

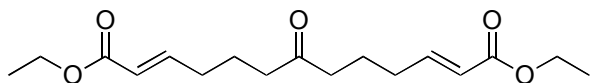
Two-Directional Cross-Metathesis

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Supplementary Information

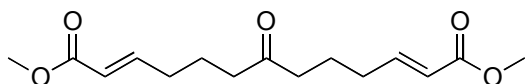
Experimental details

(2E,11E)-diethyl 7-oxotrideca-2,11-dienedioate.



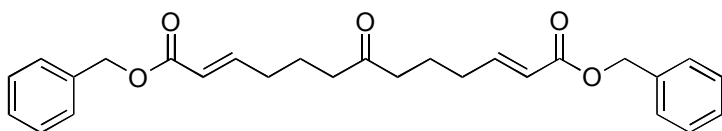
To a solution of undeca-1,10-dien-6-one (0.60 mmol, 0.10 g, 1 eq) in dichloromethane (5 mL) under Ar, was added ethyl acrylate (3.61 mmol, 0.36g, 6 eq), followed by Hoveyda-Grubbs 2nd generation catalyst (0.015 mmol, 9 mg, 2.5 mol%) as a solid. The solution was stirred for 24 h, at which time another portion of catalyst (0.015 mmol, 0.009g, 2.5 mol%) was added. The solution stirred for a further 72 h, concentrated, and purification by column chromatography (eluting with 6:1 PE/EA) gave the product as a clear oil (0.54 mmol, 168 mg, 90%): δ_{H} (400 MHz, CDCl_3) 6.85 (1H, dt, J 6.9, 15.6), 5.77 (1H, d, J 15.6), 4.13 (2H, q, J 7.1), 2.37 (2H, t, J 7.3), 2.15 (2H, q, J 7.1), 1.69 (2H, p, J 7.3), 1.23 (3H, t, J 7.1); δ_{C} (100 MHz, CDCl_3) 210, 167, 148, 122, 60, 42, 32, 22, 14; IR (thin film, ν/cm^{-1}) C=O 1712; HRMS calculated for $\text{C}_{17}\text{H}_{30}\text{NO}_5$ ($\text{M}+\text{NH}_4$) 328.2118, found 328.2117.

(2E,11E)-Dimethyl 7-oxotrideca-2,11-dienedioate



To a solution of undeca-1,10-dien-6-one (6.02 mmol, 1.0 g, 1 eq) in dichloromethane (100 mL) under N_2 , was added methyl acrylate (36.1 mmol, 3.12 g, 6 eq), followed by Hoveyda-Grubbs 2nd generation catalyst (0.15 mmol, 94 mg, 2.5 mol%) as a solid. The solution was stirred for 24 h, at which time another portion of catalyst (0.15 mmol, 94 mg, 2.5 mol%) was added. The solution stirred for a further 72 h, concentrated, and purification by column chromatography (over SiO_2 eluting with 5:1 H/EA) gave the product as a clear oil (4.48 mmol, 1.27 g, 78%): R_f 0.20 in 3:1 H/EA; δ_{H} (400 MHz, CDCl_3) 6.92 (2H, dt, J 7.0 and 15.7), 5.83 (2H, dt, J 1.5 and 15.7), 3.73 (6H, s), 2.42 (4H, t, J 7.3), 2.21 (4H, ddd, J 1.5, 7.0 and 7.3), 1.75 (4H, p, J 7.3); δ_{C} (125 MHz, CDCl_3) 209, 166, 148, 122, 51, 42, 31, 22; IR (thin film, ν/cm^{-1}) C=O 1716; HRMS calculated for $\text{C}_{15}\text{H}_{23}\text{O}_5$ ($\text{M}+\text{H}$) 283.1545, found 283.1573.

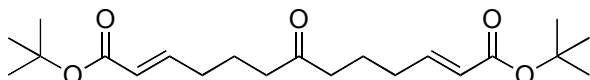
(2E,11E)-Dibenzyl 7-oxotrideca-2,11-dienedioate



To a solution of undeca-1,10-dien-6-one (1.20 mmol, 200 mg, 1 eq) in dichloromethane (20 mL) under N_2 , was added benzyl acrylate (7.22 mmol, 1.171 g, 6 eq), followed by Hoveyda-Grubbs 2nd generation catalyst (0.03 mmol, 19 mg, 2.5 mol%) as a solid. The solution was stirred for 24 h, at which time another portion of catalyst (0.03 mmol, 19 mg, 2.5 mol%) was added. The solution stirred for a further 72 h, concentrated, and purification by column chromatography (over SiO_2 eluting with 3:1 H / EA) gave the product as a clear oil (1.02 mmol, 443 mg, 85%) R_f 0.24 in 3:1 H / EA; δ_{H} (400 MHz, CDCl_3) 7.40-7.30 (10H, m, 1-H), 6.96 (2H, dt, J 6.9 and 15.6), 5.87 (2H, dt, J 1.5 and 15.7), 5.17 (4H, s), 2.41 (4H, t, J 7.3), 2.20 (4H, ddd, J 1.5, 7.3 and 7.4), 1.74 (4H, p, J 7.4); δ_{C} (125 MHz, CDCl_3) 209, 166, 148, 136,

