

A General Model for Selectivity in Olefin Cross Metathesis

Arnab K. Chatterjee, Tae-Lim Choi, Daniel P. Sanders, and Robert H. Grubbs*

Arnold and Mabel Beckman Laboratories for Chemical Synthesis

Division of Chemistry and Chemical Engineering

California Institute of Technology, Pasadena, California 91125

Fax: (626) 564-9297

Email: rhg@caltech.edu

Supplementary Information

Experimental Section

General Information:

Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 pre-coated 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 or TCI America and used as delivered unless noted otherwise. CH_2Cl_2 was purified by passage through a solvent column prior to use. Catalyst **1** and **2** were stored and manipulated on the bench. NMR spectra were recorded on a Varian Mercury 300 MHz NMR.

Representative Procedure: Olefin A (1.0 mmol) and Olefin B (1.0 mmol) were added via syringe to a stirring solution of **2** (0.05 mmol, 5.0 mol%) in CH_2Cl_2 (2.5 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with

hexane:ethyl acetate (500 ml).

Representative Procedure Using One Olefin as Solvent: Olefin A (0.28 mmol) was added *via* syringe to a stirring solution of **1** (18 mg, 0.021 mmol, 7.6 mol%) in 3,3-Dimethylbutene (1.5 ml, excess) under a nitrogen atmosphere. The flask was stirred under a continuous flow of nitrogen for 12 hours at room temperature (23 °C). The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with hexane:ethyl acetate to provide cross product.

Compound 4. *cis*-2-butene-1,4-diacetate (160 μ l, 1.0 mmol) and allylbenzene (55 μ l, 0.50 mmol) were added simultaneously via syringe to a stirring solution of **2** (11 mg, 0.014 mmol, 2.7 mol%) in CH₂Cl₂ (2.5 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 9:1 hexane:ethyl acetate (500ml). Pale oil was obtained (76 mg, 80% yield, *trans/cis* as determined by integration of peaks at 4.73 and 4.55 ppm). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.34-7.17 (5H, m), 5.92 (1H, m), 5.65 (1H, m), 4.55 (2H, app d), 3.41 (2H, d, *J* = 3.3 Hz), 2.06 (3H, unresolved s). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 171.4, 135.1, 134.0, 129.2, 129.1, 126.8, 125.8, 65.5, 60.8, 39.2, 21.6. *R_f* = 0.53 (9:1 hexane:ethyl acetate); HRMS (EI) calcd for C₁₂H₁₄O₂ [M-H]⁺ 189.0916, found 189.0916.

Compound 5. *cis*-2-butene-1,4-diacetate (160 μ l, 0.9 mmol) and 2-benzyloxy-3-butene (90 μ l, 0.51 mmol) were added simultaneously via syringe to a stirring solution of **1** (11 mg, 0.015 mmol, 2.8 mol%) in CH₂Cl₂ (2.5 ml). The flask was fitted with a condenser and refluxed under

nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 9:1 hexane:ethyl acetate (500 ml). Pale oil was obtained (48 mg, 0.19 mmol, 38% yield). Spectra compared to reported compound, see: Blackwell, H. E.; O'Leary, D. J.; Chatterjee, A. K.; Washenfelder, R. A.; Busmann, D. A. *J. Am. Chem. Soc.* **2000**, *122*, 58. $R_f = 0.36$ (9:1 hexane:ethyl acetate).

Compound 6. 5-Hexenyl-1-acetate (170 μ l, 1.0 mmol) and 2-benzyloxy-3-butene (90 μ l, 0.51 mmol) were added simultaneously via syringe to a stirring solution of **1** (15 mg, 0.018 mmol, 3.5 mol%) in CH_2Cl_2 (2.5 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 3:1 hexane:ethyl acetate (500 ml). Clear oil was obtained (121 mg, 0.42 mmol, 82% yield, 10:1 *E/Z* determined by relative ^{13}C peak heights at 71.9 and 68.0 ppm). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 8.02 (2H, t, $J = 7.2$ Hz), 7.51 (1H, t, $J = 7.2$ Hz), 7.40 (2H, t, $J = 7.8$ Hz), 5.80-5.70 (1H, m), 5.61-5.51 (2H, m), 4.02 (2H, t, $J = 6.6$ Hz), 2.09-1.98 (5H, m), 1.65-1.55 (2H, m), 1.47-1.38 (5H, m). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 171.2, 165.9, 132.9, 132.8, 130.9, 130.2, 129.7, 128.4, 71.9, 64.6, 32.1, 28.4, 25.6, 21.4, 20.9. HRMS (EI) calcd for $\text{C}_{17}\text{H}_{22}\text{O}_4$ $[\text{M} + \text{H}]^+$ 291.1596, found 291.1601. $R_f = 0.50$ (3:1 hexane:ethyl acetate).

Compound 7. 5-Hexenyl-1-acetate (170 μ l, 1.0 mmol) and 3-butene-2-ol (45 μ l, 0.52 mmol) were added simultaneously via syringe to a stirring solution of **1** (12 mg, 0.014 mmol, 2.7 mol%) in CH_2Cl_2 (2.5 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a

silica gel column (2x10 cm), eluting with 9:1 hexane:ethyl acetate (500 ml) followed by 3:1 hexane:ethyl acetate (500 ml). Brown oil was obtained (89 mg, 92% yield, 13:1 *E/Z* determined by relative ^1H integrations at 4.62 and 4.24 ppm). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 5.66-5.40 (2H, m), 4.22 (1H, quint, $J = 7.8$ Hz), 4.02 (2H, t, $J = 7.8$ Hz), 2.09-1.98 (5H, m), 1.65-1.55 (3H, m), 1.47-1.38 (2H, m), 1.32 (3H, app d). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 171.2, 134.7, 130.2, 69.7, 64.2, 32.1, 28.4, 25.6, 22.4, 20.9. $R_f = 0.26$ (3:1 hexane:ethyl acetate). Compound spectra match those of previously characterized (*Z*) compound, see: Bratt, K.; Garavelas, A.; Perlmutter, P.; Westman, G.. *J. Org. Chem.* **1996**, *61*, 2109

Compound 8. 5-Hexenyl-1-acetate (85 μl , 0.51 mmol) and 2-*tert*-butyldiphenylsilyl-3-butene (300 μl , 1.07 mmol) were added simultaneously via syringe to a stirring solution of **1** (23 mg, 0.027 mmol, 5.3 mol%) in CH_2Cl_2 (2.5 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 20:1 hexane:ethyl acetate. Brown oil was obtained (115 mg, 0.27 mmol, 53% yield, 7:1 *E/Z* determined by relative ^1H integrations at 4.58 and 4.28 ppm). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.73-7.68 (4H, m), 7.42-7.36 (6H, m), 5.58-5.45 (1H, m), 5.40-5.32 (1H, m), 4.28 (1H, quint, $J = 6.0$ Hz), 4.05 (2H, t, $J = 6.9$ Hz), 2.06 (3H, s), 1.96 (2H, q, $J = 6.9$ Hz), 1.63-1.53 (2H, m), 1.41-1.34 (2H, m), 1.17 (3H, d, $J = 6.3$ Hz), 1.08 (9H, s). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 171.3, 136.1, 136.0, 135.2, 135.1, 135.0, 134.8, 134.6, 129.7, 129.0, 127.9, 127.7, 127.6, 127.5, 70.6, 64.8, 31.9, 28.4, 27.4, 27.3, 25.8, 25.0, 24.9, 21.4, 19.6. $R_f = 0.56$ (9:1 hexane:ethyl acetate). Compound spectra match those of previously characterized (*Z*) compound, see: Bratt, K.; Garavelas, A.; Perlmutter, P.; Westman, G.. *J. Org. Chem.* **1996**, *61*, 2109.

