Supporting Information

Ruthenium-Catalyzed Cyclocarbonylation of Allenyl Alcohols and Amines:

Selective Synthesis of Lactones and Lactams

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(1) **Preparation of allenyl alcohols 1.** New allenyl alcohols **1n-1t** and **1v** were prepared from 2-prop-2-ynyloxy-tetrahydropyran with aldehydes via 2-butyne-1-ol derivatives.^{1,2}

1-(4-Chlorophenyl)buta-2,3-dien-1-ol (1n). To a mixture of 3-(tetrahydro-2-pyranyloxy)-1-propyne (4.20 g, 30 mmol)² in THF (100 mL) at -78 °C under argon, a solution of *n*-BuLi (1.6 M in hexane, 18.6 mL) was added dropwise. After stirring the solution for 1 h, a solution of 4-chlorobenzaldehyde (4.21 g, 30 mmol) in THF (100

mL) was added to the reaction mixture at -78 °C and stirred for 2 h. After stirring at room temperature for 2 h, a saturated aqueous solution of NH₄Cl was added and then the reaction mixture was extracted with ether (3 x 20 mL). The ether extract was washed with water and a saturated aqueous solution of NaCl, and dried over anhydrous MgSO₄. The ether solution was filtered and evaporated, and the residue was distilled to give 3.90 g (46% yield) of 1-(4-chlorophenyl)-4-(tetrahydropyran-2-yloxy)-but-2-yn-1-ol **1'n** as pale yellow liquid. A solution of thus prepared **1'n** (3.90 g, 14 mmol) in ether (10 mL) was added dropwise to LiAlH₄ (0.63 g 17 mmol) in ether (25 mL) at 0 °C under argon. After stirring at room temperature for 3 h, a mixture of 1:3 H₂O/THF was added, and the reaction mixture was extracted with ether (3 x 20 mL). The ether extract was washed with water and then saturated aqueous solution of NaCl, and dried over anhydrous MgSO₄. The ether solution was filtered and evaporated, and the residue was distilled to give 1.30 g (52% yield) of 1-(4-chlorophenyl)buta-2,3-dien-1-ol **1n**. Colorless liquid; bp 68 °C (0.1 mmHg); ¹H NMR (CDCl₃) 4.90 (2H, d, *J* = 6.3 Hz, C=CH₂), 5.22 (1H, d, *J* = 6.3 Hz, CH), 5.37 (1H, q, *J* = 5.8 Hz, CH), 7.30 (4H, s, Ar); ¹³C NMR (CDCl₃) 71.2, 78.2, 94.8, 127.4, 128.4, 133.3, 141.1, 207.0; IR (neat) 3367 (OH), 1956 cm⁻¹ (C=C=C); MS (EI) *m/z* 180 (M⁺); Anal. Calcd for C₁₀H₉ClO: C, 66.49; H, 5.02; Cl, 19.63. Found: C, 66.21; H, 5.09; Cl, 19.63.

1-(4-Bromophenyl)buta-2,3-butadien-1-ol (1o). Colorless liquid; bp 103 °C (0.1 mmHg); ¹H NMR (CDCl₃) 2.14 (1H, d, *J* = 3.9 Hz, OH), 4.92 (2H, d, *J* = 6.3 Hz, C=CH₂), 5.23 (1H, br, CH), 5.37 (1H, q, *J* = 5.8 Hz, C=CH), 7.27 (2H, d, *J* = 8.2 Hz,

Ar), 7.47 (2H, d, $J = 8.2$ Hz, Ar); ^{13}C NMR (CDCl_3) 71.3, 78.4, 94.8, 121.6, 127.8, 131.5, 141.7, 207.1; IR (neat) ν 3365 (OH), 1954 cm^{-1} ($\text{C}=\text{C}=\text{C}$); MS (EI) m/z 225 (M^+); Anal. Calcd for $\text{C}_{10}\text{H}_9\text{BrO}$: C, 53.36; H, 4.03; Br, 35.50. Found: C, 53.15; H, 3.84; Br, 35.32.

1-(4-Methylthiophenyl)buta-2,3-dien-1-ol (1q). Pale yellow liquid; bp 106 °C (0.1 mmHg); ^1H NMR (CDCl_3) 2.09 (1H, d, $J = 3.9$ Hz, OH), 2.48 (3H, s, SCH_3), 4.92 (2H, d, $J = 6.3$ Hz, $\text{C}=\text{CH}_2$), 5.23 (1H, br, CH), 5.42 (1H, q, $J = 5.8$ Hz, $\text{C}=\text{CH}$), 7.23 (2H, d, $J = 8.2$ Hz, Ar), 7.33 (2H, d, $J = 8.2$ Hz, Ar); ^{13}C NMR (CDCl_3) 15.7, 71.4, 78.1, 94.9, 126.5, 137.7, 139.6, 207.0; IR (neat) 3375 (OH), 1980 cm^{-1} (OH); MS (EI) m/z 192 (M^+); Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{OS}$: C, 68.71; H, 6.29; S, 16.68. Found: C, 68.76; H, 6.40; S, 16.47.