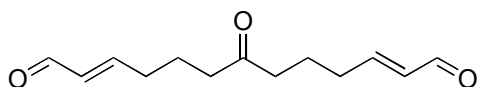
129, 128, 122, 66, 42, 31, 22; IR (thin film, ν/cm^{-1}) C=O 1712, 1654, Ar 3034; HRMS calculated for $\text{C}_{27}\text{H}_{31}\text{O}_5$ (M+H) 435.2171, found 435.2195

(2E,11E)-Di-*tert*-butyl 7-oxotrideca-2,11-dienedioate



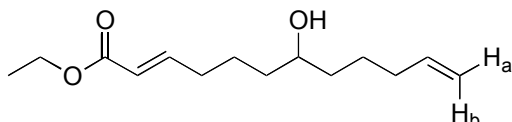
To a solution of undeca-1,10-dien-6-one (1.20 mmol, 200 mg, 1 eq) in dichloromethane (20 mL) under N_2 , was added *tert*-butyl acrylate (7.22 mmol, 0.925 g, 6 eq), followed by Hoveyda-Grubbs 2nd generation catalyst (0.03 mmol, 19 mg, 2.5 mol%) as a solid. The solution was stirred for 24 h, at which time another portion of catalyst (0.03 mmol, 19 mg, 2.5 mol%) was added. The solution stirred for a further 72 h, concentrated, and purification by column chromatography (over SiO_2 eluting with 6:1 H / EA) gave the product as a clear oil (0.939 mmol, 344 mg, 78%) R_f 0.37 in 3:1 H / EA; δ_{H} (400 MHz, CDCl_3) 6.80 (2H, dt, J 6.9 and 15.6), 5.74 (2H, dt, J 1.6 and 15.6), 2.41 (4H, t, J 7.3), 2.18 (4H, ddd, J 1.5, 7.0 and 7.4), 1.74 (4H, p, J 7.4), 1.48 (9H, s); δ_{C} (125 MHz, CDCl_3) 210, 166, 147, 124, 80, 42, 31, 28, 22; IR (thin film, ν/cm^{-1}) C=O 1707; HRMS calculated for $\text{C}_{21}\text{H}_{35}\text{O}_5$ (M+H) 397.2484, found 367.2513.

(2E,11E)-7-oxotrideca-2,11-diendial



To a solution of undeca-1,10-dien-6-one (1.34 mmol, 222 mg, 1 eq) in dichloromethane (26 mL) under N_2 , was added acrolein (6.69 mmol, 0.45 mL, 5 eq), followed by Hoveyda-Grubbs 2nd generation catalyst (0.03 mmol, 20 mg, 2.5 mol%) as a solid. The solution was stirred for 24 h, at which time another portion of catalyst (0.03 mmol, 20 mg, 2.5 mol%) was added. The solution stirred for a further 144 h, concentrated, and purification by column chromatography (over SiO_2 eluting with 1:1 ether/hexane to 7:3 ether / hexane) gave the product as a clear oil (0.837 mmol, 186 mg, 63%). δ_{H} (400 MHz, CDCl_3) 9.48 (d, J = 8.0 Hz, 2H), 6.78 (dt, J = 8.0, 15.5 Hz, 2H), 6.08 (dd, J = 8.0, 15.5 Hz), 2.43 (t, J = 7.0 Hz, 4H), 2.32 (dt, J = 7.0, 8.0 Hz, 4H), 1.78 (q, J = 7.0 Hz, 4H); δ_{C} (CDCl_3 , 100MHz) 209, 194.0, 157.0, 132.5, 42.0, 32.0, 21.5; HRMS $m/z/(MH^+)$: calcd for $\text{C}_{13}\text{H}_{19}\text{O}_3$: 223.1334, found: 223.1329.

