

Electronic Supplementary Information for:
**Copper-catalyzed cascade reactions of *N*-(2-bromoallyl)amines with
KHCO₃: an efficient process for the synthesis of oxazolidin-2-ones**

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General experimental

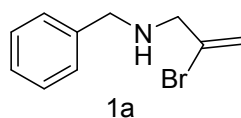
All solvents were dried by standard procedures. Reactions were followed by TLC using SILG/UV 254 silica gel plates which were visualized via a UV fluorescent lamp or iodine fumigation. Melting points were obtained using micro melting point apparatus and were uncorrected. Infrared spectra were measured by using a Nicolet FT-IR 6700 spectrometer and reported in cm^{-1} . $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectrums were obtained on a Bruker 500MHz instrument. Coupling constants were reported in Hertz (Hz). Low-resolution MS and HRMS were obtained by using EI and ESI ionizations. 2, 3-dibromopropene was commercially available and (Z)-(2,3-dibromoprop-1-enyl) benzene was synthesized from cinnamaldehyde (Lit: *J. Chem. Soc., Perkin Trans. 1*. 2002, 58-68).

General procedure for the synthesis of *N*-(2-bromoallyl)amines

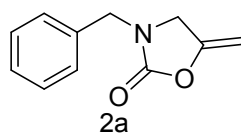
To a solution of benzylamine (35 mmol) in 20 mL CH_3CN was added 2,3-dibromopropene (10 mmol) dropwisely in an ice bath. After one hour addition was completed, the reaction mixture was stirred for other three hours in room temperature until the reaction was completed. The reaction mixture was partitioned between ethyl acetate and brine. The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel with petroleum ether and ethyl acetate (10:1 to 12:1) to afford the desired product (**1a**).

General procedure for the synthesis of oxazolidin-2-ones.

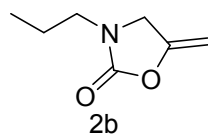
N-benzyl-2-bromoprop-2-en-1-amine (**1a**) (0.5mmol), CuI (0.1 mmol), DMEDA (0.2 mmol), KHCO_3 (1.0 mmol), K_2CO_3 (0.05 mmol), dry DMSO (2 mL) and a stirred bar were sealed in a pressurized process vial. The vial was heated to 120 °C and the mixture was stirred in an oil bath for 4 hrs. After cooling to room temperature, the reaction mixture was partitioned between ethyl acetate and water. The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel with petroleum ether and ethyl acetate (10:1 to 12:1) to afford the desired product (**2a**).



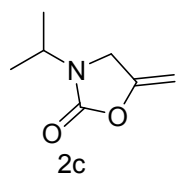
N-Benzyl-2-bromoprop-2-en-1-amine (1a): Faint yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 7.40 – 7.25 (m, 5H), 5.83 (dd, $J = 2.8, 1.2$ Hz, 3H), 5.63 (d, $J = 1.8$ Hz, 3H), 3.77 (s, 6H), 3.49 (s, 6H), 2.04 (s, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 139.6, 133.4, 128.4, 128.2, 127.1, 117.9, 56.6, 51.5; Lit: R. Grigg and V. Savic, *Chem. Commun.*, 2000, 873–874.



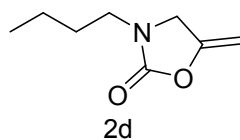
3-Benzyl-5-methyleneoxazolidin-2-one (2a): White solid; ^1H NMR (500 MHz, CDCl_3) δ 7.40 – 7.25 (m, 5H), 5.83 (dd, $J = 2.8, 1.2$ Hz, 3H), 5.63 (d, $J = 1.8$ Hz, 3H), 3.77 (s, 6H), 3.49 (s, 6H), 2.04 (s, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 139.6, 133.4, 128.4, 128.2, 127.1, 117.9, 56.6, 51.5; EI-MS calcd for $\text{C}_{11}\text{H}_{11}\text{NO}_2$ 189.2 found 189.0; Lit: M. Yoshida, T. Mizuguchi, and K. Shishido, *Chem. Eur. J.*, 2012, **18**, 15578 – 15581.



