

Ruthenium-Catalyzed Tandem Cross-Metathesis/Wittig Olefination: Generation of Conjugated Dienoic Esters from Terminal Olefins

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General Information

Unless otherwise stated, all reactions are carried out in flame-dried vials with Teflon-sealed screwcaps. For slow addition at refluxing temperatures, the vial is fitted with rubber septa pierced with a hole adequate for a cold-finger. Starting materials and reagents were purchased from chemical suppliers and used without further purification except the following: CH_2Cl_2 and toluene were dried on alumina columns using a solvent dispensing system; methacrolein was distilled over CaSO_4 , stored at $-20\text{ }^\circ\text{C}$, and used within one month of distillation.

Infrared (**IR**) spectra bands are characterized as broad (br), strong (s), medium (m) and weak (w). **¹H-NMR** chemical shifts are reported with the solvent as the internal standard (CHCl_3 δ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. **¹³C-NMR** chemical shifts are reported in ppm with the solvent as an internal reference (CDCl_3 δ 77.2 ppm). Reactions monitored by Gas Chromatography used a 100 % methyl polysiloxane column.

Experimental Procedures

Procedure A: (2E,4E)-Ethyl 4-methylundeca-2,4-dienoate (8a)¹.

A solution of methacrolein (20 μ L, 0.24 mmol), octene (76 μ L, 0.48 mmol), and Grubbs' vinylidene catalyst **IV** (10 mg, 0.012 mmol) in CH_2Cl_2 (500 μ L) was heated in a sealed vial at 60 °C for 10-12 h, or until deemed complete by ¹H NMR. Triphenylphosphine (126 mg, 0.484 mmol) was then added to the reaction, a condenser was connected, and ethyl diazoacetate (81 μ L, 0.73 mmol) dissolved in CH_2Cl_2 (500 μ L) was added slowly over 4 h at reflux. After the addition was complete, the vial was again sealed and heated to 60 °C for 4-8 h. Concentration and silica gel chromatography (20:1 hexanes: diethyl ether) afforded the desired product **8a** as a clear oil (42 mg, 82% yield). **FTIR** (NaCl, thin film) 2968(s), 2864(m), 1705(s), 1620(m), 1390(m), 1319(m), 1149(s), 972(m) cm^{-1} . **¹H-NMR** (400 MHz, CDCl_3): δ 0.82-0.90 (m, 3H), 1.20-1.34 (m, 7H), 1.44-1.34 (m, 2H), 1.55-1.44 (m, 2H), 1.74 (s, 3H), 2.16 (q, J = 7.3 Hz, 2H), 4.18 (q, J = 7.3 Hz, 2H), 5.75 (d, J = 15.4 Hz, 1H), 5.87 (t, J = 7.3 Hz, 1H), 7.29 (d, J = 15.4 Hz, 1H). **¹³C-NMR** (100 MHz, CDCl_3): δ 167.6, 149.7, 142.5, 132.8, 115.5, 60.4, 32.0, 29.3, 29.1, 29.1, 22.9, 14.7, 14.4, 12.5.

(2E,4E)-*t*-Butyl 4-methylundeca-2,4-dienoate (8b).

*Following procedure A, replacing ethyl diazoacetate with *t*-butyl diazoacetate (101 μ L, 0.726 mmol) and purifying with silica gel chromatography (20:1 hexanes:diethyl ether) afforded a clear oil **8b** (53 mg, 87% yield). **FTIR** (NaCl, thin film) 3026(s), 2914(s), 2856(s), 1708(s), 1621(m), 1366(w), 1162(s) cm^{-1} . **¹H-NMR** (400 MHz, CDCl_3): δ 0.79-0.92 (t, J = 6.6 Hz, 3H), 1.20-1.33 (m, 6H), 1.35-1.45 (m, 2H), 1.49 (s, 9H), 1.74 (s, 3H), 2.17 (q, J = 7.3 Hz, 2H), 5.70 (d, J = 16.1 Hz, 1H), 5.85 (t, J = 7.3 Hz, 1H), 7.21 (d, J = 16.1 Hz, 1H). **¹³C-NMR** (100 MHz, CDCl_3): δ 167.0, 148.7, 141.7, 132.7, 117.4, 80.1, 32.0, 29.4, 29.3, 29.1, 28.5, 22.9, 14.4, 12.5. **HRMS** (EI+) *m/z* calcd for $\text{C}_{16}\text{H}_{28}\text{O}_2$: 252.2089. Mass Found: 252.2091.*

(2E,4E)-Ethyl 13-(*t*-butyldimethylsilyloxy)-4-methyltrideca-2,4-dienoate (8c).