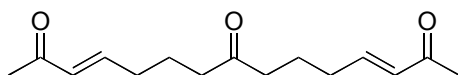
(E)-Ethyl 7-hydroxydodeca-2,11-dien-2-oate



To a solution of undeca-1,10-dien-6-ol (0.59 mmol, 100 mg, 1 eq) in dichloromethane (5 mL) under Ar, was added ethyl acrylate (3.61 mmol, 360 mg, 6 eq), followed by Hoveyda-Grubbs 2nd generation catalyst (0.015 mmol, 9 mg, 2.5 mol%) as a solid. The solution was stirred for 72 h, at which time another portion of catalyst (0.015 mmol, 9 mg, 2.5 mol%) was added. The solution was stirred for a further 48 h, concentrated, and purification by column chromatography (eluting with

6:1 PE / EA) gave the mono-substituted product as a clear oil (0.204 mmol, 49 mg, 35%); HRMS calculated for $C_{14}H_{25}O_3$ (M+H) 241.1798, found 241.1797; δ_H (400 MHz, $CDCl_3$) 6.89 (1H, dt, J 15.6 and 7.0), 5.80-5.66 (2H, m), 4.94 (1H, dd, J 1.6 and 17.1), 4.89 (1H, dd, J 1.2 and 10.9), 4.10 (2H, q, J 7.1), 3.53 (1H, m), 2.21-2.07 (2H, m), 2.06-1.94 (2H, m), 1.63-1.25 (8H, m), 1.22 (3H, t, J 7.1); δ_C (100 MHz, $CDCl_3$) 167, 149, 139, 122, 115, 72, 60, 37, 34, 32, 25, 24, 14; IR (thin film, ν/cm^{-1}) OH 3442 C=O 1718. And gave the disubstituted product as a clear oil (0.083 mmol, 26 mg, 14%): HRMS calculated for $C_{17}H_{29}O_5$ (M+H) 313.2010, found 313.2007; δ_H (400 MHz, $CDCl_3$) 6.90 (2H, dt, J 15.6 and 7.0), 5.77 (2H, d, J 15.6), 4.12 (4H, t, J 7.1), 3.55 (1H, m), 2.18 (4H, d, J 6.8), 1.60-1.52 (4H, m), 1.42 (4H, m), 1.24 (6H, q, J 7.1); δ_C (100 MHz, $CDCl_3$) 167, 149, 122, 72, 60, 37, 32, 24, 14; IR (thin film, ν/cm^{-1}) OH 3483 C=O 1717

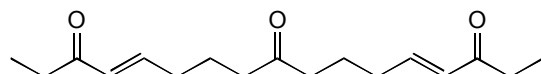
(3E,12E)-Pentadeca-3,12-diene-2,8,14-trione



To a solution of undeca-1,10-dien-6-one (0.60 mmol, 100 mg, 1 eq) and buten-4-one (3.61 mmol, 253 mg, 6 eq) in dichloromethane (5 mL) under Ar, was added Hoveyda-Grubbs 2nd generation catalyst (0.015 mmol, 9 mg, 2.5 mol%) The green solution slowly turned brown, and was stirred for 1 week, after which time the solution was concentrated. Purification by column chromatography (eluting with 8:1 PE / EA, followed by dichloromethane) afforded the di-substituted product as a clear oil (0.116 mmol, 29 mg, 19%)

To a solution of undeca-1,10-dien-6-one (0.30 mmol, 50 mg, 1 eq) and buten-4-one (1.81 mmol, 127 mg, 6 eq) in dichloromethane (5 mL) under Ar, was added Hoveyda-Grubbs 2nd generation catalyst (0.015 mmol, 9 mg, 5.0 mol%) The vial was sealed and irradiated in a microwave reactor for 2 h at 120 °C (pressure 12 bar). Another portion of catalyst (0.015 mmol, 9 mg, 5.0 mol%) was added, and the vial irradiated for 1.5 h at 120 °C (9 bar), after which time the solvent was removed. Purification by column chromatography (eluting with column chromatography (eluting with 8:1 PE / EA, followed by dichloromethane) afforded the disubstituted product as a clear oil (0.116 mmol, 29 mg, 76%): HRMS calculated for $C_{15}H_{22}O_3Na$ (M+Na) 273.1461, found 273.1462; δ_H (400 MHz, $CDCl_3$) 6.74 (1H, dt, J 6.8 and 16.0), 6.07 (1H, d, J 16.0), 2.42 (2H, t, J 7.2), 2.24 (3H, s), 1.75 (2H, t, J 7.2), 1.58 (2H, m); δ_C (100 MHz, $CDCl_3$) 213, 200, 147, 132, 42, 32, 27, 22; IR (thin film, ν/cm^{-1}) CO 1710, 1669, 1624