Compound 9. 5-Hexenyl-1-acetate (170 μ l, 1.02 mmol) and 3-methyl-1-penten-3-ol (60 μ l, 0.51 mmol) were added simultaneously via syringe to a stirring solution of **1** (20 mg, 0.024 mmol, 4.8 mol%) in CH_2Cl_2 (2.5 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 3:1 hexane:ethyl acetate. Brown oil was obtained (100 mg, 0.47 mmol, 93% yield). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 5.58 (1H, dt, J = 15.6, 6.6 Hz), 5.46 (1H, d, J = 15.6 Hz), 4.02 (1H, t, J = 6.6 Hz), 2.06-1.92 (5H, m), 1.61-1.35 (6H, m), 1.18 (3H, s), 0.81 (3H, t, J = 6.9 Hz). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 171.3, 137.4, 127.5, 73.2, 64.7, 35.6, 32.1, 28.4, 28.4, 27.7, 26.0, 21.4, 8.7 HRMS (EI) calcd for $\text{C}_{12}\text{H}_{22}\text{O}_3$ 214.1569, found 214.1579. R_f = 0.40 (3:1 hexane:ethyl acetate).

Compound 10. 5-Hexenyl-1-acetate (50 μ l, 0.30 mmol) and 3,3-Dimethyl-1-hexene (95 μ l, 0.61 mmol) were added simultaneously via syringe to a stirring solution of **1** (12 mg, 0.014 mmol, 4.7 mol%) in CH_2Cl_2 (1.5 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 20:1 hexane:ethyl acetate. Clear oil was obtained (61 mg, 0.27 mmol, 90% yield, only one olefin isomer observed by ^1H -NMR). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 5.38-5.18 (2H, m), 4.04 (2H, t, J = 6.6 Hz), 2.04 (3H, obs s), 2.01 (2H, q, J = 6.9 Hz), 1.67-1.57 (2H, m), 1.43-1.37 (2H, m), 1.20 (4H, app d, J = 3.3 Hz), 0.93 (6H, s), 0.87-0.82 (3H, m). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 171.3, 140.1, 125.2, 64.8, 46.0, 36.0, 32.6, 29.3, 28.3, 27.7, 26.3, 21.3, 18.1, 15.2. HRMS (EI) calcd for $\text{C}_{14}\text{H}_{26}\text{O}_2$ 226.1933, found 226.1934. R_f = 0.68 (5:1 hexane:ethyl acetate).

Compound 11. To a flask charged with 4-pentenyl benzoate (41.1 mg, 0.22 mmol) and **1** (9.2 mg, 0.011 mmol, 5 mol%) 3,3-Dimethyl-1-butene (1 ml, 7.75 mmol) was added via syringe. The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 30:1 hexane:ethyl acetate. Clear oil was obtained (53.1 mg, 0.22 mmol, 99% yield, only one olefin isomer observed by ¹H-NMR). ¹H NMR (300 MHz, CDCl₃, ppm): δ 8.05 (2H, d, *J* = 7.8 Hz), 7.56 (1H, t, *J* = 6.6 Hz), 7.44 (2H, t, *J* = 7.5 Hz), 5.50 (1H, d, *J* = 15.6 Hz), 5.34 (1H, dt, *J* = 15.9, 6.0 Hz), 4.32 (t, *J* = 6.6 Hz), 2.15(dd, *J* = 6.6, 7.2 Hz), 1.84 (dt, d, *J* = 6.6, 7.2 Hz), 0.99 (s). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 166.7, 142.8, 133.0, 130.7, 129.7, 128.5, 123.3, 64.8, 33.2, 30.1, 29.3, 29.1 HRMS (FAB+) calcd for C₁₆H₂₃O₂ [M-H⁺] 247.1698, found 247.1701. *R_f* = 0.62 (9:1 hexane:ethyl acetate).

Compound 12. 5-Hexenyl-1-acetate (81 μl, 0.48 mmol) and 2-methyl-2-vinyl-1,3-dioxolane (50 μl, 0.48 mmol) were added simultaneously via syringe to a stirring solution of **1** (14 mg, 0.017 mmol, 3.7 mol%) in CH₂Cl₂ (2.5 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 5:1 hexane:ethyl acetate. Clear oil was obtained (100 mg, 0.44 mmol, 91% yield, only one olefin isomer observed by ¹H-NMR). ¹H NMR (300 MHz, CDCl₃, ppm): δ 5.77 (1H, dt, *J* = 15.3, 6.9 Hz), 5.42 (1H, dt, *J* = 15.6, 1.5 Hz), 4.05 (2H, t, *J* = 6.6 Hz), 3.96-3.82 (4H, m), 2.14-1.98 (5H, m), 1.55-1.45 (2H, m), 1.42-1.35 (5H, m). *R_f* = 0.31 (9:1 hexane:ethyl acetate). Spectra match those of known compounds that are related, see: Camps, J.; Font, J.; de March, P. *Tetrahedron* **1981**, *37*, 2499.

Compound 13. Styrene (32 μ l, 0.28 mmol) and 2-methyl-2-vinyl-1,3-dioxolane (63 μ l, 0.55 mmol) were added simultaneously via syringe to a stirring solution of **1** (7 mg, 0.008 mmol, 3.0 mol%) in CH_2Cl_2 (1.3 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 20:1 hexane:ethyl acetate. Clear oil was obtained (37 mg, 0.19 mmol, 70% yield, only *E* olefin isomer observed by $^1\text{H-NMR}$). $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 7.42-7.25 (5H, m), 6.71 (1H, d, $J = 15.9$ Hz), 6.15 (1H, d, $J = 15.9$ Hz), 4.05-3.92 (4H, m), 1.57 (3H, s). $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , ppm): δ 136.3, 129.9, 128.8, 128.1, 126.9, 107.9, 64.9, 30.0, 25.6. Elemental analysis Calcd: C: 75.76, H: 7.42; Found: C: 75.47, H: 7.63. $R_f = 0.41$ (9:1 hexane:ethyl acetate).

Compound 14. 5-hexenyl-1-acetate (77 μ L, 0.49 mmol) and 2-methyl-3-buten-2-ol (113 μ l, 1.08 mmol) were added simultaneously via syringe to a stirring solution of **1** (25 mg, 0.029 mmol, 6.0 mol%) in CH_2Cl_2 (2.5 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 60:40 pentane:diethyl ether. A clear oil was obtained (56 mg, 0.28 mmol, 58% yield) and only one olefin isomer detected in $^1\text{H-NMR}$. $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 5.60-5.45 (2H, m), 4.00 (2H, t, $J = 6.63$ Hz), 2.05-1.95 (5H, m), 1.90-1.75 (1H, br s) 1.65-1.50 (2H, m), 1.45-1.30 (2H, m), 1.24 (6H, s). $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , ppm): δ 171.45, 138.76, 126.61, 70.71, 64.60, 31.88, 30.01, 28.24, 25.76, 21.20. HRMS (EI) calcd for $\text{C}_{10}\text{H}_{17}\text{O}_3$ $[\text{M}-\text{CH}_3]^+$ 185.1178, found 185.1181. $R_f = 0.27$ (70:30 hexane:ethyl acetate).

