Supporting Material

Experimental procedures and characterization (¹H and ¹³C 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 ¹H NMR data refer to the major olefin isomer unless stated otherwise. The reported ¹³C 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. CH₂Cl₂ was purified by passage through a solvent column prior to use.
**General Procedure**: To a flask charged with catalyst 1 (0.05 equiv in 0.005 to 0.006 M CH₂Cl₂), 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 (Rₚ = 0.4 in 1: 2 = EA: Hx, colorless liquid). ¹H NMR (300 MHz, CDCl₃, 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). ¹³C NMR (75 MHz, CDCl₃, 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 C₁₉H₃₀O₂, 290.2246, found, 290.2241.

8.0 mg of the product 5 in 34 % yield was obtained (Rₚ = 0.3 in 1: 2 = EA: Hx, white solid). ¹H NMR (300 MHz, CDCl₃, 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). ¹³C NMR (75 MHz, CDCl₃, 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 C₃₈H₆₀O₄, 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 (Rₚ = 0.6 in 1: 2 = EA: Hx, colorless liquid). ¹H NMR (300 MHz, CDCl₃, 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). ¹³C NMR (75 MHz, CDCl₃, 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 C₂₂H₃₆O₂, 332.2715, found, 332.2712.
9.0 mg of the product 6 in 23 % yield was obtained (Rf = 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, 15.9 Hz), 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 (Rf = 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 (Rf = 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 (Rf = 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 6.92(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 167.0, 149.6, 121.7, 64.5, 32.3, 29.4, 29.3, 29.1, 29.0, 27.5, 27.1, 26.6. HRMS (EI) calcd for C$_{24}$H$_{40}$O$_4$ 392.2927, found 392.2920.

**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 (Rf = 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 (Rf = 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 (Rf = 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), 5.83(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. (Rf = 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), 4.23(4H, m), 3.72(4H, m), 3.67(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$_{19}$H$_{26}$O$_6$ 342.1902, found 342.1906.
\(^{13}\)C NMR (75 MHz, CDCl\(_3\), ppm): \(\delta\) 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): \(\delta\) 6.83(1H, \(\text{dt, } J = 6.9, 15.6 \text{ Hz}\)), 6.71(1H, \(\text{dd, } J = 9.6, 15.6 \text{ Hz}\)), 5.81(2H, \(\text{d, } J = 1.5, 15.6 \text{ Hz}\)), 4.36(2H, \(\text{m}\)), 4.13(2H, \(\text{m}\)), 3.73(4H, \(\text{m}\)), 3.67(4H, \(\text{s}\)), 2.35 (1H, \(\text{m}\)), 2.25(2H, \(\text{m}\)), 1.79(1H, \(\text{m}\)), 1.50(1H, \(\text{m}\)). 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): \(\delta\) 6.91(2H, \(\text{m}\)), 5.81(2H, \(\text{d, } J = 15.6 \text{ Hz}\)), 4.20(4H, \(\text{m}\)), 3.72(4H, \(\text{m}\)), 3.67(4H, \(\text{s}\)), 2.20(4H, \(\text{m}\)), 1.5-1.3(3H, \(\text{m}\)), 0.95(3H, \(\text{d, } J = 6.6 \text{ Hz}\)). \(^{13}\)C NMR (75 MHz, CDCl\(_3\), ppm): \(\delta\) 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): \(\delta\) 5.60(2H, \(\text{m}\)), 5.33(2H, \(\text{dd, } J = 8.1, 15.9 \text{ Hz}\)), 5.13(2H, \(\text{m}\)) 2.10(2H, \(\text{m}\)), 2.00(6H, \(\text{s}\)), 1.60(2H, \(\text{m}\)), 1.44(4H, \(\text{m}\)), 1.23(12H, \(\text{m}\)).
1.50(2H, m), 1.40(2H, m), 1.2(24H, m). $^{13}$C NMR (75 MHz, CDCl$_3$, ppm): $\delta$ 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): $\delta$ 2.39(8H, t, $J$= 6.9 Hz), 1.58(8H, m), 1.23(24H, m). $^{13}$C NMR (75 MHz, CDCl$_3$, ppm): $\delta$ 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.