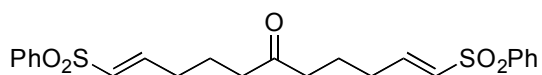
Heptadeca-4,13-diene-3,9,15-trione



To a solution of undeca-1,10-dien-6-one (250 mg, 1.50 mmol) in 35.0 mL of CH_2Cl_2 was added pentenone (0.89 mL, 9.02 mmol) and 2.5 mol % of Hoveyda-Grubbs II catalyst (23 mg, 0.038 mmol). The mixture was stirred for 4 days, upon which an additional amount of 2.5 mol% of Hoveyda-Grubbs II catalyst was added. The resulting mixture was then stirred for 3 days and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (20% EtOAc/petrol ether) to give the title compound (365 mg, 87%) as a brown oil. 1H NMR (300 MHz ,

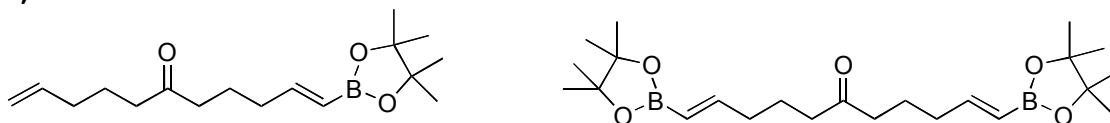
CDCl₃) δ 6.59-6.49 (m, 2H), 5.85 (dt, J = 1.5, 15.9 Hz, 2H), 2.32 (q, J = 7.2 Hz, 4H), 2.21 (t, J = 7.2 Hz, 4H), 1.98 (qd, J = 1.2, 7.2 Hz, 4H), 1.51 (quint, J = 7.2 Hz, 4H), 0.83 (t, J = 7.2 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 209.3, 200.6, 145.6, 130.3, 41.5, 32.9, 31.4, 21.7, 7.8; HRMS (ESCI+) calcd for C₁₇H₂₆O₃ 301.3865 (MNa⁺), found 301.1750.

(1E,10E)-1,11-bis(Phenylsulfonyl)undeca-1,10-dien-6-one



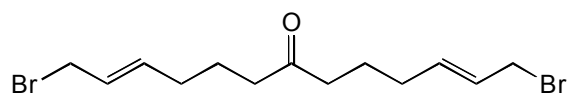
To a solution of undeca-1,10-dien-6-one (0.60 mmol, 100 mg, 1 eq) and phenyl vinyl sulfone (3.61 mmol, 607 mg, 6 eq) in dichloromethane (15 mL) under Ar, was added Hoveyda-Grubbs 2nd generation catalyst (0.0015 mmol, 9 mg, 2.5 mol%), and the solution was heated to ~50 °C and stirred for 24 h, after which time another portion of catalyst (0.0015 mmol, 9 mg, 2.5 mol%) was added. The solution was stirred at 50 °C for a further 72 h, cooled to room temperature and concentrated. Purification by column chromatography (eluting with 2:1 H / EA) yielded the product as a brown oil (0.44 mmol, 197 mg, 73%): HRMS calculated for C₂₃H₂₇O₅S₂ (M+H) 447.1300, found 447.1295; δ_H (400 MHz, CDCl₃) 7.80 (4H, d, J 8.2), 7.51 (6H, m), 6.87 (2H, dt, J 13.8 and 6.8), 6.26 (2H, d, J 14.1), 2.32 (4H, t, J 7.0), 2.16 (4H, dt, J 7.0 and 6.8), 1.65 (4H, m); δ_C (75 MHz, CDCl₃) 209, 146, 141, 133, 131, 129, 127, 41, 30, 21; IR (thin film, ν/cm^{-1}) C=O 1709 S=O 1140.

(1E,10E)-1,11-bis(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)undeca-1,10-dien-6-one



