Supplementary Material (ESI) for Chemical Communications

Two-Directional Ring-Opening Cross-Metathesis

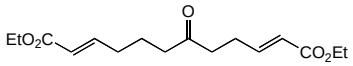
Stephen J. Roe, Jean-Christophe Legeay, Diane Robbins, Pooja Aggarwal, and

Robert A. Stockman*

Supplementary Information

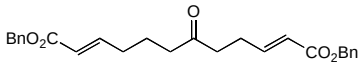
Experimental details

6-Oxododeca-2,10-dienedioic acid diethyl ester.



To a solution of cyclooct-4-en-1-one (97 mg, 0.78 mmol) in 10.0 mL of CH_2Cl_2 was added ethyl acrylate (0.51 mL, 4.68 mmol) and 2.5 mol % of Hoveyda-Grubbs second generation catalyst (12 mg, 0.020 mmol). The mixture was stirred at rt for 1 day. An additional 2.5 mol % of Hoveyda-Grubbs II catalyst was added. The resulting mixture was stirred for 1 day and was then concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (20% EtOAc/petroleum ether) to yield unsymmetrical diester **2** (179 mg, 77%) as a yellow oil. IR (thin film) cm^{-1} 2361, 1716, 1657, 1367, 1272, 1177, 1040; δ_H (400 MHz, $CDCl_3$) 6.91-6.83 (m, 2H), 5.78 (2H, dd, *J* 15.6, 1.6), 4.13 (4H, qd, *J* 7.2, 3.6), 2.53 (2H, t, *J* 7.2), 2.42 (4H, q, *J* 7.6), 2.17 (2H, dq, *J* 7.6, 1.2), 1.72 (q, *J* 7.6), 1.24 (dt, *J* 7.2, 3.6); δ_C (75 MHz, $CDCl_3$) 208.1, 166.4, 166.3, 147.8, 147.0, 122.1, 122.0, 60.2, 41.7, 40.6, 31.3, 25.9, 21.8, 14.2; *m/z* (ESI) 319 (M+23, 100%), 314 (1), 297 (1); Found: 319.1521. $C_{16}H_{24}O_5$ ($M+Na^+$) Requires 319.1516.

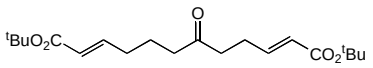
(2*E*,10*E*)-Dibenzyl 6-oxododeca-2,10-dienedioate



To a solution of cyclooct-4-en-1-one (51.1 mg, 0.41 mmol) in dichloromethane (4 mL) was added sequentially benzyl acrylate (406.9 mg, 2.50 mmol) and Hoveyda-Grubbs second generation catalyst (6.5 mg, 0.01 mmol). The mixture was stirred at room temperature for 24 hours. More catalyst (6.5 mg, 0.01 mmol) was then added and the reaction was stirred for further 24 hours. Then the solvent was evaporated and the

resulting brown oil was purified by column chromatography on silica, using a mixture of petroleum ether and ethyl acetate (8:2) as eluent, to afford (2*E*,10*E*)-dibenzyl 6-oxododeca-2,10-dienedioate (122.0 mg, 72 %) as a yellow oil. $\nu_{max}(CH_2Cl_2/cm^{-1})$ 1712, 1654, 1265, 1165; δ_H(300 MHz; $CDCl_3$) 1.75 (2H, quint, *J* 7.2), 2.21 (2H, dq, *J* 7.2 and *J* 1.4), 2.41-2.58 (6H, m), 5.16 (2H, s), 5.17 (2H, s), 5.87 (2H, dq, *J* 15.7 and *J* 1.5), 6.96 (2H, m), 7.36 (10H, m); δ_C(75 MHz, $CDCl_3$) 21.6, 25.8, 31.3, 40.5, 41.6, 67.0 , 121.6, 121.7, 128.1, 128.4, 135.9, 135.94, 147.7, 148.5, 166.0, 166.1, 207.9 .*m*/*z* (ESI) 443.1825 (($[M+Na]^+$. $C_{26}H_{28}NaO_5$ requires 443.1834).