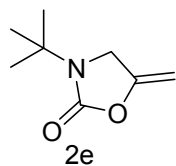
5-Methylene-3-propyloxazolidin-2-one (2b): Faint yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 4.74 (q, $J = 5.6, 2.7$ Hz, 1H), 4.29 (q, $J = 3.0, 2.2$ Hz, 1H), 4.17 (t, $J = 2.4$ Hz, 2H), 3.30 – 3.25 (m, 2H), 1.64 – 1.54 (m, 2H), 0.94 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.7, 149.2, 86.4, 47.8, 45.4, 20.6, 11.0; EI-MS calcd for $\text{C}_8\text{H}_{13}\text{NO}_2$: 155.19, found: 155.2; Lit: Y. Kayaki, M. Yamamoto, T. Suzuki and T. Ikariya, *Green Chem.*, 2006, **8**, 1019–1021.



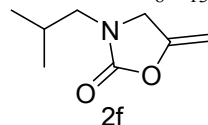
3-Isopropyl-5-methyleneoxazolidin-2-one (2c): Faint yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 4.73 (q, $J = 2.7$ Hz, 1H), 4.29 (q, $J = 2.6$ Hz, 1H), 4.13 – 4.19 (m, $J = 13.6, 6.8$ Hz, 1H), 4.12 (t, $J = 2.4$ Hz, 2H), 1.20 (d, $J = 6.8$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 154.7, 149.4, 86.2, 44.6, 43.1, 19.6; IR: (cm^{-1}) ν 2977, 2925, 1780, 1693, 1471, 1422, 1286, 1227, 1036; HRMS (ESI $^+$): Calcd for $\text{C}_{10}\text{H}_{15}\text{NO}_2$ (M+H) $^+$: 142.0868; Found: 142.0871.



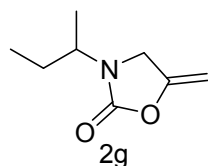
3-Butyl-5-methyleneoxazolidin-2-one (2d): Faint yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 4.73 (q, $J = 2.7$ Hz, 1H), 4.28 (q, $J = 5.2, 2.2$ Hz, 1H), 4.16 (t, $J = 2.4$ Hz, 2H), 3.33 – 3.27 (m, 2H), 1.54 (m, $J = 12.6, 7.5$ Hz, 2H), 1.34 (m, $J = 14.7, 7.4$ Hz, 2H), 0.94 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.6, 149.1, 86.3, 47.7, 43.4, 29.2, 19.7, 13.5; EI-MS: Calcd for $\text{C}_8\text{H}_{13}\text{NO}_2$: 155.19, found: 155.2; Lit: A-H. Liu, R. Ma, C. Song, Z-Z Yang, A .Yu, Y, Cai, L-N. He, Y-N. Zhao, B Yu, and Q-W. Song, *Angew. Chem. Int. Ed.* 2012, **51**, 11306-11310.



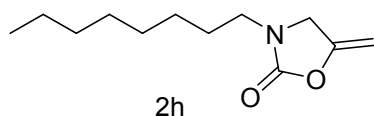
3-tert-Butyl-5-methyleneoxazolidin-2-one (2e): Faint yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 4.66 (q, $J = 2.7$ Hz, 1H), 4.24 (t, $J = 2.3$ Hz, 2H), 4.22 (q, $J = 4.8, 2.4$ Hz, 1H), 1.42 (s, 9H); IR: (cm^{-1}) ν 2977, 1779, 1683, 1471, 1423, 1285, 1227, 1036; ^{13}C NMR (125 MHz, CDCl_3) δ 154.1, 149.2, 85.3, 53.8, 46.7, 27.5; HRMS (EI^+) m/z : Calcd for $\text{C}_8\text{H}_{13}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 155.0946; Found: 155.0953.



