Ring Expansion via Olefin Metathesis

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Supporting Material

Experimental procedures and characterization (^{1}H and ^{13}C NMR, HRMS) employed in the preparation of metathesis products.

General Experimental Section. NMR spectra were recorded on Varian-300 NMR. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) with reference to internal solvent. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), and multiplet (m). The reported ^{1}H NMR data refer to the major olefin isomer unless stated otherwise. The reported ^{13}C NMR data include all peaks observed and no peak assignments were made. High-resolution mass spectra (EI) were provided by the UCLA Mass Spectrometry Facility (University of California, Los Angeles).

Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 precoated plates (0.25 mm thickness) with a fluorescent indicator. Flash column chromatography was performed using silica gel 60 (230-400 mesh) from EM Science. All other chemicals were purchased from the Aldrich, Strem, or Nova Biochem Chemical Companies, and used as delivered unless noted otherwise. CH_2Cl_2 was purified by passage through a solvent column prior to use.[i]

General Procedure: To a flask charged with catalyst **1** (0.05 equiv in 0.005 to 0.006 M CH_2Cl_2), α,β-unsaturated carbonyl compounds, and cycloalkenes were added via syringe. The flask was fitted with a condenser and refluxed under argon for 12 hours. The reaction was monitored by TLC. After the solvent was evaporated, the product was purified directly on a silica gel column.

Compound 4 and 5. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 4 = ethyl acetate: hexane. 10.0 mg of the product **4** in 43 % yield was obtained (R_f = 0.4 in 1: 2 = EA: Hx, colorless liquid). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.80(2H, dt, *J*=6.9, 15.9 Hz), 6.15(2H, dt, *J*= 1.5, 15.9 Hz), 2.49(4H, t, *J*= 6.9 Hz), 2.29(4H, dq, *J*=1.2, 6.9Hz), 1.70(6H, m), 1.29(12H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 202.2, 146.8, 131.2, 40.0, 31.4, 28.6, 28.5, 28.3, 26.7, 25.7. HRMS (EI) calcd for $C_{19}H_{30}O_2$, 290.2246, found, 290.2241.

8.0 mg of the product **5** in 34 % yield was obtained (R_f = 0.3 in 1: 2 = EA: Hx, white solid).). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.79(4H, dt, *J*= 6.9, 15.9 Hz), 6.10(4H, dt, *J*= 1.5, 15.9 Hz), 2.52(8H, t, *J*= 7.29 Hz), 2.24(8H, q, *J*= 6.6 Hz), 1.67(12H, m), 1.27(24H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 201.0, 145.2, 131.1, 40.4, 31.9, 29.6, 29.4, 29.3, 26.8, 24.5. HRMS (EI) calcd for $C_{38}H_{60}O_4$, 580.4492, found, 580.4486.

Compound 6 and 7. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 9 = ethyl acetate: hexane. 10.0 mg of the product **7** in 23 % yield was obtained (R_f = 0.6 in 1: 2 = EA: Hx, colorless liquid). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.80(2H, m), 6.07(2H, d, *J*= 15.6 Hz), 5.37(2H, m), 2.51(4H, t, *J*= 6.9 Hz), 2.20(4H, m), 2.00(4H, m), 1.6- 1.27(24H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 201.5, 147.8, 130.8, 130.7, 130.5, 40.0, 32.7, 32.6, 28.1-29.8 (m), 24.7. HRMS (EI) calcd for $C_{22}H_{36}O_2$, 332.2715, found, 332.2712.

9.0 mg of the product **6** in 23 % yield was obtained (R_f = 0.5 in 1: 2 = EA: Hx, colorless liquid). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.78(2H, dt, *J*= 7.2, 15.9 Hz), 6.09(2H, dt, *J*= 1.5, 15.9Hz), 2.49(4H, t, *J*= 6.9 Hz), 2.22(4H, dq, *J*= 1.5, 6.9 Hz), 1.63(4H, m), 1.47(4H, m), 1.24 (16H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 202.2, 148.0, 131.1, 39.8, 32.3, 29.2, 29.0, 28.8, 28.5, 28.1, 25.8. HRMS (EI) calcd for $C_{30}H_{50}O_2$, 442.3811, found, 442.3806.

Compound 8. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 3 = ethyl acetate: hexane. 13.0 mg of the product in 43 % yield was obtained (R_f = 0.4 in 1: 2 = EA: Hx, colorless liquid). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.78(2H, m), 6.12(2H, d, *J*= 16.2 Hz), 4.87(1H, m), 2.50(4H, m), 2.22(4H, m), 2.06(3H, s), 1.6- 1.25(14H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 201.6, 170.8, 146.8, 146.1, 131.2, 131.1, 72.7, 40.2, 40.1, 33.5, 32.9, 32.0, 29.1, 28.9, 28.8, 28.5, 25.7, 25.6, 24.1, 21.6. HRMS (EI) calcd for $C_{24}H_{38}O_4$, 390.2770, found, 390.2770.