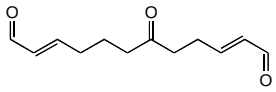
(2*E*,10*E*)-Di-*tert*-butyl 6-oxododeca-2,10-dienedioate



To a solution of `cyclooct-4-en-1-one` (46 mg, 0.37 mmol) in 4.0 mL of CH_2Cl_2 was added *t*-butyl acrylate (0.32 mL, 2.22 mmol) and 2.5 mol% of Hoveyda-Grubbs second generation catalyst (6 mg, 0.0093 mmol). The mixture was stirred at rt for 1 d. An additional 2.5 mol% of Hoveyda-Grubbs second generation catalyst was added. The resulting mixture was stirred for 2 d and was then concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (20% EtOAc/petroleum ether) to afford the product (77 mg, 60%) as a clear oil. IR (thin film) cm^{-1} 2978, 2934, 1713, 1654, 1457, 1392, 1368, 1291, 1256, 1155, 981, 851; δ_H (300 MHz, $CDCl_3$) 6.81-6.70 (2H, m), 5.72 (1H, q, *J* 1.5), 5.67 (1H, q, *J* 1.5), 2.51 (2H, t, *J* 6.6), 2.39 (4H, t, *J* 7.2), 2.13 (2H, dq, *J* 7.2, 1.5), 1.70 (2H, quint, *J* 7.2), 1.42 (18H, d, *J* 2.4); δ_C (75 MHz, $CDCl_3$) 208.3, 165.8, 146.6, 145.7, 123.8, 80.1, 41.7, 40.7, 31.2, 28.1, 25.7, 21.9; m/z

(ESI) 375 (M+23, 100%), 370 (3), 353 (1); Found: 375.2147. $C_{20}H_{32}O_5$ ($M+Na^+$) Requires 375.2142.

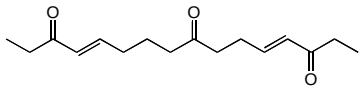
(2*E*,10*E*)-6-Oxododeca-2,10-dienedial



To a solution of `cyclooct-4-en-1-one` (45.2 mg, 0.36 mmol) in dichloromethane (4 mL)

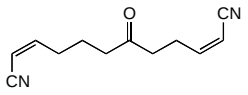
was added sequentially acrolein (0.154 mL, 2.19 mmol) and Hoveyda-Grubbs second generation catalyst (6 mg, 0.01 mmol). The mixture was stirred at room temperature for 24 hours. More catalyst (6 mg, 0.01 mmol) was then added and the reaction was stirred for further 24 hours. Then the solvent was evaporated and the resulting brown oil was purified by column chromatography on silica, using a mixture of petroleum ether and ethyl acetate (8:2) as eluent, to afford (2*E*,10*E*)-6-oxododeca-2,10-dienedial (22.4 mg, 30%) as a brown oil $\nu_{max}(CH_2Cl_2/cm^{-1})$ 2358, 1685, 1266, 1134 and 974; δ_H(300 MHz; $CDCl_3$) 1.83 (2H, quint, *J* 7.2), 2.32-2.52 (4H, m), 2.63 (4H, m), 6.10 (2H, m), 6.83 (2H, m), 9.49 (1H, d, *J* 5.1), 9.52 (1H, d, *J* 5.1); δ_C(75 MHz, $CDCl_3$) 207.6, 193.8, 193.7, 157.0, 156.2, 133.4, 133.3, 41.6, 40.4, 31,9, 26.3, 21.5.*m*/*z* (ESI) 231.0993 (($[M+Na]_+$. $C_{12}H_{16}NaO_3$ requires 231.0992).

Hexadeca-4,12-diene-3,8,14-trione



To a solution of cyclooct-4-en-1-one (52 mg, 0.42 mmol) in 4.0 mL of CH_2Cl_2 was added pentenone (0.25 mL, 2.51 mmol) and 2.5 mol % of Hoveyda-Grubbs second generation catalyst (7 mg, 0.010 mmol). The mixture was stirred at rt for 1 d. An additional 2.5 mol % of Hoveyda-Grubbs II catalyst was added. The resulting mixture was stirred for 2 d and was then concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (20-100% EtOAc/petroleum ether gradient) to afford unsymmetrical trione **5** (98 mg, 89%) as a dark brown oil. IR (thin film) cm^{-1} 2976, 2939, 1713, 1672, 1630, 1459, 1413, 1360, 1201, 1125, 980, 845; δ_H (300 MHz, $CDCl_3$) 6.76-6.65 (2H, m), 6.01 (2H, dd, *J* 15.9, 1.5), 2.56-2.29 (10H, m), 2.14 (2H, dq, *J* 7.2, 1.2), 1.68 (2H, quint, *J* 7.2), 1.04-0.93 (6H, m); δ_C (75 MHz, $CDCl_3$) 208.3, 200.9, 200.7, 145.6, 144.8, 130.5, 130.4, 41.7, 40.6, 35.8, 33.2, 31.5, 26.0, 21.8, 19.0, 8.0; LRMS: m/z (ESI) 287 (M+23, 100%), 265 (17), 282 (1); HRMS: Found: 282.2079. $C_{16}H_{24}O_3$ ($M+NH_4^+$) Requires 282.2064.