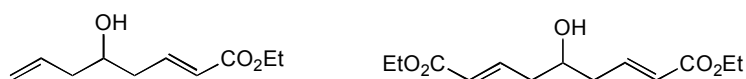
To a stirring solution of undeca-1,10-dien-6-one (0.60 mmol, 100 mg, 1 eq) and vinyl boronic acid pinacol ester (1.81 mmol, 278 mg, 3 eq) in dichloromethane (5 mL) under argon, was added Hoveyda-Grubbs 2nd generation catalyst (0.0015 mmol, 9 mg, 2.5 mol%). The green solution slowly turned brown, and was stirred for 1 week, after which time another portion of catalyst (0.0015 mmol, 9 mg, 2.5 mol%) was added. The solution was stirred for a further week, and concentrated. Purification by column chromatography (eluting with 6:1 PE/EA) gave the mono-substituted product as a clear oil (0.28 mmol, 82 mg, 47%) HRMS calculated for C₁₇H₂₉BO₃Na (M+Na⁺) 315.2102, found 315.2102; δ_H (400 MHz; CDCl₃) 6.55 (1H, dt, J 6.5 and 18.0), 5.74 (1H, dtd, J 1.6, 6.7 and 16.9), 5.42 (1H, d, J 18.0), 5.04-4.91 (2H, m), 2.37 (4H, t, J 7.4), 2.14 (2H, q, J 6.4), 2.03 (2H, q, J 7.1), 1.66 (4H, m), 1.25 (12H, s); δ_C (100 MHz, CDCl₃) 22.1, 22.8, 24.6, 24.7, 24.8, 24.8, 33.1, 35.0, 41.9, 42.0, 83.1, 83.4, 115.2, 115.3, 138.0, 153.3, 210.8; IR (thin film, ν/cm^{-1}) CO 1713; and the di-substituted product as a clear oil (0.053 mmol, 22 mg, 9%) HRMS calculated for C₂₃H₄₀B₂O₅Na (M+Na⁺) 441.2954, found 441.2953; δ_H (400 MHz; CDCl₃) 6.50 (2H, dt, J 6.5 and 17.9), 5.36 (2H, dt, J 1.3 and 18.0), 2.32 (4H, t, J 7.4), 2.08 (4H, dtd, J 1.5, 6.7 and 13.7), 1.63 (4H, tt, J 7.4 and 13.5), 1.20 (12H, s); δ_C (100 MHz, CDCl₃) 22, 25, 35, 42, 83, 115, 153, 211; IR (thin film, ν/cm^{-1}) CO 1712

1,13-Dibromo-trideca-2,11-dien-7-one



To a solution of undeca-1,10-dien-6-one (100 mg, 0.60 mmol) in 7.0 mL of CH_2Cl_2 was added allyl bromide (0.32 mL, 3.61 mmol) and 2.5 mol % of Hoveyda-Grubbs II catalyst (9 mg, 0.015 mmol). The mixture was stirred at rt for 8 days under nitrogen, and then a second portion of Hoveyda-Grubbs II catalyst (2.5 mol%) was added. The resulting mixture was then stirred for 2 days and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (10% EtOAc/petrol ether) to give the title compound (74 mg, 35%) as a brown oil. ν_{max} (thin film)/ cm^{-1} 2972, 1709, 1661, 1591, 1371, 1265, 1155, 1091, 1047, 965; δ_{H} (300 MHz, CDCl_3) 5.73-5.69 (m, 4H), 3.94 (d, $J = 6.3$ Hz, 4H), 2.40 (d, $J = 7.2$ Hz, 4H), 2.07 (q, $J = 7.2$ Hz, 4H), 1.67 (quint, $J = 7.2$ Hz, 4H); δ_{C} (75 MHz, CDCl_3) 210.3, 135.5, 127.2, 41.8, 33.2, 31.3, 22.7. m/z (ES+) 273 (M-81, 16%), 271 (17), 191 (11), 353 (8); HRMS: Found: 271.0692. $\text{C}_{13}\text{H}_{20}^{79}\text{Br}_2\text{O}$ (M- ^{79}Br) Requires 271.0698.

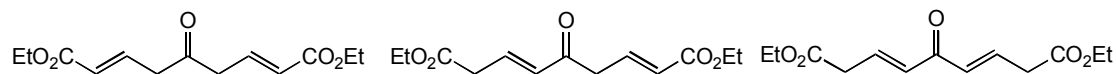
5-Hydroxynona-2,7-dienedioic acid diethyl ester and 5-hydroxy-octa-2,7-dienoic acid ethyl ester



General procedure I was followed using ethyl acrylate (1.17 mL, 10.7 mmol), 295 (100 mg, 0.892 mmol) and stirring over 89 hours. Purification by column chromatography over silica gel (eluting with 1:3 ethyl acetate / hexane) gave the *title compound* 302 (101 mg, 44%) as a colourless oil; R_f 0.13 (1:2 ethyl acetate / hexane); ν_{max} (thin film)/ cm^{-1} 3481 (alcohol), 1709 (ester), 1654 (olefin); δ_{H} (400 MHz, CDCl_3) 6.92 (2H, dt, J 15.7 and 7.3), 5.86 (2H, d, J 15.7), 4.13 (4H, q, J 7.1), 3.92-3.83 (1H, m), 2.83 (1H, d, J 4.3), 2.42-2.27 (4H, m), 1.23 (6H, t, J 7.1); δ_{C} (101 MHz, CDCl_3) 166.2, 144.4, 124.0, 69.0, 60.3, 39.6, 14.1; m/z (CI) 274.2 (M+ NH_4^+ , 28%), 257.1 (M+ H^+ , 50), 132.0 (100); HRMS: Found 274.1649. $\text{C}_{13}\text{H}_{24}\text{NO}_5$ (M+ NH_4^+) Requires 274.1649.