Compound 15. 5-hexenyl-1-acetate (40 μ l, 0.24 mmol) was added via syringe to a stirring solution of **1** (12 mg, 0.014 mmol, 6.0 mol%) and 2-*tert*-butyldimethylsilyloxy-2-methyl-3-butene (106 mg, 0.53 mmol) in CH_2Cl_2 (1.5 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 9:1 hexane:ethyl acetate (500 ml) followed by 3:1 hexane:ethyl acetate (300 ml). A clear oil was obtained (73 mg, 0.23 mmol, 97% yield) and only one olefin isomer detected in ^1H -NMR. ^1H NMR (300 MHz, CDCl_3 , ppm): δ 5.60-5.50 (2H, m), 4.05 (2H, t, $J = 6.6$ Hz), 2.04-1.99 (5H, m), 1.70-1.58 (2H, m), 1.47-1.40 (2H, m), 1.26 (6H, s), 0.85 (9H, s), 0.03 (6H, s). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 171.3, 139.6, 125.9, 73.1, 64.7, 32.1, 30.9, 28.5, 26.2, 26.0, 21.4, 18.4, -1.66. HRMS (EI) calcd for $\text{C}_{17}\text{H}_{34}\text{O}_3\text{Si}$ 314.2277, found 314.2269 $R_f = 0.18$ (9:1 hexane:ethyl acetate).

Compound 16. 1-Benzyloxy-2-Methyl-2-propene (90 μ l, 0.51 mmol) and 5-Hexenyl-1-acetate (170 μ l, 1.0 mmol) were simultaneously added *via* syringe to a stirring solution of **1** (21 mg, 0.026 mmol, 5.0 mol %) in CH_2Cl_2 (2.5 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 20:1 hexane:ethyl acetate (500 ml) and then elute with 9:1 hexane:ethyl acetate. Clear oil was obtained (120 mg, 81% yield, 4:1 *E/Z* based on integration of ^1H peaks at 5.41, 5.63 ppm). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 8.03 (2H, d, $J = 6.9$ Hz), 7.54 (1H, t, $J = 7.4$ Hz), 7.42 (2H, t, $J = 7.6$ Hz), 5.63 (1H, m), 4.67 (2H, s), 4.00 (2H, t, $J = 6.3$ Hz), 2.18-2.01 (5H, m), 1.97 (3H, s), 1.61 (2H, m), 1.43 (2H, m). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 171.3, 166.6, 133.0, 130.7, 130.6, 130.5, 129.7, 129.3, 128.5,

70.7, 64.5, 28.4, 25.8, 21.6, 14.2. R_f = 0.43 (9:1 hexane:ethyl acetate); HRMS (EI) calcd for $C_{17}H_{22}O_4$ $[M + H]^+$ 291.1596, found 291.1589. Elemental analysis Calcd: C: 70.32, H: 7.64; Found: C: 69.89, H: 7.76.

Compound 17. To a flask charged with methacrylamide (17.2 mg, 0.20 mmol), TBS protected 9-decen-1-ol (65 mg, 0.24 mmol) and **1** (8.5mg, 0.01 mmol, 5 mol%), solvent of 1 ml CH_2Cl_2 was added via syringe. The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 2:1 hexane:ethyl acetate. Clear oil was obtained (46.6 mg, 71% yield, >20:1 = *E/Z*). 1H NMR (300 MHz, $CDCl_3$, ppm): δ 6.39 (1H, t, J = 7.5 Hz), 5.87 (2H, br), 3.55 (2H, J = 6.6 Hz), 2.10 (2H, m), 1.80 (3H, s), 1.2- 1.48 (12H, m), 0.86 (9H, s), 0.00 (6H, s). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 171.7, 138.2, 129.9, 63.6, 33.2, 29.8, 29.7, 29.7, 29.1, 28.8, 26.3, 26.1, 18.7, 13.1, -4.8. R_f = 0.35 (1:1 hexane:ethyl acetate); HRMS (EI) calcd for $C_{18}H_{37}NO_2Si$ 327.2594, found 327.2594.

Compound 18. To a solution of **1** (10.0mg, 0.012 mmol, 5 mol%), in 1 ml CH_2Cl_2 methacrylic acid (20 μ l, 0.236 mmol), and 1-dodecene (0.260 mmol) was added via syringe. The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm); eluting with 5:1 hexane:ethyl acetate. Clear oil was obtained (46.6 mg, 71% yield, >4:1 = *E/Z*). 1H NMR (300 MHz, $CDCl_3$, ppm): δ 6.92 (1H, t, J = 7.8 Hz), 2.18 (2H, m), 1.83 (3H, s), 1.2- 1.48 (16H, m), 0.88 (3H, t, J = 6.6 Hz), ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 173.7, 145.7, 127.0, 32.3, 30.0, 29.9, 29.8, 29.7, 29.7, 29.3, 28.8, 23.1, 14.5, 12.4. R_f = 0.30 (1:5 hexane:ethyl acetate); HRMS

(EI) calcd for C₁₄H₂₆O₂ 226.1933, found 226.1930.

Compound 19. Methacrolein (10 μ l, 0.12 mmol) was added via syringe to a stirring solution of **1** (6 mg, 0.007 mmol, 6.3 mol%) and 1-acetoxy-5-methyl-2-hexene (19 mg, 0.11 mmol) in CH₂Cl₂ (1.0 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 9:1 hexane:ethyl acetate. Clear oil was obtained (20 mg, 0.1086 mmol, 97% yield) and all *trans* olefin by ¹H and ¹³C spectra. ¹H NMR (300 MHz, CDCl₃, ppm): δ 9.41 (1H, s), 6.51 (1H, app t), 4.02 (2H, t, J = 6.9 Hz), 2.37 (2H, q, J = 7.2 Hz), 2.04 (3H, app s), 1.74-1.54 (7H, m). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 195.2, 171.2, 153.9, 139.8, 64.2, 28.8, 28.5, 25.1, 21.3, 9.6. R_f = 0.11 (9:1 hexane:ethyl acetate). Spectra matches those of previously characterized compound by J. P. Morgan, Grubbs group.

Compound 20. *cis*-2-butene-1,4-diacetate (95 μ l, 0.60 mmol) was added via syringe to a stirring solution of **1** (15 mg, 0.018 mmol, 5.7 mol%) and 2-propene-*tert*-butyldimethylsilyloxyphenol (76 mg, 0.31 mmol) in CH₂Cl₂ (2.0 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 20:1 hexane:ethyl acetate. Clear oil was obtained (88 mg, 0.29 mmol, 94% yield) and all *trans* olefin by coupling constants in ¹H spectra. ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.45 (1H, dd, J = 7.5, 1.2 Hz), 7.14 (1H, app t, J = 7.5 Hz), 7.02-6.90 (2H, m), 5.80-5.70 (1H, dd, J = 8.1, 1.2 Hz), 6.22 (1H, dt, J = 16.2, 6.0 Hz), 4.73 (2H, dd, J = 6.0, 1.5 Hz), 2.10 (3H, s), 1.03 (9H, s), 0.21 (6H, s) ppm. ¹³C NMR (75 MHz, CDCl₃, ppm): δ 170.8, 153.0, 129.0, 128.9, 127.7, 126.6, 123.0, 121.5, 119.7, 65.6, 26.1,

21.3, 18.6, -3.9. $R_f = 0.51$ (9:1 hexane:ethyl acetate); HRMS (EI) calcd for $C_{17}H_{26}SiO_3$ $[M]^+$ 306.1651, found 306.1648. $R_f = 0.51$ (9:1 hexane:ethyl acetate).