1-(4-(N,N-Dimethylamino)phenyl)buta-2,3-dien-1-ol (1r). Pale yellow liquid; b.p. 85 °C (0.1 mmHg) ^1H NMR (CDCl_3) d 2.94 (6H, s, $\text{CH}_3 \times 2$), 4.87-4.95 (2H, m, CH_2), 5.18 (1H, br, CH), 5.44 (1H, q, $J = 6.5$ Hz, CH), 6.71 (2H, d, $J = 8.2$ Hz, Ar), 7.27 (2H, d, $J = 8.2$ Hz, Ar); ^{13}C NMR (CDCl_3) d 40.5, 71.6, 77.8, 95.2, 112.4, 127.4, 130.7, 150.3, 206.9; IR (neat) 3370 (OH), 1955 cm^{-1} ($\text{C}=\text{C}=\text{C}$); MS (EI) m/z 189 (M^+); Anal. Calcd for $\text{C}_{12}\text{H}_{15}\text{NO}$: C, 76.16; H, 7.99; N, 7.40%. Found: C, 76.36; H, 8.05; N, 7.64.

1-(4-Nitrophenyl)buta-2,3-dien-1-ol (1s). Pale yellow liquid; b.p. 140 °C (0.1 mmHg); ^1H NMR (CDCl_3) 4.94 (2H, br, $\text{C}=\text{CH}_2$), 5.38 (2H, br, CH, $\text{C}=\text{CH}$), 7.56 (2H, d, $J = 8.5$ Hz, Ar), 8.20 (2H, d, $J = 9.0$ Hz, Ar); ^{13}C NMR (CDCl_3) 71.1, 78.7,

94.4, 123.6, 126.7, 147.2, 149.8, 207.3; IR (neat) 3389 (OH), 1955 (C=C=C), 1518, 1345 cm^{-1} (NO_2); MS (EI) m/z 191 (M^+); Anal. Calcd for $\text{C}_{10}\text{H}_9\text{NO}_3$: C, 62.83; H, 4.74; N, 7.33. Found: C, 62.83; H, 4.74; N, 7.23.

1-Ferrocenylbuta-2,3-butadien-1-ol (1t). Yellow crystal; mp 65 °C; ^1H NMR (CDCl_3) 2.05 (1H, s, OH), 4.12-4.25 (4H, m, Cp), 4.20 (5H, s, Cp), 4.89 (2H, d, J = 6.3 Hz, $\text{C}=\text{CH}_2$), 4.91-4.95 (1H, m, CH), 5.48 (1H, q, J = 6.5 Hz, $\text{C}=\text{CH}$); ^{13}C NMR (CDCl_3) 66.4, 66.9, 67.9, 68.1, 68.2, 68.4, 77.5, 92.2, 96.1, 207.4; IR (KBr) 3307 (-OH), 1956 cm^{-1} ($\text{C}=\text{C}=\text{C}$); MS (FAB) m/z 254 (M^+); Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{FeO}$: C, 66.18; H, 5.55. Found: C, 66.17; H, 5.47.

1-Cyclopropylbuta-2,3-dien-1-ol (1v). Colorless liquid; bp 78 °C (30 mmHg); ^1H NMR (CDCl_3) 0.25-0.33 (1H, m, CH_2), 0.34-0.41 (1H, m, CH_2), 0.49-0.60 (2H, m, CH_2), 1.00-1.08 (1H, m, CH), 1.87 (1H, br, OH), 3.56-3.61 (1H, m, CH), 4.84-4.89 (2H, m, $\text{C}=\text{CH}_2$), 5.31 (1H, d, J = 6.5 Hz, $\text{C}=\text{CH}$); ^{13}C NMR (CDCl_3) 1.9, 3.0, 17.6, 73.7, 77.5, 93.7, 207.0; IR (neat) 3350 (OH), 1960 cm^{-1} ($\text{C}=\text{C}=\text{C}$); MS (EI) m/z 110 (M^+); Anal. Calcd for $\text{C}_7\text{H}_{10}\text{O}$: C, 76.33; H, 9.15. Found: C, 76.23; H, 8.99%.