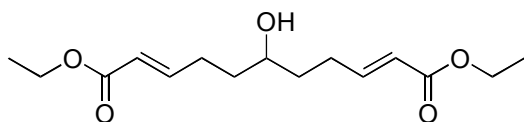
The column chromatography also yielded the *title compound* 301 (31.8 mg, 19%) as a colourless oil; R_f 0.23 (1:2 ethyl acetate / hexane); ν_{max} (thin film)/ cm^{-1} 3465 (alcohol), 1708 (ester), 1653 (olefin); δ_{H} (400 MHz, CDCl_3) 6.97 (1H, dt, J 15.7 and 7.4), 5.90 (1H, dd, J 15.7 and 1.3), 5.86-5.74 (1H, m), 5.15 (1H, d, J 11.2), 5.14 (1H d, J 15.8), 4.17 (2H, q, J 7.1), 3.85-3.76 (1H, m), 2.46-2.26 (3H, m), 2.24-2.13 (1H, m), 1.92 (1H, d, J 2.9), 1.27 (3H, t, J 7.1); δ_{C} (101 MHz, CDCl_3) 166.3, 144.9, 134.0, 123.9, 118.7, 69.3, 60.3, 41.5, 39.3, 14.2; m/z (CI) 202.1 (M+ NH_4^+ , 100%), 185.1 (30), 158.0 (31); HRMS: Found 202.1439. $\text{C}_{10}\text{H}_{20}\text{NO}_3$ (M+ NH_4^+) Requires 202.1438.

5-Oxonona[2,6]/[2,7]/[3,6]dienedioic acid diethyl esters



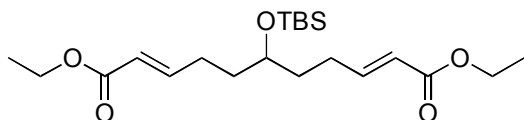
To a solution of the hept-1,7-dien-4-one (100 mg, 0.908 mmol in DCM (5 mL) under argon was added ethyl acrylate ((0.59 mL, 5.45 mmol), 6 eq) followed by Grubbs Hoveyda 2nd generation catalyst (2.5 mol%). The solution was stirred at ambient temperature for 24 hours then additional catalyst (2.5 mol%) was added. The reaction was stirred for a further 65 hours after which the reaction was concentrated *in vacuo* and the crude purified directly by column chromatography over silica gel (eluting with 1:3 ethyl acetate / hexane) gave the *title compounds* (18.0 mg, 8.0%) as an inseparable mixture of olefin regioisomers as a colourless oil; R_f 0.12-0.14 (1:3 ethyl acetate / hexane); ν_{\max} (neat)/ cm^{-1} 1750-1650 (broad carbonyl bands); δ_{H} (400 MHz, CDCl_3) 7.10-6.84 (2H, m, 3-H, 7-H), 6.47-5.84 (2H, m), 4.22-4.11 (4H, m), 3.51-3.21 (4H, m), 1.30-1.22 (6H, m); δ_{C} (101 MHz, CDCl_3) 202.2, 195.3 and 188.4, 169.8, 169.7, 165.7 and 165.6, 140.0, 139.4, 138.8 and 138.8, 132.1, 131.1, 125.5 and 125.0, 61.3, 61.2, 60.6 and 60.5, 45.4, 42.9, 37.8, 37.6, 14.2 and 14.1.

(2E,9E)-Diethyl 6-hydroxyundeca-2,9-dienedioate



To a solution of nona-1,8-dien-5-ol (0.71 mmol, 100 mg, 1 eq) in dichloromethane (5 mL) under Ar, was added ethyl acrylate (4.28 mmol, 428 mg, 6 eq), followed by Hoveyda-Grubbs 2nd generation catalyst (0.018 mmol, 11 mg, 2.5 mol%) as a solid. The solution was stirred for 150 h, monitoring by TLC, after which time another portion of catalyst (0.018 mmol, 11 mg, 2.5 mol%) and was stirred for a further 24 h. The reaction mixture was concentrated and purification by column chromatography (eluting with 6:1 H / EA) gave the product as a clear oil (0.10 mmol, 29 mg, 14%): HRMS calculated for $\text{C}_{15}\text{H}_{25}\text{O}_5$ (M+H) 285.1697, found 283.1700; δ_{H} (400 MHz, CDCl_3) 6.92 (2H, dt, J 6.9 and 16.1), 5.83 (2H, dd, J 1.3 and 16.0), 4.17 (2H, q, J 7.0), 3.65-3.52 (1H, m), 2.42-2.09 (4H, m), 1.62-1.49 (4H, m), 1.25 (3H, t, J 7.0); δ_{C} (100 MHz, CDCl_3) 167, 148, 122, 71, 60, 36, 29, 14.