Compound 21. Ethyl acrylate (65 μ l, 0.60 mmol) was added via syringe to a stirring solution of **1** (13 mg, 0.015 mmol, 5.0 mol%) and 2-propene-*tert*-butyldimethylsilyloxy-phenol (75 mg, 0.30 mmol) in CH_2Cl_2 (1.7 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 20:1 hexane:ethyl acetate. Clear oil was obtained (28 mg, 0.09 mmol, 30% yield) and all *trans* olefin by coupling constants in 1H spectra. 1H NMR (300 MHz, $CDCl_3$, ppm): δ 8.09 (1H, d, $J = 16.2$ Hz), 7.55 (1H, dd, $J = 7.8, 1.5$ Hz), 7.28-7.22 (1H, m), 6.99-6.82 (2H, m), 6.37 (1H, d, $J = 16.5$ Hz), 4.24 (2H, q, $J = 7.2$ Hz), 1.32 (3H, app t, $J = 7.2$ Hz), 1.03 (9H, s), 0.22 (6H, s). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 167.3, 154.7, 140.0, 131.4, 127.4, 126.1, 121.7, 120.1, 117.9, 60.5, 26.1, 18.6, 14.6, -3.9. HRMS (EI) calcd for $C_{17}H_{26}O_3Si$ 306.1651, found 306.1644. $R_f = 0.45$ (9:1 hexane:ethyl acetate).

Compound 22. Ethyl acrylate (95 μ l, 0.88 mmol) was added via syringe to a stirring solution of **1** (13 mg, 0.015 mmol, 3.4 mol%) and 2-propene-acetoxyphenol (78 mg, 0.44 mmol) in CH_2Cl_2 (2.0 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 20:1 hexane:ethyl acetate (300 ml) followed by 3:1 hexane:ethyl acetate (500 ml). Clear oil was obtained (90 mg, 0.38 mmol, 87% yield) and all *trans* olefin by coupling constants by 1H -NMR. 1H NMR (300 MHz, $CDCl_3$, ppm): δ 7.73 (1H, d, $J = 15.9$ Hz), 7.62 (1H, dd, $J = 7.8, 1.5$ Hz), 7.39 (1H, td, $J = 7.8, 1.5$ Hz), 7.27-7.22 (1H, m), 7.11 (1H, dd, $J =$

7.8, 1.2 Hz), 6.43 (1H, d, $J = 16.2$ Hz), 4.25 (2H, q, $J = 7.2$ Hz), 2.37 (3H, app s), 1.32 (3H, t, $J = 7.2$ Hz). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 169.2, 166.7, 149.3, 137.9, 131.1, 127.7, 127.2, 126.4, 123.2, 120.4, 60.8, 21.2, 14.5. $R_f = 0.20$ (9:1 hexane:ethyl acetate). Elemental analysis Calcd: C: 66.66, H: 6.02; Found: C: 66.54, H: 6.07.

Compound 23. *cis*-2-butene-1,4-diacetate (25 μl , 0.16 mmol) was added via syringe to a stirring solution of **2** (4 mg, 0.005 mmol, 9.0 mol%) and 3,7-octadiene-2-one (9 mg, 0.054 mmol) in CH_2Cl_2 (1.0 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 4:1 hexane:ethyl acetate. Yellow oil was obtained (10 mg, 0.23 mmol, 78% yield) as a 4.5:1 *E/Z* olefin mixture by ^1H NMR integration at 4.60 and 4.51 ppm. ^1H NMR (300 MHz, CDCl_3 , ppm): δ 6.76 (1H, dt, $J = 15.9, 6.0$ Hz), 6.06 (1H, d, $J = 15.9$ Hz), 5.74 (1H, m), 5.60 (1H, m), 4.49 (2H, $J = 6.0$ Hz), 2.30 (4H, m), 2.23 (3H, s), 2.04 (3H, s), ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 198.7, 171.0, 147.1, 134.4, 131.9, 125.4, 65.1, 31.9, 30.9, 27.3, 21.3. HRMS (EI) calcd for $\text{C}_{11}\text{H}_{16}\text{O}_3$ 196.1099, found 196.1108. $R_f = 0.50$ (3:1 hexane:ethyl acetate).

Compound 24. To an oven dried, 100 ml Fischer-Porter bottle with Teflon stir bar, ruthenium metathesis catalyst **1** (14 mg, 0.017 mmol, 7.0 mol%) was added. The bottle was capped with a rubber septum and flushed with dry nitrogen and cooled to -78 $^\circ\text{C}$. 1,5-Hexadiene (85 μl , 0.72 mmol) and methyl vinyl ketone (20 μl , 0.24 mmol) was injected into the bottle. Once the substrates were frozen, a pressure regulator was attached to the bottle. The bottle was evacuated and backfilled with dry nitrogen 3 times. Subsequently, isobutylene (10 ml) was condensed into

the bottle. The bottle was backfilled to ~2 psi with nitrogen, sealed, and allowed to slowly warm to room temperature, at which time it was transferred to an oil bath at 40 °C. After stirring for 12 hours, the bottle was removed from the oil bath and allowed to cool to room temperature. The isobutylene was slowly vented off at room temperature until the pressure apparatus could be safely disassembled. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 10:1 hexane:ethyl acetate. Clear oil was obtained (32 mg, 0.21 mmol, 89% yield). ¹H NMR (300 MHz, CDCl₃, ppm): δ 6.78 (1H, dt, *J* = 15.9, 6.6 Hz), 6.07 (1H, dt, *J* = 15.9, 1.5 Hz), 5.12-5.06 (1H, m), 2.26-2.14 (7H, m), 1.69 (3H, s), 1.60 (3H, s). *R_f* = 0.53 (9:1 hexane:ethyl acetate). Spectra matches that of a previous characterization, see: Coxon, J. M.; Garland, R. P.; Hartshorn, M. P. *Aust. J. Chem.* **1972**, *25*, 353.

Compound 25. 1,5-Hexadiene (70 μl, 0.59 mmol) and methyl vinyl ketone (25 μl, 0.30 mmol) were added simultaneously *via* syringe to a stirring solution of **1** (18 mg, 0.021 mmol, 7.1 mol %) in CH₂Cl₂ (2.0 ml) under a nitrogen atmosphere. The flask was fitted with a reflux condenser stirred at 40 °C with a continuous flow of nitrogen for 3 hours. At that point, a solution of styrene (25 μl, 0.30 mmol) and catalyst **1** (16 mg, 0.019 mmol, 6.2 mol%) in CH₂Cl₂ was cannula transferred. The reaction mixture was stirred at 40 °C for an additional 8 hours. The resulting solution was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 15:1 hexane:ethyl acetate to provide cross product (*R_f* = 0.33 in 9:1 hexane:ethyl acetate) as a clear oil (28 mg, 0.14 mmol, 47% yield). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.35-7.21 (5H, m), 6.87-6.79 (1H, m), 6.42 (1H, d, *J* = 15.9 Hz), 6.27-6.10 (2H, m), 2.41 (4H, app s), 2.26 (3H, s). Spectra matches that of a previously characterized compound,

see: Johns, A.; Murphy, J. A.; Sherburn, M. S. *Tetrahedron* **1989**, *45*, 7835.