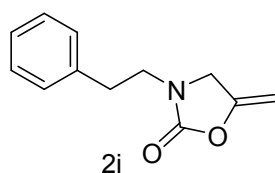
3-Isobutyl-5-methyleneoxazolidin-2-one (2f): Faint yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 4.74 (q, $J = 2.7$ Hz, 1H), 4.29 (q, $J = 5.2, 2.2$ Hz, 1H), 4.17 (t, $J = 2.4$ Hz, 2H), 3.10 (d, $J = 7.5$ Hz, 2H), 1.90 (dp, $J = 14.0, 6.9$ Hz, 1H), 0.94 (d, $J = 6.7$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.9, 149.2, 86.3, 51.5, 48.5, 26.8, 19.8; IR: (cm^{-1}) ν 2962, 2874, 1789, 1692, 1470, 1428, 1284, 1242, 1054; HRMS (EI^+) m/z : Calcd for $\text{C}_8\text{H}_{13}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 155.0946; Found: 155.0952.



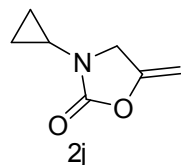
3-sec-Butyl-5-methyleneoxazolidin-2-one (2g): Faint yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 4.72 (q, $J = 5.6, 2.7$ Hz, 1H), 4.29 – 4.25 (q, 1H), 4.13 – 4.01 (m, 2H), 3.92 – 3.83 (m, 1H), 1.50 (p, $J = 7.4$ Hz, 2H), 1.16 (d, $J = 6.8$ Hz, 3H), 0.90 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.2, 149.5, 86.2, 50.5, 43.1, 26.9, 17.7, 10.7; IR: (cm^{-1}) ν 2970, 2859, 2930, 1779, 1694, 1423, 1284, 1228, 1050; HRMS (EI^+) m/z : Calcd for $\text{C}_8\text{H}_{13}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 155.0946; Found: 155.0949.



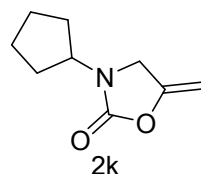
5-Methylene-3-octyloxazolidin-2-one (2h): Faint yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 4.75 (q, $J = 2.7$ Hz, 1H), 4.29 (q, $J = 5.2, 2.2$ Hz, 1H), 4.16 (t, $J = 2.4$ Hz, 2H), 3.34 – 3.25 (m, 2H), 1.60 – 1.51 (m, 2H), 1.36 – 1.21 (m, 10H), 0.89 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.6, 149.2, 86.4, 47.8, 43.8, 31.7, 29.1 (d, $J = 1.2$ Hz), 27.3, 26.6, 22.6, 14.0; IR: (cm^{-1}) ν 2927, 2860, 1789, 1693, 1427, 1384, 1283, 1064; HRMS (EI^+) m/z : Calcd for $\text{C}_{12}\text{H}_{21}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 211.1572; Found: 211.1578.



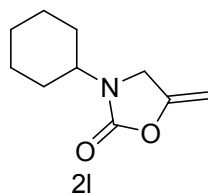
5-Methylene-3-phenethylloxazolidin-2-one (2i): Faint yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 7.43 – 7.16 (m, 5H), 4.72 (q, $J = 2.7$ Hz, 1H), 4.23 (q, $J = 2.3$ Hz, 1H), 4.01 (t, $J = 2.2$ Hz, 2H), 3.57 (t, $J = 7.3$ Hz, 2H), 2.91 (t, $J = 7.3$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.4, 149.1, 137.9, 128.7, 128.6, 126.8, 86.3, 48.4, 45.2, 33.9; IR: (cm^{-1}) ν 3024, 2924, 1779, 1681, 1473, 1429, 1282, 1243, 1087, 1061; HRMS (EI^+) m/z : Calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 203.0946; Found: 203.0943.



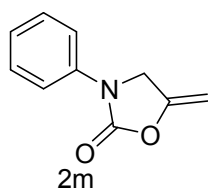
3-Cyclopropyl-5-methyleneoxazolidin-2-one (2j): Faint yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 4.70 (q, $J = 5.6, 2.7$ Hz, 1H), 4.26 (q, $J = 3.0, 2.2$ Hz, 1H), 4.14 (t, $J = 2.4$ Hz, 2H), 2.60 – 2.55 (m, 1H), 0.84 – 0.74 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.5, 149.1, 86.4, 48.9, 25.3, 5.7; IR: (cm^{-1}) ν 2926, 1785, 1675, 1469, 1423, 1392, 1280, 1120, 1025; HRMS (EI^+) m/z : Calcd for $\text{C}_7\text{H}_9\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 139.0633; Found: 139.0632.