*Following procedure A, replacing 1-octene with *t*-butyl(dec-9-enyloxy)dimethylsilane (130 mg, 0.484 mmol) and purifying with silica gel chromatography (10:1 hexanes:diethyl ether) afforded a clear oil **8c** (69 mg, 75% yield). **FTIR** (NaCl, thin film) 3047(m), 2969(s), 2870(s), 1712(s), 1646(m), 1477(w), 1169(s), 842(m) cm^{-1} . **¹H-NMR** (400 MHz, CDCl_3): δ 0.03 (s, 6H), 0.88 (s, 9H), 1.20-1.34 (m, 11H), 1.44-1.34 (m, 2H), 1.55-1.44 (m, 2H), 1.75 (s, 3H), 2.18 (q, J = 7.3 Hz, 2H), 3.58 (t, J = 6.6 Hz, 2H), 4.20 (q, J = 7.3 Hz, 2H), 5.77 (d, J = 15.4 Hz, 1H), 5.89 (t, J = 7.3 Hz, 1H), 7.31 (d, J =*

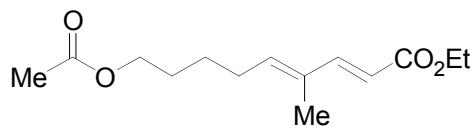
¹ For an earlier citation describing this molecule, see: Kukovinets, O. S.; Zainullin, R. A.; Kasradze, V. G.; Burov, V. N.; Mokrousova, E. P.; Odinokov, V. N.; Tolstikov, G. A. *Agrokhimiya* **1999**, 9, 60-63.

15.4 Hz, 1H). **¹³C-NMR** (100 MHz, CDCl₃): δ 167.5, 149.7, 142.4, 132.7, 115.5, 63.5, 60.3, 33.1, 29.7, 29.6, 29.5, 29.3, 29.1, 26.8, 22.1, 18.7, 14.7, 12.4, -4.9. **HRMS** (TOF MS ES+) *m/z* calcd for C₂₂H₄₃O₃Si: 383.2981. Mass Found: 383.2979.

(2E,4E)-Ethyl 10-(benzyloxy)-4-methyldeca-2,4-dienoate (8d). *Following procedure A, replacing 1-octene with ((hept-6-enyloxy)methyl)benzene (98 mg, 0.48 mmol), and purifying with silica gel chromatography (10:1 hexanes:diethyl ether) afforded a clear oil **8d** (55 mg, 72% yield).*

FTIR (NaCl, thin film) 3040(s), 2936(m), 2857(m), 1718(s), 1273(w), 1280(m), 1182(m) cm⁻¹. **¹H-NMR** (400 MHz, CDCl₃): δ 1.26-1.33 (m, 2H), 1.30 (t, *J* = 7.3 Hz, 3H), 1.36-1.47 (m, 4H), 1.59-1.66 (m, 2H), 1.76 (s, 3H), 2.20 (q, *J* = 7.3 Hz, 2H), 3.39 (t, *J* = 6.6 Hz, 2H), 4.20 (q, *J* = 7.3 Hz, 2H), 4.50 (s, 2H), 5.78 (d, *J* = 15.4 Hz, 1H), 5.88 (t, *J* = 7.3 Hz, 1H), 7.20-7.44 (m, 6H). **¹³C-NMR** (100 MHz, CDCl₃): δ 167.5, 149.6, 142.1, 138.6, 132.9, 128.4, 127.7, 127.6, 115.6, 73.1, 70.4, 60.3, 29.9, 29.2, 29.0, 26.2, 14.7, 12.4. **HRMS** (TOF MS ES+) *m/z* calcd for C₂₀H₂₈O₃Na: 339.1936. Mass Found: 339.1929.