Compound 10. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 10 = ethyl acetate: hexane. 13.3 mg of the product in 45 % yield was obtained (R_f = 0.3 in 1: 5 = EA: Hx, colorless liquid). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.86(2H, dt, *J*= 6.9, 15.6 Hz), 5.73(2H, dt, *J*= 1.5, 15.6 Hz), 4.21(4H, m), 2.20(4H, m), 1.81(4H, m), 1.50(4H, m), 1.23(4H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 166.7, 149.8, 121.9, 64.0, 31.1, 27.7, 27.1, 26.3. HRMS (EI) calcd for $C_{16}H_{24}O_4$ 280.1675, found 280.1680.

Compound 11. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 10 = ethyl acetate: hexane. 18.0 mg of the product was obtained in 45 % yield (R_f = 0.45 in 1: 10 = EA: Hx, colorless liquid). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.89(2H, dt, *J*= 6.9, 15.6 Hz), 5.75(2H, d, *J*= 15.6 Hz),

4.15(4H, m), 2.21(4H, m), 1.7(4H, m), 1.45(4H, m), 1.24(12H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 166.6, 149.7, 122.0, 63.8, 32.3, 29.2, 28.7, 28.1, 27.9, 25.9. HRMS (EI) calcd for $C_{20}H_{32}O_4$ 336.2301, found 336.2308.

Compound 13. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 15 = ethyl acetate: hexane. 25.7 mg of the product was obtained in 47% yield(R_f = 0.4 in 1: 10 = EA: Hx, colorless liquid). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.93(2H, dt, *J*= 6.9, 15.6 Hz), 5.82(2H, dt, *J*= 1.8, 15.6 Hz), 4.14(4H, t, *J*= 5.7 Hz), 2.20(4H, m),1.63(4H, m), 1.5-1.3 (16H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 166.9, 149.2, 121.7, 64.9, 31.4, 29.5, 29.0, 27.5, 27.1, 26.6. HRMS (EI) calcd for $C_{20}H_{32}O_4$ 336.2301, found 336.2298.

Compound 14. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 15 = ethyl acetate: hexane. 28.2 mg of the product was isolated in 42 % yield. (R_f = 0.4 in 1: 10 = EA: Hx, colorless liquid). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.92(2H, dt, *J*= 6.9, 15.6 Hz), 5.82(2H, dt, *J*= 1.2, 15.6 Hz), 4.11(4H, t, *J*= 5.7 Hz), 2.20 (4H, m), 1.60 (4H, m), 1.5-1.2 (24H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 167.0, 149.6, 121.7, 64.5, 32.3, 29.4, 29.3, 29.1, 29.0, 28.5, 28.0, 26.2. HRMS (EI) calcd for $C_{24}H_{40}O_4$ 392.2927, found 392.2920.

Compound 16. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 1 = ethyl acetate: hexane. 9.0 mg of the product was obtained in 52 % yield (R_f = 0.3 in 1: 1 = EA: Hx, white solid). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.85(2H, dt, *J*= 7.2, 15.6 Hz), 5.84(2H, dt, *J*= 1.5, 15.6 Hz), 4.26(4H, m), 3.72(4H, m), 3.67(4H, s), 2.29(4H, m), 1.77(2H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 166.4, 148.1, 123.2, 70.7, 69.3, 63.9, 31.7, 24.6. HRMS (EI) calcd for $C_{15}H_{22}O_6$ 298.1416, found 298.1416.

Compound 17. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 1 = ethyl acetate: hexane. 7.0 mg of the product was obtained in 39 % yield (R_f = 0.35 in 1: 1 = EA: Hx, white solid). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.85(2H, dt, *J*= 7.2, 15.6 Hz), 5.84(2H, dt, *J*= 1.5, 15.6 Hz), 4.26(4H, m), 3.75(4H, m), 3.67(4H, s), 2.23(4H, m), 1.45(4H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 166.5, 149.2, 122.1, 71.0, 69.4, 64.0, 31.2, 26.3. HRMS (EI) calcd for $C_{16}H_{24}O_6$ 312.1573, found 312.1584.

Compound 18. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 1 = ethyl acetate: hexane. 12.0 mg of the product was obtained in 63 % yield (R_f = 0.35 in 1: 1 = EA: Hx, white solid). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.92(2H, dt, *J*=7.2, 15.6 Hz), 5.83(2H, dt, *J*= 1.5, 15.6 Hz), 4.28(4H, m), 3.73(4H, m), 3.66(4H, s), 2.24(4H, m), 1.48(4H, m), 1.24(2H, m).^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 166.7, 149.4, 121.9, 71.2, 69.5, 64.1, 32.2, 27.8, 27.7. HRMS (EI) calcd for $C_{17}H_{26}O_6$ 326.1729, found 326.1732.