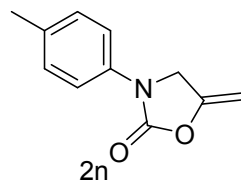
3-Cyclopentyl-5-methyleneoxazolidin-2-one (2k): Faint yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 4.71 (q, $J = 2.9$ Hz, 1H), 4.27 (m, $J = 2.9, 2.2$ Hz, 1H), 4.24 (q, $J = 15.9, 8.0$ Hz, 1H), 4.14 (t, $J = 2.4$ Hz, 2H), 1.95 – 1.84 (m, 2H), 1.75 – 1.49 (m, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.1, 149.4, 86.2, 54.3, 44.3, 28.8, 23.8; IR: (cm^{-1}) ν 2960, 2871, 1780, 1693, 1472, 1423, 1366, 1284, 1061; HRMS (EI^+) m/z : Calcd for $\text{C}_9\text{H}_{13}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 167.0946; Found: 167.0948.



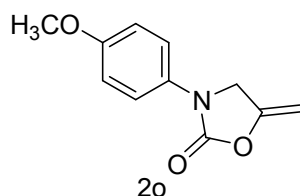
3-Cyclohexyl-5-methyleneoxazolidin-2-one (2l): Faint yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 4.73 (q, $J = 5.6, 2.7$ Hz, 1H), 4.28 (q, $J = 3.0, 2.2$ Hz, 1H), 4.14 (t, $J = 2.4$ Hz, 2H), 3.74 (m, $J = 11.0, 6.9, 3.0$ Hz, 1H), 1.83 (m, $J = 5.3, 4.0$ Hz, 4H), 1.67 (m, $J = 1.5$ Hz, 1H), 1.43 – 1.27 (m, 4H), 1.16 – 1.02 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 154.4, 149.1, 85.7, 51.8, 43.6, 29.7, 24.7; IR: (cm^{-1}) ν 2933, 2856, 1778, 1692, 1421, 1370, 1285, 1230, 1051; HRMS (ESI $^+$): Calcd for $\text{C}_{10}\text{H}_{15}\text{NO}_2$ (M+H) $^+$: 182.1181; Found: 182.1187.



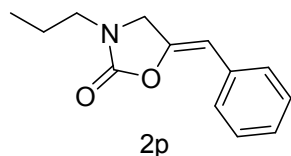
5-Methylene-3-phenyloxazolidin-2-one (2m): White solid; ^1H NMR (500 MHz, CDCl_3) δ 7.60 – 7.53 (m, 2H), 7.45 – 7.38 (m, 2H), 7.19 (t, $J = 7.4$ Hz, 1H), 4.87 (q, $J = 5.9, 2.6$ Hz, 1H), 4.66 (t, $J = 2.4$ Hz, 2H), 4.45 (m, $J = 3.4, 2.2$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 152.3, 147.7, 137.2, 129.2, 124.6, 118.2, 87.1, 77.3, 77.0, 76.8, 48.4; EI-MS calcd for $\text{C}_{10}\text{H}_9\text{NO}_2$: 175.1, found: 175.2; Lit: M. Shimizu and H. Yoshioka, *J. Chem. Soc., Chem. Commun.*, 1987, 689-690.



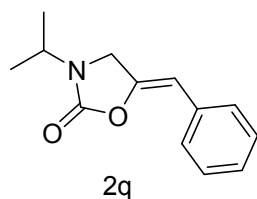
5-Methylene-3-p-tolyloxazolidin-2-one (2n): White solid; ^1H NMR (500 MHz, CDCl_3) δ 7.45 – 7.39 (m, 2H), 7.20 (d, $J = 8.4$ Hz, 2H), 4.84 (q, $J = 5.8, 2.7$ Hz, 1H), 4.61 (t, $J = 2.4$ Hz, 2H), 4.42 (m, $J = 3.1, 2.2$ Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 147.9, 134.7, 134.3, 129.7, 118.3, 86.9, 48.6, 20.7; IR: (cm^{-1}) ν 2922, 1782, 1679, 1520, 1461, 1405, 1386, 1117; HRMS (EI $^+$) m/z : Calcd for $\text{C}_{11}\text{H}_{11}\text{NO}_2$ (M+H) $^+$: 189.0790; Found: 189.0794.