6-Oxododeca-2,10-dienedinitrile



To a solution of cyclooct-4-en-1-one (35.0 mg, 0.28 mmol) in dichloromethane (2.8 mL)

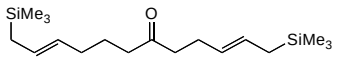
was added sequentially acrylonitrile (0.06 mL, 0.91 mmol) and Hoveyda-Grubbs second generation catalyst (8 mg, 0.013 mmol). The mixture was stirred at 140°C under microwave irradiation for 2 hours. More catalyst (8 mg, 0.013 mmol) was then added and

the reaction was stirred at 120°C under microwave irradiation for further 2 hours. Then the solvent was evaporated and the resulting brown oil was purified by column chromatography on silica, using a mixture of petroleum ether and ethyl acetate (1:1) as eluent, to afford a mixture of isomer (cis-cis, cis-trans, trans-cis : 2/1/1) of 6-oxododeca-2,10-dienedinitrile (41.6 mg, 73%) as a brown oil.ν_{max}(CH_2Cl_2/cm^{-1}) 2933, 2222, 1713, 1622, 1412, 1374 and 1106; (mixture of isomers)δ_H(300 MHz; $CDCl_3$) 1.78 (2H, m), 2.39-2.70 (8H, m), 5.32-5.39 (2H, m), 6.42-6.73 (2H, m). *m*/*z* (ESI) 225.0996 (([M+Na]$^+$. $C_{12}H_{14}N_2NaO_1$ requires 225.0998).

(2Z,10Z)-6-oxododeca-2,10-dienedinitrile (major isomer) :

δ_H(300 MHz; $CDCl_3$) 1.57 (2H, quint, *J* 7.3), 2.29-2.18 (4H, m), 2.48-5.35 (4H, m), 5.13 (2H, m, *J* 10.9 and 3.0), 6.35-6.20 (2H, m, *J* 10.9). δ_C(75 MHz, $CDCl_3$) 207.4, 155.7, 153.8, 153.2, 115.6, 100.34, 100.30, 41.2, 40.6, 31.0, 25.6, 21.7.*m*/*z* (ESI) 225.0996 (([M+Na]$^+$. $C_{12}H_{14}N_2NaO_1$ requires 225.0998).

1,12-Bis(trimethylsilanyl)-dodeca-2,10-dien-6-one



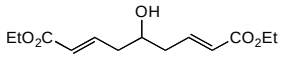
To a solution of `cyclooct-4-en-1-one` (45 mg, 0.36 mmol) in 3.6 mL of CH_2Cl_2 was added

allyltrimethyl silane (0.69 mL, 4.32 mmol) and 2.5 mol % of Hoveyda-Grubbs second generation catalyst(6 mg, 0.0091 mmol). The mixture was stirred at rt for 1 day. An additional 2.5 mol % of Hoveyda-Grubbs second generation catalyst was added. The resulting mixture was stirred for 1 day

and was then concentrated *in vacuo*. The residue was purified by flash column

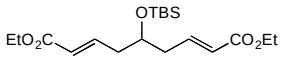
chromatography on silica gel (10% EtOAc/petroleum ether) to afford unsymmetrical dienone product (16 mg, 14%) as a clear oil. IR (thin film) cm^{-1} 3008, 2954, 2096, 1716, 1659, 1598, 1484, 1409, 1368, 1291, 1248, 1154, 1093, 966, 855; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.35-5.22 (2H, m), 5.14-5.03 (2H, m), 2.29 (4H, dquint, *J* 7.2, 2.7), 2.14 (2H, q, *J* 6.9), 1.98-1.83 (2H, m), 1.62-1.45 (2H, m), 1.38-1.22 (4H, m), -0.11--0.14 (18H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.9, 127.8, 127.2, 126.6, 125.5, 43.2, 42.8, 42.3, 42.1, 33.1, 32.2, 27.1, 26.4, 23.8, 22.6, 21.5, 18.5, -1.9; LRMS: m/z (ESI) 347 (M+23, 100%), 325 (92), 342 (6); HRMS: Found: 347.2187. $C_{18}H_{36}OSi_2$ ($M+Na^+$) Requires 347.2197.