Compound 26. To an oven dried, 100 ml Fischer-Porter bottle with Teflon stir bar, ruthenium metathesis catalyst **1** (31.8 mg, 0.037 mmol, 5.0 mol%) was added. The bottle was capped with a rubber septum and flushed with dry nitrogen and cooled to $-78\text{ }^{\circ}\text{C}$. 1,5-Hexadiene (266 μl , 2.25 mmol) and ethyl acrylate (81 μl , 0.75 mmol) was injected into the bottle. Once the substrates were frozen, a pressure regulator was attached to the bottle. The bottle was evacuated and backfilled with dry nitrogen 3 times. Subsequently, isobutylene (10 ml) was condensed into the bottle. The bottle was backfilled to ~ 2 psi with nitrogen, sealed, and allowed to slowly warm to room temperature, at which time it was transferred to an oil bath at $40\text{ }^{\circ}\text{C}$. After stirring for 12 hours, the bottle was removed from the oil bath and allowed to cool to room temperature. The isobutylene was slowly vented off at room temperature until the pressure apparatus could be safely disassembled. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (4x15 cm), eluting with 20:1 pentanes:diethyl ether. Clear oil was obtained (82 mg, 0.45 mmol, 60% yield). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 6.92 (1H, dt, $J = 15.6, 6.3$ Hz), 5.77 (1H, dt, $J = 15.6, 1.5$ Hz), 5.12-5.02 (1H, m), 4.13 (2H, q, $J = 7.2$ Hz), 2.26-2.05 (4H, m), 1.64 (3H, s), 1.56 (3H, s), 1.24 (3H, t, $J = 7.8$ Hz). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 166.85, 149.08, 132.86, 123.04, 121.56, 60.25, 32.59, 26.73, 25.80, 17.85, 14.41. $R_f = 0.39$ (20:1 hexane:ethyl acetate). HRMS (GC-EI) calcd for $\text{C}_{11}\text{H}_{18}\text{O}_2$ [M^{\bullet}] 182.1307, found 182.1314.

Compound 27. To an oven dried, 100 ml Fischer-Porter bottle with Teflon stir bar, ruthenium metathesis catalyst **1** (31.8 mg, 0.037 mmol, 5.0 mol%) was added. The bottle was capped with

a rubber septum and flushed with dry nitrogen and cooled to $-78\text{ }^{\circ}\text{C}$. 1,5-Hexadiene (266 μl , 2.25 mmol) and diethyl vinyl phosphonate (115 μl , 0.75 mmol) was injected into the bottle. Once the substrates were frozen, a pressure regulator was attached to the bottle. The bottle was evacuated and backfilled with dry nitrogen 3 times. Subsequently, isobutylene (10 ml) was condensed into the bottle. The bottle was backfilled to ~ 2 psi with nitrogen, sealed, and allowed to slowly warm to room temperature, at which time it was transferred to an oil bath at $40\text{ }^{\circ}\text{C}$. After stirring for 12 hours, the bottle was removed from the oil bath and allowed to cool to room temperature. The isobutylene was slowly vented off at room temperature until the pressure apparatus could be safely disassembled. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (4x15 cm), eluting with 1:2 hexane:ethyl acetate. A clear oil was obtained (104 mg, 0.427 mmol, 57% yield) $E:Z = 8:1$. *E* isomer: ^1H NMR (300 MHz, CDCl_3 , ppm): δ 6.85-6.60 (1H, m), 5.59 (1H, dd, $J = 21.3, 17.1$ Hz), 5.10-4.95 (1H, m), 4.01 (4H, q, $J = 7.2$ Hz), 2.35-2.00 (4H, m), 1.62 (3H, s), 1.54 (3H, s), 1.26 (3H, t, $J = 7.2$ Hz). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 153.66, 132.89, 122.92, 117.07 (d, $J = 186$ Hz), 61.73, 53.58, 34.58, 34.30, 26.47, 25.79, 17.87, 16.53. ^{31}P NMR (121 MHz, CDCl_3 , ppm): δ 19.85. $R_f = 0.24$ (1:2 hexane:ethyl acetate). HRMS (FAB) calcd for $\text{C}_{12}\text{H}_{24}\text{O}_3\text{P}$ $[\text{M} + \text{H}]^+$ 247.1463, found 247.1455.

Compound 28. 1,5-Hexadiene (33 μl , 0.28 mmol) was added *via* syringe to a stirring solution of **1** (18 mg, 0.021 mmol, 7.6 mol %) and ethyl acrylate (30 μl , 0.28 mmol) in 3,3-dimethylbutene (1.5 ml, excess) under a nitrogen atmosphere. The flask was stirred under a continuous flow of nitrogen for 12 hours at room temperature ($23\text{ }^{\circ}\text{C}$). The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting

with 8:1 hexane:ethyl acetate to provide cross product ($R_f = 0.37$ in 20:1 hexane:ethyl acetate) as a viscous oil (39 mg, 0.19 mmol, 67% yield). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 6.95 (1H, dt, $J = 15.9, 6.6$ Hz), 5.80 (1H, dt, $J = 15.9, 1.5$ Hz), 5.50-5.40 (1H, m), 5.27 (1H, dt, $J = 15.3, 6.6$ Hz), 4.05 (2H, q, $J = 6.6$ Hz), 2.26-2.12 (4H, m), 1.28 (3H, t, $J = 7.2$ Hz), 0.98 (9H, s). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 166.86, 148.86, 143.06, 123.07, 121.69, 60.28, 33.01, 32.58, 31.26, 29.85, 25.80, 14.44. HRMS (FAB) calcd for $\text{C}_{13}\text{H}_{23}\text{O}_2$ $[\text{M} + \text{H}]^+$ 211.1698, found 211.1702.

Compound 29. 1,5-Hexadiene (63 μl , 0.53 mmol) and ethyl acrylate (58 μl , 0.53 mmol) were added simultaneously *via* syringe to a stirring solution of **1** (22 mg, 0.026 mmol, 5.2 mol %) in CH_2Cl_2 (2.5 ml) under a nitrogen atmosphere. The flask was fitted with a reflux condenser stirred at 40 °C with a continuous flow of nitrogen for 1.5 hours. At that point, styrene (180 μl , 1.57 mmol) was added *via* syringe. The reaction mixture was stirred at 40 °C for an additional 11 hours. The resulting solution was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 10:1 hexane:ethyl acetate to provide cross product ($R_f = 0.38$ in 9:1 hexane:ethyl acetate) as a clear oil (41 mg, 0.18 mmol, 34% yield). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.35-7.21 (5H, m), 7.04-6.96 (1H, m), 6.47-6.40 (1H, m), 6.24-6.16 (1H, m), 5.86 (1H, d, $J = 15.6$ Hz), 4.08 (2H, q, $J = 6.6$ Hz), 2.41 (4H, app s), 1.31 (3H, app t). Spectra matches that of a previously characterized methyl ester, see: Johns, A.; Murphy, J. A.; Sherburn, M. S. *Tetrahedron* **1989**, *45*, 7835.

Compound in Table 5, Entry 1. To flask charged with **1** (12.4 mg, 0.015 mmol, 5.0 mol%), acrylic acid (20 μl , 0.29 mmol) and 2,2-dimethyl 3-butene (1 ml, 7.75 mmol) were added *via*

syringe. The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The product was purified directly on a silica gel column, eluting with 1: 2 = ethyl acetate: hexane. 20.2 mg of the product was obtained (73%, R_f = 0.30 in 1: 2 = EA: Hx, white solid). Spectra match those of a previously characterized product, see: Freeman, F.; Kappso, J. C. *J. Org. Chem.* **1986**, *51*, 1654.

Compound in Table 5, Entry 2. To flask charged with **1** (8.5 mg, 0.01 mmol, 5.0 mol%), *t*-butyl acrylate (30 μ l, 0.21 mmol) and 2,2-dimethyl 3-butene (1 ml, 7.75 mmol) were added via syringe. The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The product was purified directly on a silica gel column, eluting with 1: 30 = ethyl acetate: hexane. 27.5 mg of the product was obtained (73%, R_f = 0.40 in 1: 20 = EA: Hx, white solid). Spectra match those of a previously characterized product, see: Inoue, S; Sato, Y. *J. Org. Chem.* **1991**, *56*, 347.

