methyl-N-(5-methylene-2-oxo-3-(p-tolyl)oxazolidin-4-yl)benzenesulfonamide (9c)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
N-(3-(4-chlorophenyl)-5-methylene-2-oxooxazolidin-4-yl)-4-methylbenzenesulfonamide (9d)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$N$-(3-(4-bromophenyl)-5-methylene-2-oxooxazolidin-4-yl)-4-methylbenzenesulfonamide (9e)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
4-methyl-N-(5-methylene-2-oxo-3-(quinolin-8-yl)oxazolidin-4-yl)benzenesulphonamide (9f)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$N$-(3-benzyl-5-methylene-2-oxooxazolidin-4-yl)-4-methylbenzenesulfonamide (9g)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$N$-(3-cyclohexyl-5-methylene-2-oxooxazolidin-4-yl)-4-methylbenzenesulfonamide (9h)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$N$-(3-buty1-5-methylene-2-oxooxazolidin-4-yl)-4-methylbenzenesulfonamide (9i)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$N$-(5-methylene-2-oxo-3-tosyloxazolidin-4-yl)benzenesulfonamide (9j)

$^1$H NMR (400 MHz, CDCl$_3$)

$^1$C NMR (100 MHz, CDCl$_3$)
N-(5-methylene-2-oxo-3-tosyloxazolidin-4-yl)methanesulfonamide (9k)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)

S56
2,4,6-trimethyl-N-(5-methylene-2-oxo-3-tosyloxazolidin-4-yl)benzenesulfonamide (9l)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
4-methoxy-\(N\)-(5-methylene-2-oxo-3-tosyloxazolidin-4-yl)benzenesulfonamide (9m)

\(^1\)H NMR (400 MHz, CDCl\(_3\))

\(^{13}\)C NMR (100 MHz, CDCl\(_3\))
$N$-(5-ethylidene-2-oxo-3-phenyloxazolidin-4-yl)-4-methylbenzenesulfonamide (9n)

$^1$H NMR (400 MHz, CDCl$_3$)

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$^{13}$C NMR (100 MHz, CDCl$_3$)
(E)-N-(5-hexylidene-2-oxo-3-phenyloxazolidin-4-yl)-4-methylbenzenesulfonamide (9o)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
4-methyl-N-(2-oxo-3-phenyl-5-(propan-2-ylidene)oxazolidin-4-yl)benzenesulfonamide (9p)

$^1$H NMR (400 MHz, CD$_2$Cl$_2$)

$^{13}$C NMR (100 MHz, CD$_2$Cl$_2$)
N-(5-cyclopentylidene-2-oxo-3-phenyloxazolidin-4-yl)-4-methylbenzenesulfonamide (9q)

$^1$H NMR (400 MHz, CD$_2$Cl$_2$)

$^{13}$C NMR (100 MHz, CD$_2$Cl$_2$)
N-(5-cyclohexylidene-2-oxo-3-phenyloxazolidin-4-yl)-4-methylbenzenesulfonamide (9r)

$^1$H NMR (400 MHz, CD$_2$Cl$_2$)

$^1$C NMR (100 MHz, CD$_2$Cl$_2$)
(E)-N-(5-(4-bromobenzylidene)-2-oxo-3-phenyloxazolidin-4-yl)-4-methylbenzenesulfonamide (9s)

$^1$H NMR (400 MHz, CD$_2$Cl$_2$)

$^{13}$C NMR (100 MHz, CD$_2$Cl$_2$)
4-methyl-N-((4R,5R)-5-methyl-2-oxo-3-tosyloxazolidin-4-yl)benzenesulfonamide (12)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)

S65
(E)-3-(tosylimino)prop-1-en-2-yl cyclohexylcarbamate (13)

$^{1}$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
NOE between H-5 and H-7

(\textit{E})-N-(5-hexylidene-2-oxo-3-phenyloxazolidin-4-y1)-4-methylbenzenesulfonamide (9o)
2D-NOESY NMR (500 MHz, CDCl$_3$)