1,9-diethyl(2*E*,7*E*)-5-hydroxynona-2,7-dienedioate



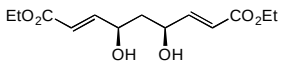
To a solution of cyclopent-3-en-1-ol (65.5 mg, 0.78 mmol) in 10.0 mL of CH_2Cl_2 was added ethyl acrylate (0.51 mL, 4.68 mmol) and 2.5 mol % of Hoveyda-Grubbs second generation catalyst(12 mg, 0.020 mmol). The mixture was stirred at rt for 1 day. An additional 2.5 mol % of Hoveyda-Grubbs second generation catalyst was added. The resulting mixture was stirred for 2 days and was then concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (20% EtOAc/petroleum ether) to yield the product (40 mg, 20%) as a yellow oil. ν_{max} (thin film)/cm^{-1} 3473, 2982, 2937, 2906, 1718, 1654, 1269, 1096, 1042; δ_H (300 MHz, $CDCl_3$) 6.81 (2H, dt, *J* 15.5 and 7.4), 5.76 (2H, dt, *J* 15.5 and 1.4), 4.04 (4H, q, *J* 7.1), 3.82 – 3.73 (1H, m), 2.25 (4H, m), 2.11 (1H, d, *J* 4.5), 1.14 (6H, t, *J* 7.1); δ_C (75MHz, $CDCl_3$) 166.1, 144.2, 124.2, 68.9, 60.2, 39.6, 14.1; *m/z* (ES) 279 (M+23 100%), 257 (M+1, 1%), 274 (M+18 0.2%); HRMS: Found: 279.1225. $C_{13}H_{20}O_5Na$ ($M+Na^+$) Requires 279.1208.

1,9-diethyl(2*E*,7*E*)-5-[*tert*-butyldimethylsilyl)oxy]nona-2,7-dienedioate



To a solution of 1-(*tert*butyldimethylsilyloxy)-cyclopent-3-ene (155 mg, 0.78 mmol) in 10.0 mL of CH_2Cl_2 was added ethyl acrylate (0.51 mL, 4.68 mmol) and 2.5 mol % of Hoveyda-Grubbs second generation catalyst (12 mg, 0.020 mmol). The mixture was stirred at rt for 1 day. An additional 2.5 mol % of Hoveyda-Grubbs second generation catalyst was added. The resulting mixture was stirred for 1 days and was then concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (20% EtOAc/petroleum ether) to yield the product (191 mg, 66%) as a colourless oil. ν_{max} (thin film)/cm^{-1} 3583, 2955, 2931, 2857, 1722, 1656, 1263, 1175, 1096, 1044; δ_H (300 MHz, $CDCl_3$) 6.77 (2H, dt, *J* 15.4 and 7.5), 5.69 (2H, dt, *J* 15.4 and 1.4), 4.04 (4H, q, *J* 7.1), 3.79 – 3.71 (1H, m), 2.20 (4H, ddt, *J* 7.5, 6.1 and 1.4), 1.13 (6H, t, *J* 7.1), 0.73 (9H, s,), -0.11 (6H, s); δ_C (75MHz, $CDCl_3$) 166.1, 144.7, 123.7, 70.1, 60.1, 39.9, 25.6, 17.9, 14.1, -4.8; *m/z* (ES) 393 (M+23, 100 %), 371 (M+1, 2 %), 388 (M+18, 1 %) HRMS: Found: 393.2060. $C_{19}H_{34}O_5{}^{28}SiNa$ ($M+Na^+$) Requires 393.2073.