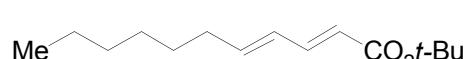
Procedure B: (2E,4E)-Ethyl 9-acetoxy-4-methylnona-2,4-dienoate (8e). A solution of methacrolein



(110 μL, 1.21 mmol), hexenyl acetate (54 μL, 0.34 mmol), and Grubbs' vinylidene catalyst **IV** (14 mg, 0.017 mmol) in CH₂Cl₂ (600 μL) was heated in a sealed vial at 60 °C for 3-4 h, or until deemed complete by ¹H NMR. The vial was

unscrewed, and the solvent was allowed to evaporate for 0.5 h, until an aliquot revealed no remaining methacrolein by ¹H NMR. CH₂Cl₂ (600 μL) and triphenylphosphine (175 mg, 0.670 mmol) were then added to the reaction, a condenser was connected, and ethyl diazoacetate (112 μL, 1.01 mmol) dissolved in CH₂Cl₂ (600 μL) was added slowly over 4 h at reflux. After the addition was complete, the vial was again sealed and heated to 60 °C for 4-8 h. Concentration and silica gel chromatography (3:1 hexanes: diethyl ether) afforded the desired product **8e** as a clear oil (71 mg, 86% yield). **FTIR** (NaCl, thin film) 3093(s), 3040(s), 1751(m), 1712(m), 1228(m) cm⁻¹. **¹H-NMR** (400 MHz, CDCl₃): δ 1.29 (t, *J* = 6.6, 3H), 1.49 (m, 2H), 1.64 (m, 2H), 1.77 (s, 3H), 2.05 (s, 3H), 2.32 (q, *J* = 7.3 Hz, 2H), 4.06 (t, *J* = 6.6 Hz, 2H), 4.20 (q, *J* = 7.3 Hz, 2H), 5.79 (d, *J* = 16.1 Hz, 1H), 5.87 (t, *J* = 7.3 Hz, 1H), 7.31 (d, *J* = 16.1 Hz, 1H). **¹³C-NMR** (100 MHz, CDCl₃) δ 171.1, 167.5, 149.3, 141.6, 133.3, 115.9, 64.4, 60.4, 28.6, 28.5, 25.7, 21.3, 14.6, 12.5. **HRMS** (TOF MS ES+) *m/z* calcd for C₁₄H₂₂O₄Na: 277.1416. Mass Found: 277.1427.

Procedure C: (2E,4E)-*t*-Butyl undeca-2,4-dienoate (8f). A solution of acrolein (112 μL, 1.68 mmol),



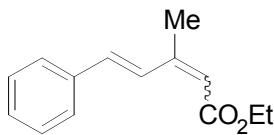
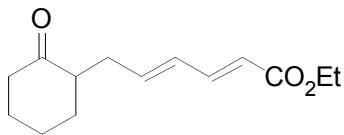
octene (54 μL, 0.34 mmol), and Hoveyda-Grubbs' II (**III**) (10 mg, 0.017 mmol) in CH₂Cl₂ (600 μL) was heated in a

sealed vial at 60 °C for 32 h, or until deemed complete by thin layer chromatography. The vial was unscrewed, and the solvent was allowed to evaporate for 0.5 h, until aliquot revealed no remaining acrolein

by $^1\text{H-NMR}$. CH_2Cl_2 (600 μL) and triphenylphosphine (175 mg, 0.670 mmol) were then added to the reaction, a condenser was connected, and *t*-butyl diazoacetate (140 μL , 1.01 mmol) dissolved in CH_2Cl_2 (600 μL) was added slowly over 4 h at reflux. After the addition was complete, the vial was again sealed and heated to 60 $^{\circ}\text{C}$ for 4-8 h. Concentration and silica gel chromatography (50:1 hexanes: diethyl ether) afforded the desired product **8f** as a clear oil (47 mg, 59% yield). **FTIR** (NaCl, thin film) 3034(m), 2923(s), 2864(w), 1705(s), 1653(m), 1372(m), 1136(s), 998(m) cm^{-1} . **$^1\text{H-NMR}$** (400 MHz, CDCl_3): δ 0.87 (t, J = 7.3 Hz, 3H), 1.20-1.40 (m, 8H), 1.47 (s, 9H), 2.14 (q, J = 7.3 Hz, 2H), 5.70 (d, J = 15.4 Hz, 1H), 6.00-6.25 (m, 2H), 7.15 (dd, J = 15.4, 10.3 Hz, 1H). **$^{13}\text{C-NMR}$** (100 MHz, CDCl_3): δ 166.6, 144.1, 144.0, 128.4, 121.2, 80.1, 33.2, 31.9, 29.1, 29.0, 28.5, 22.9, 14.4. **HRMS** (EI $^+$) m/z calcd for $\text{C}_{15}\text{H}_{26}\text{O}_2$: 238.1933. Mass Found: 238.1930.