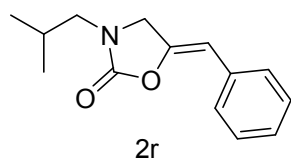
3-(4-Methoxyphenyl)-5-methyleneoxazolidin-2-one (2o): White solid; ^1H NMR (500 MHz, CDCl_3) δ 7.48 – 7.42 (m, 2H), 6.96 – 6.90 (m, 2H), 4.85 (q, $J = 5.7, 2.7$ Hz, 1H), 4.62 (t, $J = 2.4$ Hz, 2H), 4.42 (q, $J = 5.4, 2.2$ Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.8, 152.6, 147.9, 130.3, 120.3, 114.5, 86.9, 55.5, 48.9; EI-MS calcd for $\text{C}_{11}\text{H}_{11}\text{NO}_3$: 205.2, found: 205.3; Lit: R. S. Menon, A. D. Findlay, A. C. Bissember, and M. G. Banwell, *J. Org. Chem.*, 2009, **74**, 8901-8903.



(Z)-5-Benzylidene-3-propyloxazolidin-2-one (2p): Faint yellow liquid. ^1H NMR (500 MHz, CDCl_3) δ 7.57 (d, $J = 7.4$ Hz, 2H), 7.33 (t, $J = 7.8$ Hz, 2H), 7.21 (t, $J = 7.4$ Hz, 1H), 5.51 (t, $J = 2.0$ Hz, 1H), 4.30 (d, $J = 2.1$ Hz, 2H), 3.34 – 3.30 (m, 2H), 1.68 – 1.59 (m, 2H), 0.97 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.6, 142.0, 133.6, 128.5, 128.2, 126.8, 102.8, 48.8, 45.5, 20.6, 11.1; IR: (cm^{-1}) ν 2963, 2934, 1790, 1693, 1470, 1430, 1268, 1052; HRMS (EI^+) m/z : Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_2$ ($\text{M}+\text{H}^+$): 217.1103; Found: 217.1097.



(Z)-5-Benzylidene-3-isopropyloxazolidin-2-one (2q): Faint yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 7.57 (d, $J = 7.6$ Hz, 2H), 7.33 (t, $J = 7.7$ Hz, 2H), 7.21 (t, $J = 7.4$ Hz, 1H), 5.53 (t, $J = 1.9$ Hz, 1H), 4.28 (d, $J = 1.9$ Hz, 2H), 4.23 (dt, $J = 13.5, 6.8$ Hz, 1H), 1.25 (d, $J = 6.8$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 154.7, 142.3, 133.6, 128.4, 128.2, 126.7, 102.8, 44.9, 44.2, 19.8; IR: (cm^{-1}) ν 2975, 1779, 1691, 1472, 1421, 1267, 1039; HRMS (EI^+) m/z : Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_2$ ($\text{M}+\text{H}^+$): 217.1103; Found: 217.1106.



(Z)-5-Benzylidene-3-isobutyloxazolidin-2-one (2r): Faint yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 7.58 (d, $J = 7.4$ Hz, 2H), 7.34 (t, $J = 7.7$ Hz, 2H), 7.22 (t, $J = 7.4$ Hz, 1H), 5.52 (t, $J = 2.0$ Hz, 1H), 4.32 (d, $J = 2.0$ Hz, 2H), 3.17 (d, $J = 7.5$ Hz, 2H), 1.95 (m, $J = 13.9, 6.9$ Hz, 1H), 0.97 (d, $J = 6.7$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.9, 141.9, 133.5, 128.5, 128.2, 126.8, 102.8, 51.5, 49.4, 26.9, 19.9; IR: (cm^{-1}) ν

2961, 1780, 1693, 1478, 1429, 1275, 1051; HRMS (EI⁺)m/z: Calcd for C₁₄H₁₇NO₂
(M+H)⁺: 231.1260; Found: 231.1260.

Supporting NMR Spectra