Compound in Table 5, Entry 3. To a flask charged with **1** (8.5 mg, 0.01 mmol, 5.0 mol%), 2-vinyl-1,3-dioxolane (20 μ l, 0.2 mmol) and 2,2-dimethyl 3-butene (1 ml, 7.75mmol) were added via syringe. The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 10:1 hexane:ethyl acetate. Clear oil was obtained (23.4 mg, 0.15 mmol, 75% yield). Only *E*-isomer was observed by $^1\text{H-NMR}$. $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 5.93 (1H, d, J = 16.2 Hz), 5.37 (1H, dd, J = 15.9, 6.6 Hz), 5.17 (1H, d, J = 6.6 Hz), 4.00 (2H, m), 3.89 (2H, m), 1.03 (9H, s), $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , ppm): δ 148.9, 121.3, 104.9, 65.2, 33.4, 29.4. R_f = 0.30 (10:1 hexane:ethyl acetate); HRMS (EI) calcd for $\text{C}_9\text{H}_{15}\text{O}_2$ [M-H^+]

155.1072, found 155.1072.

Compound in Table 5, Entry 4. To a solution of **1** (8.5 mg, 0.01 mmol, 5.0 mol%), in 1 ml of CH₂Cl₂, acrylic acid (14 μ l, 0.2 mmol), and 2-methyl 1-heptene (126 μ l, 0.76 mmol) were added via syringe. The flask was fitted with a condenser and refluxed under nitrogen for 6 hours. The product was purified directly on a silica gel column, eluting with 1: 5 = ethyl acetate: hexane. 26.5 mg of the product was obtained (R_f = 0.3 in 1: 5 = EA: Hx, white solid). *E* / *Z* ratio was confirmed by ¹H NOE. ¹H NMR (300 MHz, CDCl₃, ppm): δ 5.67 (1H, s), [2.60 (2H, t, J = 7.5 Hz), 1.90 (3H, s) for *cis*], [2.14 (3H, s), 2.10 (2H, J = 7.0 Hz), for *trans*] 1.50 (2H, m), 1.30 (6H, m), 0.87 (3H, J = 6.6 Hz). ¹³C NMR (75 MHz, CDCl₃, ppm): δ [172.6, 163.8, 115.2, 41.5, 31.7, 27.4, 22.8, 19.4, 14.4. for *trans*] [172.6, 163.8, 115.7, 33.8, 32.2, 28.2, 25.9, 19.4, 14.4. for *cis*] HRMS (EI) calcd for C₉H₁₆O₂ 156.1150, found 156.1145.

Compound in Table 5, Entry 5. To a solution of **1** (8.5 mg, 0.01 mmol, 5.0 mol%), in 1 ml of CH₂Cl₂, ethyl crotonate (24 μ l, 0.19 mmol), and 2-methyl 1-heptene (126 μ l, 0.76 mmol) were added via syringe. The flask was fitted with a condenser and refluxed under nitrogen for 6 hours. The product was purified directly on a silica gel column, eluting with 1: 15 = ethyl acetate: hexane. 29.7 mg of the product was obtained (83%, R_f = 0.4 in 1: 10 = EA: Hx, clear oil). *E* / *Z* ratio was confirmed by ¹H NOE. ¹H NMR (300 MHz, CDCl₃, ppm): δ 5.62 (1H, s), 4.12 (2H, m), [2.58 (2H, t, J = 7.5 Hz), 1.84 (3H, s) for *cis*], [2.11 (3H, s), 2.00 (2H, J = 7.5 Hz), for *trans*] 1.50 (2H, m), 1.30 (6H, m), 0.86 (3H, J = 6.9 Hz). ¹³C NMR (75 MHz, CDCl₃, ppm): δ [167.0, 160.5, 115.6, 59.7, 41.2, 31.7, 27.4, 22.8, 19.1, 14.7, 14.4. for *trans*] [166.5, 160.9, 116.1, 59.7, 33.7, 32.3, 28.2, 25.5, 22.9, 14.7, 14.3. for *cis*] HRMS (EI) calcd for C₁₁H₂₀O₂ 184.1463,

found 184.1460.

Compound in Table 5, Entry 6. To a solution of **1** (8.5 mg, 0.01 mmol, 5.0 mol%), in 1 ml of CH_2Cl_2 , 4-hexene-3-one (22 μl , 0.19 mmol), and 2-methyl 1-heptene (126 μl , 0.76 mmol) were added via syringe. The flask was fitted with a condenser and refluxed under nitrogen for 6 hours. The product was purified directly on a silica gel column, eluting with 1: 15 = ethyl acetate: hexane. 22.0 mg of the product was obtained ($R_f = 0.4$ in 1: 10 = EA: Hx, white solid). *E* / *Z* ratio was confirmed by ^1H NOE. ^1H NMR (300 MHz, CDCl_3 , ppm): δ 6.02 (1H, s), [2.54 (2H, t, $J = 7.5$ Hz), 1.83 (3H, s) for *cis*], [2.10 (3H, s), 2.08 (2H, $J = 7.0$ Hz), for *trans*] 2.40 (2H, $J = 5.4$ Hz), 1.50 (2H, m), 1.30 (6H, m), 1.00 (3H, $J = 6.6$ Hz), 0.87 (3H, $J = 6.6$ Hz). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ [201.8, 158.7, 123.0, 41.5, 37.7, 31.8, 27.5, 22.8, 19.6, 14.4, 8.5. for *trans*] [201.2, 159.4, 123.5, 37.7, 34.1, 32.3, 28.3, 25.8, 22.9, 14.4, 8.5. for *cis*] HRMS (EI) calcd for $\text{C}_{10}\text{H}_{20}\text{O}$ 168.1514, found 168.1513.

Compound in Table 5, Entry 7. 2-Methyl-1-undecene (110 μl , 0.5 mmol) and 2-Vinyl-1,3-dioxolane (100 μl , 1.0 mmol) were simultaneously added *via* syringe to a stirring solution of **1** (12 mg, 0.015 mmol, 2.9 mol %) in CH_2Cl_2 (2.5 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 9:1 hexane:ethyl acetate. Pale yellow oil was obtained (60 mg, 67% yield, 3:1 *E/Z* based on relative intensities of ^{13}C peaks at 122.1, 121.2 ppm). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 5.48 (1H, m), 5.22 (1H, m), 4.00 (2H, app t), 3.87 (2H, app t), 1.96 (2H, m), 1.75 (3H, s), 1.46-1.25 (17H, m) ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 122.1, 121.2, 101.0, 100.6, 65.4, 40.1, 32.4, 32.1, 30.1, 30.0, 29.9, 27.9,

27.7, 23.2, 14.6. $R_f = 0.26$ (9:1 hexane:ethyl acetate); HRMS (EI) calcd for $C_{15}H_{28}O_2$ $[M]^+$ 240.2083, found 240.2089.

Compound in Table 6, Entry 1. 5-hexenyl-1-tetrahydropyranyl ether (37.9 mg, 0.21 mmol) and styrene (92 μ l, 0.84 mmol) were added sequentially via syringe to a stirring solution of **1** (9.3 mg, 0.011 mmol, 5.0 mol%) in CH_2Cl_2 (0.2 M). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 20:1 hexane:ethyl acetate. A colorless oil was obtained (37.1 mg, 0.14 mmol, 70 % yield). 1H NMR (300 MHz, $CDCl_3$, ppm): δ 7.40-7.24 (4H, m), 7.24-7.15 (1H, m), 6.50-6.33 (1H, m), 6.33-6.16 (1H, m), 4.65-4.55 (1H, m), 4.00-3.70 (2H, m), 3.70-3.30 (2H, m), 2.40-2.15 (2H, m), 2.00-1.30 (10H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 138.03, 130.97, 130.52, 130.36, 130.22, 128.67, 127.01, 126.12, 99.06, 67.62, 62.53, 33.04, 29.98, 29.52, 26.26, 25.70, 19.87 ppm. HRMS (EI) for $C_{17}H_{25}O_2$ $[M+H]^+$: Calcd 261.1854, Found 261.1847. $R_f = 0.25$ (20:1 hexane:ethyl acetate).