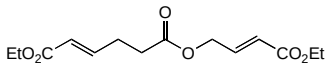
4,6-Dihydroxynona-2,7-dienedioic acid diethyl ester



To a solution of the *cis*-1,3-dihydroxycyclopent-4-ene (100 mg, 0.999 mmol) in DCM (5

mL) under argon was added ethyl acrylate (0.65 mL, 6.00 mmol), followed by Hoveyda-Grubbs second generation catalyst (2.5 mol%). The solution was stirred at ambient temperature for 24 hours then additional catalyst (2.5 mol%) was added. The reaction was stirred for a further 65 hours after which the reaction was concentrated *in vacuo*. Purification by column chromatography over silica gel (eluting with 1:1 ethyl acetate / hexane) gave the *product* (140 mg, 52%) as an amorphous beige foam; M.p. 73-75 °C; R_f 0.23 (1:1 ethyl acetate / hexane); ν_{max} (neat)/cm^{-1} 3442 (alcohol), 1710 (ester), 1659 (olefin); δ_H (400 MHz, $CDCl_3$) 6.86 (2H, dd, *J* 15.6 and 4.4), 6.01 (2H, d, *J* 15.6), 4.57-4.49 (2H, m), 4.18-4.15 (2H, m), 4.14 (4H, q, *J* 7.1), 1.80 (1H, d, *J* 14.3), 1.66 (1H, dt, *J* 14.4 and 9.5), 1.24 (6H, t, *J* 7.1); δ_C (101 MHz, $CDCl_3$) 166.6 , 149.0, 120.3, 70.5, 60.6, 41.3, 14.0; *m/z* (ES) 290.2 ($M+H_2O^+$, 98%), 273.2 ($M+H^+$, 100), 127.0 (90); HRMS: Found 273.1333. $C_{13}H_{21}O_6$ ($M+H^+$) Requires 273.1333.

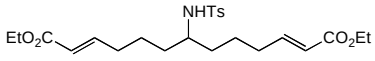
(2*E*)-(*E*)-3-(ethoxycarbonyl)allyl ethyl hex-2-enedioate



To a solution of (*Z*)-3,4-dihydrooxepin-2(7H)-one (56.5 mg, 0.50 mmol) in dichloromethane (5 mL) was added sequentially ethyl acrylate (0.330 mL, 3.03 mmol) and Hoveyda-Grubbs second generation catalyst (8 mg, 0.013 mmol). The mixture was stirred at room temperature for 24 hours. More catalyst (8 mg, 0.013 mmol) was then added and the reaction was stirred for further 48 hours. Then the solvent was evaporated and the resulting brown oil was purified by column chromatography on silica, using a mixture of petroleum ether and ethyl acetate (8:2) as eluent, to afford (2*E*)-(*E*)-3-(ethoxycarbonyl)allyl ethyl hex-2-enedioate (72.0 mg, 50%) as a clear oil. ν_{max}(CH_2Cl_2/cm^{-1}) 2926, 1718, 1654, 1465, 1263, 1178 and 1042; δ_H (300 MHz; $CDCl_3$)

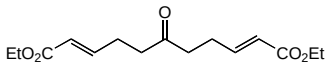
1.28 (6H, m), 2.55 (4H, m), 4.12 (2H, q, *J* 7.1), 4.2 (2H, q, *J* 7.1), 4.76 (2H, dd, *J* 4.7 and *J* 1.9), 5.86 (1H, d, *J* 15.6), 6.01 (1H, dt, *J* 15.7 and 1.9), 6.93 (2H, m); δ_C (75 MHz, $CDCl_3$) 171.5, 166.2, 165.6, 146.1, 140.8, 122.5, 122.4, 62.7, 60.6, 60.3, 32.2, 27.0, 14.3, 14.2 .*m*/*z* (ESI) 307.1160 (([M+Na]+. $C_{14}H_{20}NaO_6$ requires 307.1152).

6-(Toluene-4'-sulfonylamino)undeca-2,9-dienedioic acid diethyl ester



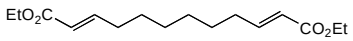
To a solution of the 1-(toluene-4'-sulfonylamino)-cyclohep-4-ene (100 mg, 0.377 mmol) in DCM (5 mL) under argon was added ethyl acrylate (0.25 mL, 2.26 mmol), followed by Hoveyda-Grubbs second generation catalyst (2.5 mol%). The solution was stirred at ambient temperature for 24 hours then additional catalyst (2.5 mol%) was added. The reaction was stirred for a further 24 hours after which the reaction was concentrated *in vacuo* and purification by column chromatography over silica gel (eluting with 1:3 ethyl acetate / hexane) gave the *product* (130 mg, 79%) as a colourless oil; R_f 0.18 (1:2 ethyl acetate / hexane); ν_{max} (thin film)/cm^{-1} 3277 (N-H), 1717 (ester), 1653 (olefin); δ_H (400 MHz, $CDCl_3$) 7.68 (2H, d, *J* 7.9), 7.23 (2H, d, *J* 7.9), 6.69 (2H, dt, *J* 15.7 and 6.7), 5.58 (2H, d, *J* 15.7), 5.39 (1H, d, *J* 8.2), 4.09 (4H, q, *J* 7.1), 3.22-3.11 (1H, m), 2.35 (3H, s), 2.13-1.91 (4H, m), 1.54-1.31 (4H, m), 1.20 (6H, t, *J* 7.1); δ_C (101 MHz, $CDCl_3$) 66.3, 147.5, 143.4, 138.0, 129.6, 126.8, 121.7, 60.1, 52.9, 33.2, 27.8, 21.3, 14.1; *m/z* (CI) 455.2 ($M+NH_4^+$, 6%), 108.1 (100); HRMS: Found 455.2211. $C_{22}H_{35}N_2O_6S$ ($M+NH_4^+$) Requires 455.2210.