Compound 19. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 1 = ethyl acetate: hexane. 29.4 mg of the product was obtained in 59 % yield (R_f = 0.40 in 1: 1 = EA: Hx, colorless liquid). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.98(2H, dt, *J*= 6.9, 15.6 Hz), 5.84(2H, dt, *J*= 1.5, 15.6 Hz), 4.29(4H, m), 3.74(4H, m), 3.68(4H, s), 2.21(4H, dq, *J*= 1.5, 6.6 Hz), 1.50(4H, m), 1.29(4H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 166.7, 149.8, 121.5, 71.2, 69.6, 64.0, 31.2, 27.3, 26.9. HRMS (EI) calcd for $C_{18}H_{28}O_6$ 340.1886, found 340.1893.

Compound 20. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 2 = ethyl acetate: hexane. 31.3 mg of the product was isolated in 55 % yield. (R_f = 0.55 in 1: 1 = EA: Hx, colorless liquid). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.95(2H, dt, *J*= 7.2, 15.6 Hz), 5.81(2H, dt, *J*= 1.5, 15.6

Hz), 4.26(4H, m), 3.70(4H, m), 3.65(4H, s), 2.20 (4H, m), 1.44(4H, m), 1.23(12H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 166.8, 150.2, 121.4, 71.1, 69.8, 64.0, 32.2, 29.1, 28.9, 28.4, 27.7. HRMS (EI) calcd for $C_{22}H_{36}O_6$ 396.2512, found 396.2507.

Compound 21. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 1 = ethyl acetate: hexane. 9.0 mg of the product was isolated in 50 % yield. (R_f = 0.35 in 1: 1 = EA: Hx, colorless liquid). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.83(1H, dt, *J*= 6.9, 15.6 Hz), 6.71(1H, dd, *J*= 9.6, 15.6 Hz), 5.81(2H, dt, *J*= 1.5, 15.6 Hz), 4.36(2H, m), 4.13(2H, m), 3.73(4H, m), 3.67(4H, s), 2.35 (1H, m), 2.25(2H, m), 1.79(1H, m), 1.50(1H, m)1.04(3H, d, *J*= 6.9). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 166.7, 166.5, 153.0, 148.4, 123.0, 121.6, 70.7, 70.5, 69.2, 69.2, 63.8, 63.8, 37.2, 33.1, 30.7, 21.1. HRMS (EI) calcd for $C_{16}H_{24}O_6$ 312.1573, found 312.1581.

Compound 22. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 1 = ethyl acetate: hexane. 7.0 mg of the product was isolated in 37 % yield. (R_f = 0.35 in 1: 1 = EA: Hx, colorless liquid). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.91(2H, m), 5.81(2H, d, *J*= 15.6 Hz), 4.20(4H, m), 3.72(4H, m), 3.67(4H, s), 2.20(4H, m), 1.5-1.3(3H, m), 0.95(3H, d, *J*= 6.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 166.5, 149.3, 148.3, 122.8, 121.9, 71.1, 70.1, 69.4, 69.3, 64.1, 39.2, 33.5, 31.3, 29.1, 20.6. HRMS (EI) calcd for $C_{17}H_{26}O_6$ 326.1729, found 326.1728.

Compound 24. see **General Procedure**. This time 8 mol% of catalyst **2** was used. The product was purified directly on a silica gel column, eluting with 1: 10 = ethyl acetate: hexane. 25.4 mg of the product was isolated in 59 % yield. (R_f = 0.5 in 1: 5 = EA: Hx, colorless liquid).). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 5.60(2H, m), 5.33(2H, dd, *J*= 8.1, 15.9 Hz), 5.13(2H, m) 2.10(2H, m), 2.00(6H, s), 1.60(2H, m),

1.50(2H, m), 1.40(2H, m), 1.2(24H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 170.5, 134.8, 128.9, 75.5, 34.4, 32.1, 29.8, 29.6, 29.2, 29.1, 28.6, 28.2, 24.9, 21.8. HRMS (EI) calcd for $C_{26}H_{44}O_4$ 420.3240, found 420.3247.

Compound 25. see **General Procedure**. After metathesis reaction was done, the pot was pressured up with 50 psi hydrogen gas, and ran for overnight. The product was purified directly on a silica gel column, eluting with 1: 10 = ethyl acetate: hexane. 13.0 mg of the product was isolated in 48 % yield. (R_f = 0.45 in 1: 4 = EA: Hx, white solid). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.39(8H, t, *J*= 6.9 Hz), 1.58(8H, m), 1.23(24H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 212.5, 41.6, 29.1, 29.0,28.8, 24.1. HRMS (EI) calcd for $C_{22}H_{40}O_2$ 336.3028, found 336.3024.

(i) The solvent columns are composed of activated alumina (A-2) and supported copper redox catalyst (Q-5 reactant). See: Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.