Compound in Table 6, Entry 3. 5-hexenyl-1-acetate (70 μ l, 0.45 mmol) and 2-bromostyrene (170 μ l, 1.36 mmol) were added simultaneously via syringe to a stirring solution of **1** (19 mg, 0.021 mmol, 4.8 mol%) in CH_2Cl_2 (2.5 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 20:1 hexane:ethyl acetate. A light brown oil was obtained (130 mg, 0.44 mmol, 98% yield) and only one olefin isomer detected in 1H -NMR. 1H NMR (300 MHz, $CDCl_3$, ppm): δ 7.52-7.43 (2H, m), 7.29-7.02 (2H, m), 6.70 (1H, d, $J = 15.9$ Hz), 6.13 (1H, dt, $J = 15.9, 6.9$ Hz), 4.09 (2H, t, $J = 6.6$ Hz), 2.28 (2H,

app q), 2.04 (3H, s), 1.74-1.53 (4H, m). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 171.3, 139.6, 133.4, 132.9, 129.3, 128.4, 127.5, 126.9, 126.2, 64.6, 32.8, 28.4, 25.8, 21.4 ppm. HRMS (EI) for $\text{C}_{14}\text{H}_{17}\text{BrO}_2$: Calcd 296.0412, Found 296.0403. $R_f = 0.34$ (9:1 hexane:ethyl acetate).

Compound in Table 6, Entry 5. *cis*-2-butene-1,4-diacetate (75 μl , 0.48 mmol) and 2-fluorostyrene (24 μl , 0.20 mmol) were added simultaneously via syringe to a stirring solution of **1** (8 mg, 0.009 mmol, 5.0 mol%) in CH_2Cl_2 (1.0 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 10:1 hexane:ethyl acetate. A brown oil was obtained (38 mg, 0.20 mmol, 97% yield) and only one olefin isomer detected in ^1H -NMR. ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.48-7.22 (1H, m), 7.24-7.19 (1H, m), 7.12-7.00 (2H, m), 6.79 (1H, d, $J = 16.2$ Hz), 6.36 (1H, dt, $J = 15.9, 6.3$ Hz), 4.74 (2H, dd, $J = 6.3, 1.2$ Hz), 2.11 (3H, s). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 170.8, 162.0, 158.7, 129.5 (d, $J = 8.3$ Hz), 127.6 (d, $J = 3.5$ Hz), 126.4 (d, $J = 3.8$ Hz), 125.9 (d, $J = 5.2$ Hz), 124.2 (d, $J = 3.7$ Hz), 115.8 (d, $J = 21.9$ Hz), 65.3, 21.3 ppm. ^{19}F NMR (282 MHz, CDCl_3 , ppm): δ -118.2 (t, $J = 5.9$ Hz). HRMS (EI) calcd for $\text{C}_{11}\text{H}_{11}\text{FO}_2$ 194.0743, found 194.0746. $R_f = 0.34$ (9:1 hexane:ethyl acetate).

Compound in Table 6, Entry 6. *cis*-2-butene-1,4-diacetate (160 μl , 1.01 mmol) and 2,5-difluorostyrene (62 μl , 0.50 mmol) were added simultaneously via syringe to a stirring solution of **1** (13 mg, 0.015 mmol, 3.0 mol%) in CH_2Cl_2 (2.5 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 9:1 hexane:ethyl acetate. A dark brown oil was obtained (53 mg, 0.25 mmol, 50% yield) and only one olefin

isomer detected in $^1\text{H-NMR}$. $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 7.42-7.10 (2H, m), 6.90-6.80 (2H, m), 6.71-6.55 (1H, m), 4.75 (2H, app d), 2.11 (3H, s) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , ppm): δ 162.7, 159.4, 134.3, 130.5, 128.8, 120.0, 123.3, 111.8, 65.6, 21.3. $R_f = 0.48$ (9:1 hexane:ethyl acetate). HRMS(EI) for $\text{C}_{11}\text{H}_{10}\text{F}_2\text{O}_2$ Calcd: 212.0649, Found: 212.0644.

Compound in Table 6, Entry 7. *cis*-2-butene-1,4-diacetate (24 μl , 0.15 mmol) was added via syringe to a stirring solution of **1** (4 mg, 0.015 mmol, 3.0 mol%) and *trans*-stilbene (23 mg, 0.13 mmol) in CH_2Cl_2 (1.3 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 9:1 hexane:ethyl acetate. A clear yellow oil was obtained (23 mg, 0.13 mmol, 51% yield) and only one olefin isomer detected in $^1\text{H-NMR}$. $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 7.42-7.26 (5H, m), 6.65 (1H, d, $J = 15.9$ Hz), 6.29 (1H, dt, $J = 15.9, 6.3$ Hz), 4.75 (2H, app d), 2.11 (3H, s) ppm. $R_f = 0.41$ (9:1 hexane:ethyl acetate).

Compound spectra match that of *trans*-cinnamyl acetate in Aldrich compound library.

Compound in Table 7, Entry 1. Methyl acrylate (90 μl , 1.00 mmol) and styrene (60 μl , 0.52 mmol) were added simultaneously via syringe to a stirring solution of **1** (20 mg, 0.024 mmol, 4.5 mol%) in CH_2Cl_2 (2.5 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 20:1 hexane:ethyl acetate. A white crystalline solid was obtained (78 mg, 0.48 mmol, 92% yield) and only *E* olefin isomer detected (by coupling constants) in $^1\text{H-NMR}$. $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 7.64 (1H, d, $J = 15.6$ Hz), 6.40 (1H, d, $J = 15.9$ Hz), 3.83 (3H, s). $R_f = 0.53$ (9:1 hexane:ethyl acetate). Compound spectra

match that of *trans*-methyl cinnamate in Aldrich compound library.

Compound in Table 7, Entry 2. Ethyl acrylate (110 μ l, 1.02 mmol) and 2,4-dimethylstyrene (75 μ l, 0.51 mmol) were added simultaneously via syringe to a stirring solution of **1** (10 mg, 0.012 mmol, 2.4 mol%) in CH_2Cl_2 (2.5 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 20:1 hexane:ethyl acetate. A clear oil was obtained (91 mg, 0.45 mmol, 87% yield) and only *E* olefin isomer detected (by coupling constants) in ^1H -NMR. ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.95 (1H, d, $J = 15.9$ Hz), 7.48-7.45 (1H, m), 7.02-7.00 (2H, m), 6.33 (1H, d, $J = 16.2$ Hz), 4.26 (2H, q, $J = 6.9$ Hz), 2.41 (3H, s), 2.33 (3H, s), 1.34 (3H, t, $J = 7.2$ Hz). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 167.3, 142.2, 140.3, 137.7, 131.6, 127.2, 126.4, 118.2, 60.6, 21.6, 20.0, 14.6. HRMS (EI) for $\text{C}_{13}\text{H}_{16}\text{O}_2$: Calcd 204.1150, Found 204.1155. Elemental analysis Calcd: C: 76.44, H: 7.90; Found: C: 76.07, H: 8.05. $R_f = 0.70$ (9:1 hexane:ethyl acetate).