Diethyl (2*E*,9*E*)-6-oaxoundeca-2,9-dienedioate



To a solution of (Z)-cyclohept-4-enone (31.1 mg, 0.31 mmol) in dichloromethane (3 mL) was added sequentially ethyl acrylate (0.205 mL, 1.88 mmol) and Hoveyda-Grubbs second generation catalyst (5 mg, 0.008 mmol). The mixture was stirred at room temperature for 24 hours. More catalyst (5 mg, 0.008 mmol) was then added and the reaction was stirred for further 24 hours. Then the solvent was evaporated and the resulting brown oil was purified by column chromatography on silica, using a mixture of petroleum ether and ethyl acetate (8:2) as eluent, to afford Diethyl (2*E*,9*E*)-6-oaxoundeca-2,9-dienedioate (54.8 mg, 63%) as a clear oil ν_{max}(CH_2Cl_2/cm^{-1}) 2983, 2906, 1710, 1654, 1312, 1176 and 1040; δ_H(400 MHz; $CDCl_3$) 1.28 (6H, t, *J* 7.1), 2.48 (4H, m), 2.58 (4H, t), 4.18 (4H, q, *J* 7.1), 5.82 (2H, dt, *J* 15.7 and 1.6), 6.91 (2H, dt, *J* 15.6 and 6.7); δ_C(101 MHz, $CDCl_3$) 206.8, 166.2, 146.8, 122.2, 60.2, 40.5, 25.8, 14.1.*m*/*z* (ESI) 305.1360 ($[M+Na]^+$. $C_{15}H_{22}NaO_5$ requires 305.1359).

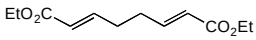
Dodeca-2,10-dienedioic acid diethyl ester



To a solution of the cyclooctene (100 mg, 0.907 mmol) in DCM (5 mL) under argon was added ethyl acrylate (0.59 mL, 5.44 mmol), followed by Hoveyda-Grubbs second generation catalyst (2.5 mol%). The solution was stirred at ambient temperature for 24 hours then additional catalyst (2.5 mol%) was added. The reaction was stirred for a further 65 hours after which the reaction was concentrated *in vacuo* and purification by column chromatography over silica gel (eluting with 1:9 ethyl acetate / hexane) gave the

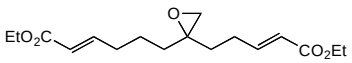
product (189 mg, 74%) as a colourless oil; R_f 0.42 (1:3 ethyl acetate / hexane); ν_{max} (thin film)/cm^{-1} 1717 (ester), 1653 (olefin); δ_H (400 MHz, $CDCl_3$) 6.86 (2H, dt, *J* 15.6 and 7.0), 5.71 (2H, dd, *J* 15.6 and 1.4), 4.08 (4H, q, *J* 7.1), 2.10 (4H, dt, *J* 7.0 and 7.3), 1.41-1.31 (4H, m), 1.27-1.21 (4H, m), 1.19 (6H, t, *J* 7.1); δ_C (101 MHz, $CDCl_3$) 166.4, 148.9, 121.1, 59.8, 31.9, 28.6, 27.7, 14.0; *m/z* (CI) 300.3 ($M+NH_4^+$, 21%), 282.2 ($M+H^+$, 100); Found 283.1901. $C_{16}H_{27}O_4$ ($M+H^+$) Requires 283.1904.