(2E,4E)-Ethyl 6-(2-oxocyclohexyl)hexa-2,4-dienoate (8g). Following procedure C, replacing *t*-butyl diazoacetate and 1-octene with ethyl diazoacetates (81 μL , 0.726 mmol) and 97% 2-allylcyclohexanone (50 μL , 0.325 mmol) respectively, and purifying with silica gel chromatography (10:1 hexanes:diethyl ether) afforded a clear oil **8g** (50 mg, 63% yield). **FTIR** (NaCl, thin film) 3047(m), 2942(m), 2870(m), 1712(s), 1640(m), 1247(m), 1129(m) cm^{-1} . **$^1\text{H-NMR}$** (400 MHz, CDCl_3): δ 1.00-1.50 (m, 2H), 1.26 (t, J = 7.3 Hz, 2H), 1.75-1.95 (m, 2H), 1.95-2.21 (m, 2H), 2.21-2.47 (m, 3H), 2.60 (dt, J = 14.6, 5.8 Hz 1H), 4.17 (q, J = 7.3 Hz, 2H), 5.77 (d, J = 15.4 Hz, 1H), 6.06 (dt, J = 15.4, 7.3 Hz, 1H), 6.15 (dd, J = 15.4, 11.0 Hz, 1H), 7.18-7.24 (dd, J = 15.4, 10.3 Hz, 1H). **$^{13}\text{C-NMR}$** (100 MHz, CDCl_3): δ 211.6, 167.1, 144.6, 141.8, 130.1, 119.8, 60.4, 50.5, 42.3, 33.9, 33.2, 28.2, 25.4, 14.6. **HRMS** (TOF MS ES $^+$) m/z calcd for $\text{C}_{14}\text{H}_{20}\text{O}_3\text{Na}$: 259.1310. Mass Found: 259.1317.

Procedure D: (4E)-Ethyl 3-methyl-5-phenylpenta-2,4-dienoate (9) and stereoisomer (9b) A solution of methyl vinyl ketone (20 μL , 0.24 mmol), styrene (80 μL , 0.66 mmol), and Grubbs' vinylidene catalyst (**IV**) (13 mg, 0.016 mmol) in toluene (1.2 mL) was heated in a sealed vial at 50 $^{\circ}\text{C}$ for 10-12 h, or until deemed complete by ^1H NMR. Triphenylphosphine (345 mg, 1.32 mmol) and benzoic acid (20 mg, 0.14 mmol) were then added to the reaction. Ethyl diazoacetate (140 μL , 1.01 mmol) was added slowly over 10 h at 90 $^{\circ}\text{C}$, and the reaction was held at this temperature for another 20 h. Concentration and silica gel chromatography (20:1 hexanes:diethyl ether) afforded the desired products **9** and **9b** as a mixture of cis/trans isomers (37 mg, 71% yield). **9:** **$^1\text{H-NMR}$** (400 MHz, CDCl_3): δ 8.42 (d, J = 16.8 Hz, 1H), 7.22-7.62 (m, aromatic), 6.92 (d, J = 16.1 Hz, 1H), 5.75 (s, 1H), 4.20 (q, J = 7.3 Hz, 2H), 2.13 (s, 3H), 1.32 (t, J = 7.3 Hz, 2H). **9b:** 7.22-7.62 (m, aromatic), 6.94 (d, J = 16.1 Hz, 1H), 6.81 (d, J = 16.1 Hz, 1H), 5.91 (s, 1H), 4.20 (q, J = 7.3 Hz, 2H), 2.41 (s, 3H), 1.32 (t, J = 7.3 Hz, 2H). *E/Z ratio was determined by $^1\text{H NMR}$*



integration of the methyl groups (2.13 ppm vs. 2.41 ppm), and the configuration is determined by comparison to known data.²

² Lee, M.; Chen, Y.; Zhang, X. P. *Organometallics*, **2003**, *22*, 4905-4909.