(2) Characterization data for furanones (2b – 2h, 2j – 2l, 2n, 2p), 2-pyranones (4a, 4c), and piperidin-2-one (7a).

3,5,5-Trimethyl-2[5H]-furanone (2b). Colorless solid; ^1H -NMR 1.44 (6H, s, CH_3 x 2), 1.88 (3H, s, CH_3), 6.98 (1H, s, $\text{C}=\text{CH}$); ^{13}C -NMR 10.4, 25.6, 128.2, 153.9, 173.6; IR (KBr) 1755 cm^{-1} ($\text{C}=\text{O}$); MS (EI) m/z 126 (M^+).

5-Ethyl-3-methyl-2[5H]-furanone (2c). Pale yellow oil; $^1\text{H-NMR}$ 0.98 (3H, t, $J = 7.3$ Hz, CH_3), 1.68-1.85 (2H, m, CH_2), 1.92 (3H, s, CH_3), 4.82-4.86 (1H, m, CH), 7.02 (1H, s, $\text{C}=\text{CH}$); $^{13}\text{C-NMR}$ 9.1, 10.6, 26.5, 82.0, 130.1, 148.3, 174.3; IR (neat) 1755 cm^{-1} ($\text{C}=\text{O}$); MS (EI) m/z 126 (M^+).

3-Methyl-5-phenyl-2[5H]-furanone (2d). Colorless oil; $^1\text{H-NMR}$ 1.99 (3H, s, CH_3), 5.87 (1H, s, CH), 7.13 (1H, s, $\text{C}=\text{CH}$), 7.25-7.29 (2H, m, Ar), 7.33-7.41 (3H, m, Ar); $^{13}\text{C-NMR}$ 10.6, 82.1, 126.4, 128.9, 129.0, 135.1, 148.3, 174.3; IR (KBr) 1760 cm^{-1} ($\text{C}=\text{O}$); MS (EI) m/z 174 (M^+).

3-Methyl-2[5H]-furanone (2e). Colorless oil; $^1\text{H-NMR}$ 1.93 (3H, s, CH_3), 4.92 (1H, d, $J = 6.8$ Hz, CH_2), 7.41 (1H, br, $\text{C}=\text{CH}$); $^{13}\text{C-NMR}$ 17.6, 67.6, 131.6, 135.6, 165.0; IR (neat) 1760 cm^{-1} ($\text{C}=\text{O}$); MS (EI) m/z 98 (M^+).

3,4-Dimethyl-2[5H]-furanone (2f). Colorless solid; $^1\text{H-NMR}$ 1.71 (3H, s, CH_3), 1.95 (3H, s, CH_3), 4.85 (2H, s, CH_2); $^{13}\text{C-NMR}$ 11.1, 18.2, 74.5, 124.2, 145.0, 171.0; IR(neat) 1744 cm^{-1} ($\text{C}=\text{O}$); MS(EI) m/z 112 (M^+).

3-Methyl-4-isopropyl-2[5H]-furanone (2g). $^1\text{H-NMR}$ 1.11 (6H, d, $J = 7.2$ Hz, $\text{CH}_3 \times 2$), 1.97 (3H, s, CH_3), 2.52 (1H, br, CH), 4.92 (2H, s, CH_2); $^{13}\text{C-NMR}$ 11.7, 19.8, 29.0, 69.5, 119.6, 154.3, 171.0; IR (KBr) 1755 cm^{-1} ($\text{C}=\text{O}$); MS (EI) m/z 140 (M^+).

3-Methyl-4-methoxy-1-oxaspiro-[4,5]-3-decen-2-one (2h). Pale yellow solid; $^1\text{H-NMR}$ 1.50 -1.73 (10H, m, $\text{CH}_2 \times 5$), 1.99 (3H, s, CH_3), 4.10 (3H, s, OCH_3); $^{13}\text{C-NMR}$

NMR 8.5, 21.8, 24.5, 33.0, 58.9, 82.4, 95.1, 174.5, 177.4; IR (KBr) 1750 cm⁻¹ (C=O); MS (EI) m/z 196 (M⁺).

5-Ethyl-3-methyl-4-methoxy-2[5H]-furanone (2j). Pale yellow oil; ¹H-NMR 0.94 (3H, t, *J* = 7.3 Hz, CH₃), 1.55-1.62 (2H, m, CH₂), 1.98 (3H, s, CH₃), 4.09 (3H, s, OCH₃), 4.56-4.59 (1H, m, CH); ¹³C-NMR 8.2, 8.3, 24.9, 58.7, 78.4, 97.5, 173.1, 175.1; IR (neat) 1752 (C=O), 1670 cm⁻¹ (C=C); MS (EI) m/z 156 (M⁺).