Octa-2,6-dienedioic acid diethyl ester



To a solution of the cyclooca-1,4-diene (100 mg, 0.924 mmol) in DCM (5 mL) under argon was added ethyl acrylate (1.21 mL, 11.1 mmol), followed by Hoveyda-Grubbs second generation catalyst (2.5 mol%). The solution was stirred at ambient temperature for 24 hours then additional catalyst (2.5 mol%) was added. The reaction was stirred for a further 65 hours after which the reaction was concentrated *in vacuo* and purification by column chromatography over silica gel (eluting with 1:5 ethyl acetate / hexane) gave the product (300 mg, 72%) as a colourless oil; R_f 0.33 (1:3 ethyl acetate / hexane); δ_H (400 MHz, $CDCl_3$) 6.89 (2H, dt, *J* 15.7 and 6.6), 5.81 (2H, d, *J* 15.7), 4.14 (4H, q, *J* 7.1), 2.33 (4H, d, *J* 6.6), 1.24 (6H, t, *J* 7.1). Other data matched the literature: T. R. Hoye, L. C. Kopel, and T. D. Ryba, *Synthesis*, 2006, 1572.

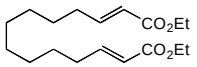
6-[2-(4-Ethoxycarbonyl-but-3-enyl)-oxiranyl]-hex-2-enoic acid ethyl ester



To a solution of (*Z*)-1-oxaspiro[2.7]dec-6-ene (28 mg, 0.20 mmol) in 3.0 mL of CH_2Cl_2 was added ethyl acrylate (0.13 mL, 1.22 mmol) and 2.5 mol % of Hoveyda-Grubbs

second generation catalyst (3 mg, 0.0051 mmol). The mixture was stirred at rt for 1 day. An additional 2.5 mol % of Hoveyda-Grubbs II catalyst was added. The resulting mixture was stirred for 1 day and was then concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (20% EtOAc/petroleum ether) to afford unsymmetrical epoxide product (42 mg, 67%) as a clear oil. IR (thin film) cm^{-1} 2982, 2940, 2870, 1719, 1655, 1447, 1392, 1368, 1313, 1269, 1187, 1095, 1043, 979, 857, 711; δ_H (300 MHz, $CDCl_3$) 6.98-6.87 (2H, m), 5.85 (1H, quint, *J* 1.5), 5.80 (1H, quint, *J* 1.5), 4.11 (4H, q, *J* 7.2), 2.60 (2H, s), 2.29-2.18 (4H, m), 1.83-1.46 (6H, m), 1.25 (6H, t, *J* 7.2); δ_C (75 MHz, $CDCl_3$) 171.1, 166.5, 148.1, 147.8, 121.8, 60.3, 58.4, 53.4, 52.1, 33.6, 32.2, 27.3, 23.2, 21.0, 14.2; m/z (ESI) 333 (M+23, 100%), 311 (13), 328 (6); Found: 333.1690. $C_{17}H_{26}O_5$ ($M+Na^+$) Requires 333.1672.

(2*E*,12*E*)-diethyl tetradeca-2,12-dienedioate



To a solution of (E)-cyclodecene (70.3 mg, 0.51 mmol) in dichloromethane (5 mL) was added sequentially ethyl acrylate (0.335 mL, 3.07 mmol) and Hoveyda-Grubbs second generation catalyst (8 mg, 0.01 mmol). The mixture was stirred at room temperature for 24 hours. More catalyst (8 mg, 0.01 mmol) was then added and the reaction was stirred for further 24 hours. Then the solvent was evaporated and the resulting brown oil was purified by column chromatography on silica, using a mixture of petroleum ether and ethyl acetate (8:2) as eluent, to afford (2*E*,12*E*)-diethyl tetradeca-2,12-dienedioate (91.6 mg, 58%) as a clear oil $\nu_{max}(CH_2Cl_2/cm^{-1})$ 2931, 2854, 1719, 1654, 1266 and 1180; δ_H(300 MHz; $CDCl_3$) 1.29 (6H, t, *J* 7.1), 1.47-1.83 (12 H, m), 2.2 (4H, qd, *J* 7.0 and *J*

1.5), 4.18 (4H, q, *J* 7.1), 5.80 (2H, dt, *J* 15.6 and *J* 1.6), 7.00 (2H, dt, *J* 15.6 and *J* 7.0); δ_C(75 MHz, $CDCl_3$) 166.7, 149.3, 121.2, 60.1, 32.1, 29.2, 29.0, 27.9, 14.2,.*m*/z (ESI) 333.2045 (($[M+Na]^+$. $C_{18}H_{30}NaO_4$ requires 333.2042).