Compound in Table 7, Entry 4. Ethyl acrylate (75 μ l, 0.69 mmol) and 2-trifluoromethylstyrene (50 μ l, 0.34 mmol) were added simultaneously via syringe to a stirring solution of **1** (15 mg, 0.018 mmol, 5.1 mol%) in CH_2Cl_2 (2.0 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 9:1 hexane:ethyl acetate. A brown oil was obtained (37 mg, 0.15 mmol, 44% yield) and only *E* olefin isomer detected (by coupling constants) in ^1H -NMR. ^1H NMR (300 MHz, CDCl_3 , ppm): δ 8.05 (1H, app d), 7.70-7.31 (4H, m), 6.43 (1H, app d), 4.20 (2H, q, $J = 6.9$ Hz), 1.31 (3H, app t). $R_f = 0.70$ (9:1

hexane:ethyl acetate). Compound matches spectra previously reported of the methyl ester, see: Vallgård, J.; Appelberg, U.; Csöreg, I.; Hacksell, U. *J. Chem. Soc. Perkin Trans. 1* **1994**, 461.

Compound in Table 7, Entry 5. Ethyl acrylate (81 μ l, 0.56 mmol) and 3,4-dimethoxystyrene (56 μ l, 0.38 mmol) were added simultaneously via syringe to a stirring solution of **1** (13 mg, 0.015 mmol, 4.0 mol%) in CH_2Cl_2 (2.0 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 9:1 hexane:ethyl acetate. A clear oil was obtained (96 mg, 0.36 mmol, 96% yield) and only *E* olefin isomer detected (by coupling constants) in $^1\text{H-NMR}$. $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 7.62 (1H, d, $J = 15.9$ Hz), 7.10 (1H, dd, $J = 8.4, 2.0$ Hz), 7.05 (1H, d, $J = 2.1$ Hz), 6.85 (1H, d, $J = 8.1$ Hz), 6.30 (1H, d, $J = 15.9$ Hz), 4.20 (2H, t, $J = 6.6$ Hz), 3.91 (6H, s), 1.73-1.62 (2H, m), 1.50-1.38 (2H, m), 0.96 (3H, t, $J = 7.2$ Hz). $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , ppm): δ 167.5, 151.2, 149.3, 144.6, 127.6, 122.8, 116.1, 111.2, 109.7, 64.6, 56.2, 56.1, 31.1, 19.5, 14.1. HRMS (EI) calcd for $\text{C}_{15}\text{H}_{20}\text{O}_4$ 264.1362, found 264.1352. $R_f = 0.24$ (9:1 hexane:ethyl acetate).

Compound in Table 7, Entry 6. Methyl acrylate (90 μ l, 1.00 mmol) and 4-nitrostyrene (75 μ l, 0.51 mmol) were added simultaneously via syringe to a stirring solution of **1** (10 mg, 0.012 mmol, 2.3 mol%) in CH_2Cl_2 (2.5 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 9:1 hexane:ethyl acetate. A white crystalline solid was obtained (93 mg, 0.45 mmol, 89% yield) and only *E* olefin isomer detected (by coupling constants) in $^1\text{H-NMR}$. $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 8.25 (1H, dd, $J = 7.2,$

2.1 Hz), 7.74-7.66 (4H, m), 6.55 (1H, d, $J = 16.2$ Hz), 3.84 (3H, app s). $R_f = 0.30$ (9:1 hexane:ethyl acetate). Spectra match those of previously characterized compound, see: Huang, X.; Xie, L.; Wu, H. *J. Org. Chem.* **1988**, *53*, 4862.

Compound in Table 7, Entry 7. Ethyl acrylate (110 μ l, 1.02 mmol) and 4-vinylbenzaldehyde (75 μ l, 0.49 mmol) were added simultaneously via syringe to a stirring solution of **1** (16 mg, 0.019 mmol, 3.8 mol%) in CH_2Cl_2 (2.5 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 9:1 pentane:ethyl acetate. A dark yellow oil was obtained (85 mg, 0.42 mmol, 83% yield) and only *E* olefin isomer detected (by coupling constants) in $^1\text{H-NMR}$. $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 10.00 (1H, s), 7.90-7.64 (4H, m), 6.52 (1H, d, $J = 15.9$ Hz), 4.26 (2H, q, $J = 7.2$ Hz), 1.33 (3H, t, $J = 7.2$ Hz). $R_f = 0.28$ (9:1 hexane:ethyl acetate). Spectra match those of previously characterized compound, see: Syper, L.; Mlochowski, J. *Synthesis* **1984**, 747.

Compound in Table 7, Entry 8. Ethyl acrylate (110 μ l 1.02 mmol) and 2-fluorostyrene (60 μ l, 0.50 mmol) were added simultaneously via syringe to a stirring solution of **1** (12 mg, 0.014 mmol, 2.8 mol%) in CH_2Cl_2 (2.5 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 9:1 hexane:ethyl acetate. A clear oil was obtained (70 mg, 0.36 mmol, 72% yield) and only *E* olefin isomer detected (by coupling constants) in $^1\text{H-NMR}$. $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 7.80 (1H, d, $J = 16.2$ Hz), 7.55-7.49 (1H, m), 7.35-7.30 (1H, m), 7.17-7.05 (2H, m), 6.52 (1H, d, $J = 16.2$ Hz), 4.26 (2H, q, $J =$

6.9 Hz), 1.33 (3H, $J = 7.2$ Hz). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 166.9, 137.3, 133.8, 131.9, 129.2, 124.6, 121.1, 121.0, 116.5, 61.0, 14.7. $R_f = 0.39$ (9:1 hexane:ethyl acetate). Spectra match those of previously characterized compound, see: Houghton, R. P.; Voyle, M.; Price, R. J. *Organomet. Chem.* **1983**, 259, 183.

Compound in Table 7, Entry 9. Ethyl acrylate (96 μl , 0.89 mmol) and 2-chlorostyrene (57 μl , 0.44 mmol) were added simultaneously via syringe to a stirring solution of **1** (19 mg, 0.022 mmol, 5.0 mol%) in CH_2Cl_2 (2.5 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 10:1 hexane:ethyl acetate. A clear oil was obtained (58 mg, 0.27 mmol, 62% yield) and only *E* olefin isomer detected (by coupling constants) in ^1H -NMR. ^1H NMR (300 MHz, CDCl_3 , ppm): δ 8.07 (1H, d, $J = 15.9$ Hz), 7.62-7.59 (1H, m), 7.42-7.26 (3H, m), 7.17-7.05 (2H, m), 6.43 (1H, d, $J = 15.9$ Hz), 4.26 (2H, q, $J = 6.9$ Hz), 1.33 (3H, $J = 7.2$ Hz). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 166.6, 140.5, 133.8, 132.9, 131.2, 130.3, 127.8, 127.2, 121.1, 61.6, 14.7. $R_f = 0.63$ (9:1 hexane:ethyl acetate). Spectra match those of previously characterized compound, see: Berrier, C.; Gesson, J. P.; Jacquesy, J. C.; Renoux, A. *Tetrahedron* **1983**, 40, 4973.

Compound in Table 7, Entry 10. Ethyl acrylate (73 μl , 0.67 mmol) and 2-bromostyrene (42 μl , 0.33 mmol) were added simultaneously via syringe to a stirring solution of **1** (22 mg, 0.026 mmol, 7.7 mol%) in CH_2Cl_2 (2.5 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 10:1 hexane:ethyl acetate. A clear oil was

obtained (42 mg, 0.17 mmol, 49% yield) and only *E* olefin isomer detected (by coupling constants) in $^1\text{H-NMR}$. $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 8.07 (1H, d, $J = 15.9$ Hz), 7.62-7.59 (2H, m), 7.35-7.22 (2H, m), 6.39 (1H, d, $J = 15.9$ Hz), 4.26 (2H, q, $J = 6.9$ Hz), 1.33 (3H, $J = 7.2$ Hz). $R_f = 0.60$ (9:1 hexane:ethyl acetate). Spectra match those of previously characterized compound, see: Dyker, G.; Grundt, P. *Helv. Chim. Acta.* **1999**, *82*, 588.