3-Methyl-4-methoxy-5-phenyl-2[5H]-furanone (2k). Colorless solid; ¹H-NMR 2.01 (3H, s, CH₃), 3.95 (3H, s, OCH₃), 5.56 (1H, s, CH), 7.29-7.32 (2H, m, Ar), 7.34-7.40 (3H, m, Ar); ¹³C-NMR 8.0, 58.7, 78.9, 97.6, 126.9, 128.8, 129.3, 134.5, 172.7, 174.7; IR (KBr) 1738 (C=O), 1652 cm⁻¹ (C=C); MS (EI) m/z 204 (M⁺).

3-Ethyl-2[5H]-furanone (2l). Pale yellow solid; ¹H-NMR 1.06 (3H, t, *J* = 7.2 Hz, CH₃), 2.00 (2H, q, *J* = 7.3 Hz, CH₂), 4.85 (2H, d, *J* = 5.6 Hz, CH₂), 7.41 (1H, br, C=CH); ¹³C-NMR 11.2, 25.3, 67.9, 134.8, 136.2, 165.0; IR (neat) 1752 cm⁻¹ (C=O); MS (EI) m/z 112 (M⁺).

3-Methyl-5-(4-chlorophenyl)-2[5H]-furanone (2n). ¹H-NMR 1.99 (3H, s, CH₃), 5.84 (1H, s, CH), 7.09 (1H, s, C=CH), 7.19 (2H, d, *J* = 8.3 Hz, Ar), 7.38 (2H, d, *J* = 8.1 Hz, Ar); ¹³C-NMR 10.5, 81.1, 127.7, 129.0, 129.6, 133.5, 134.8, 147.8, 173.9; IR (KBr) 1752 cm⁻¹ (C=O); MS (EI) m/z 208 (M⁺).

3-Methyl-5-(4-methoxyphenyl)-2[5H]-furanone (2p). Colorless oil; ¹H-NMR 1.99 (3H, s, CH₃), 3.73 (3H, s, OCH₃), 5.90 (1H, s, CH), 7.41 (1H, s, C=CH), 6.70 (2H, d, *J* = 8.3 Hz, Ar), 7.08 (2H, d, *J* = 8.1 Hz, Ar); ¹³C-NMR 17.9, 56.0, 82.9, 114.3, 128.3,

133.2, 131.6, 135.6, 160.9, 165.0; IR (KBr) 1750 cm^{-1} (C=O); MS (EI) m/z 204 (M^+).

3-Methyl-5,6-dihdropyran-2-one (4a). Pale yellow oil; $^1\text{H-NMR}$ 1.93 (3H, s, CH_3), 2.39-2.44 (2H, m, CH_2), 4.37 (2H, t, $J = 6.6\text{ Hz}$, OCH_2), 6.63 (1H, s, $\text{C}=\text{CH}$); $^{13}\text{C-NMR}$ 17.2, 24.3, 66.6, 128.7, 139.4, 165.4; IR (neat) 1718 cm^{-1} (C=O); MS (EI) m/z 112 (M^+).

3,5-Mimethyl-5,6-dihdropyran-2-one (4c); $^1\text{H-NMR}$ 1.10 (3H, d, $J = 7.3\text{ Hz}$, CH_3), 1.91 (3H, s, CH_3), 2.66 (1H, br, CH), 4.02 (1H, dd, $J = 8.5, 10.7\text{ Hz}$, CH_2), 4.35 (1H, dd, $J = 4.8, 10.9\text{ Hz}$, CH_2), 6.49 (1H, s, $\text{C}=\text{CH}$); $^{13}\text{C-NMR}$ 15.6, 17.0, 29.1, 72.1, 127.2, 145.6, 165.3; IR (neat) 1714 cm^{-1} (C=O); MS(EI) m/z 126 (M^+).

3-Methylenepiperidin-2-one (7a). pale yellow oil; $^1\text{H NMR}$ (CDCl_3) 1.84-1.90 (2H, m, CH_2), 2.56-2.59 (2H, m, CH_2), 3.37-3.41 (2H, m, NCH_2), 5.32 (1H, br, $\text{C}=\text{CH}_2$), 6.21 (1H, br, $\text{C}=\text{CH}_2$), 6.69 (1H, br, NH); $^{13}\text{C NMR}$ (CDCl_3) 23.0, 29.7, 42.6, 122.0, 137.4, 165.9; IR(neat) 3244 (NH), 1674 (C=O), 1622 cm^{-1} (C=C); MS (EI) m/z 111 (M^+).

References

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