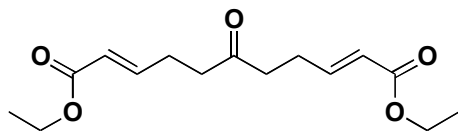
(2E,9E)-Diethyl 6-*tert*-butyldimethylsilyloxyundeca-2,9-dienedioate



To a solution of *tert*-butyldimethyl(nona-1,8-dien-5-yloxy)silane (0.39 mmol, 100 mg, 1 eq) in dichloromethane (5 mL) under Ar, was added ethyl acrylate (2.36 mmol, 354 mg, 6 eq), followed by Hoveyda-Grubbs 2nd generation catalyst (0.01 mmol, 6 mg, 2.5 mol%) as a solid. The solution was stirred for 120 h, monitoring by TLC, after which time the reaction mixture was concentrated and purification by column chromatography (eluting with 9:1 H / EA) gave the product as a clear oil (0.23 mmol, 90 mg, 57%): HRMS calculated for $\text{C}_{21}\text{H}_{39}\text{O}_5\text{Si}$ (M+H) 399.2561, found 399.2568; δ_{H} (400 MHz, CDCl_3) 6.96 (2H, dt, J 15.6 and 7.2) 5.83 (2H, d, J 15.6), 4.19 (4H, q, J 7.2), 3.60 (1H, m), 2.46 (4H, m), 1.61 (4H, m), 1.30 (6H, t, J 7.2),

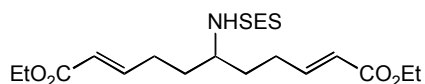
0.90 (9H, s), 0.05 (6H, s); δ_C (100 MHz, CDCl_3) 166, 149, 121, 70, 60, 35, 28, 26, 18, 14, -4; IR (thin film, ν/cm^{-1}) C=O 1721.

Diethyl (2E,9E)-6-oxoundeca-2,9-dienedioate :



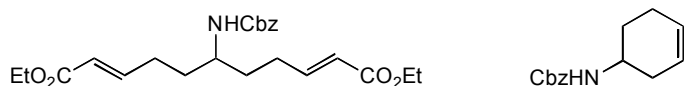
To a solution of nona-1,8-dien-5-one (1.54 g, 11.09 mmol) in dichloromethane (60 cm^3) under inert N_2 atmosphere, was added sequentially ethyl acrylate (7.25 cm^3 , 66.6 mmol) and Hoveyda-Grubbs second generation catalyst (174 mg, .28 mmol). The mixture was stirred at room temperature for 5 days. More catalyst (90 mg, 0.14 mmol) was then added and the reaction was stirred for further 2 days. After TLC monitoring, more catalyst (40 mg, 0.06 mmol) was added and the reaction mixture was allowed to stir for 2 days. 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 (75:25) as eluent, to afford the title compound (2.07 g, 66%) as a clear oil $\nu_{\text{max}}(\text{CH}_2\text{Cl}_2/\text{cm}^{-1})$ 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, J 6.8), 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) 14.1, 25.8, 40.5, 60.2, 122.1, 146.8, 166.2, 206.8. m/z (ESI) 305.1360 (M^+ . $\text{C}_{15}\text{H}_{22}\text{NaO}_5$ requires 305.1359).

6-[[2'-(Trimethylsilyl)ethyl]sulfonylamino]undeca-2,9-dienedioic acid diethyl ester



To a solution of the 5-[[2'-(trimethylsilyl)ethyl]sulfonylamino]nona-1,8-diene (100 mg, 0.329 mmol) in DCM (5 mL) under argon was added ethyl acrylate (0.22 mL, 1.98 mmol, 6 eq) followed by Grubbs Hoveyda 2nd 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 the crude purified directly by column chromatography over silica gel (eluting with 1:3 ethyl acetate / hexane) gave the *title compound* 305 (114 mg, 77%) as a colourless oil; R_f 0.27 (1:2 ethyl acetate / hexane); ν_{max} (thin film)/ cm^{-1} 3278 (N-H), 1716 (ester), 1654 (olefin), 1369 and 1142 (sulfonamide); δ_H (400 MHz, CDCl_3) 6.91 (2H, dt, J 15.6 and 6.8), 5.83 (2H, dt, J 15.6 and 1.4), 4.53 (1H, d, J 9.3), 4.16 (4H, q, J 7.1), 3.44-3.33 (1H, m), 2.93-2.86 (2H, m), 2.39-2.20 (4H, m), 1.74-1.55 (4H, m), 1.26 (6H, t, J 7.1), 1.03-0.96 (2H, m), 0.03 (9H, s); δ_C (101 MHz, CDCl_3) 166.3, 147.3, 122.1, 60.3, 53.4, 50.3, 34.1, 28.3, 14.2, 10.7, -2.0; m/z (ES) 465.4 ($\text{M}+\text{H}_2\text{O}^+$, 90%), 448.3 ($\text{M}+\text{H}^+$, 100); HRMS: Found 448.2182. $\text{C}_{20}\text{H}_{38}\text{NO}_6\text{S}^{28}\text{Si}$ ($\text{M}+\text{H}^+$) Requires 448.2184.

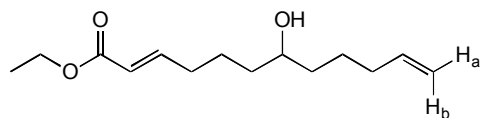
5-Benzyloxycarbonylamino-deca-2,8-dienedioic acid diethyl ester



To a solution of the 4-benzyloxycarbonylamino-octa-1,7-diene (40 mg, 0.135 mmol) in DCM (5 mL) under argon was added ethyl acrylate (0.18 mL, 1.63 mmol, 6 eq) followed by Grubbs Hoveyda 2nd 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 the crude purified directly by column chromatography over silica gel (eluting with 1:3 ethyl acetate / hexane) which gave the *title compound* (10.0 mg, 18%) as a colourless oil; R_f 0.35 (1:3 ethyl acetate / hexane); ν_{\max} (thin film)/ cm^{-1} 1717 (ester and carbamate); δ_H (400 MHz, CDCl_3) 7.39-7.30 (5H, m), 6.96-6.82 (2H, m), 5.87 (1H, d, J 16.0), 5.82 (1H, d, J 15.7), 5.09 (2H, s), 4.58 (1H, d, J 8.8), 4.19 (2H, q, J 7.1), 4.18 (2H, q, J 7.1), 3.87-3.76 (1H, m), 2.49-2.35 (2H, m), 2.31-2.20 (2H, m), 1.73-1.62 (1H, m), 1.61-1.51 (1H, m), 1.29 (3H, t, J 7.1), 1.28 (3H, t, J 7.1); δ_C (101 MHz, CDCl_3) 166.1, 155.9, 147.4, 143.6, 136.5, 128.7, 128.3, 128.2, 124.8, 122.2, 66.9, 60.4, 60.2, 50.0, 37.7, 33.1, 28.6, 14.1; m/z (ES) 421.3 ($\text{M}+\text{H}_2\text{O}^+$, 35%), 404.2 ($\text{M}+\text{H}^+$, 100), 296.2 (70); HRMS: Found 404.2066. $\text{C}_{22}\text{H}_{30}\text{NO}_6$ ($\text{M}+\text{H}^+$) Requires 404.2068.

The column chromatography also yielded 77% of the ring-closed product: M.p. 64-66 °C, (lit.¹ 64-67 °C); R_f 0.37 (1:4 ethyl acetate / hexane); δ_H (400 MHz, CDCl_3) 7.36-7.29 (5H, m), 5.67 (1H, m), 5.59 (1H, m), 5.09 (2H, s), 4.80 (1H, br s), 3.87 (1H, m), 2.39 (1H, m), 2.12 (2H, m), 1.94-1.86 (2H, m), 1.63-1.50 (1H, m).

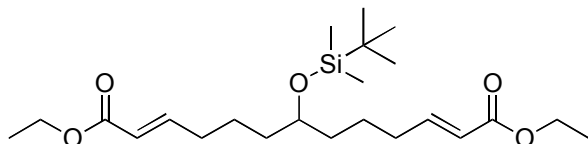
(*E*)-Ethyl 7-hydroxydodeca-2,11-dienoate



To a solution of undeca-1,10-dien-6-ol (0.59 mmol, 100 mg, 1 eq) in dichloromethane (5 mL) under Ar, was added ethyl acrylate (3.61 mmol, 360 mg, 6 eq), followed by Hoveyda-Grubbs 2nd generation catalyst (0.015 mmol, 9 mg, 2.5 mol%) as a solid. The solution was stirred for 72 h, at which time another portion of catalyst (0.015 mmol, 9 mg, 2.5 mol%) was added. The solution was stirred for a further 48 h, concentrated, and purification by column chromatography (eluting with 6:1 PE / EA) gave the mono-substituted product as a clear oil (0.204 mmol, 49 mg, 35%); HRMS calculated for $\text{C}_{14}\text{H}_{25}\text{O}_3$ ($\text{M}+\text{H}$) 241.1798, found 241.1797; δ_H (400 MHz, CDCl_3) 6.89 (1H, dt, J 15.6 and 7.0), 5.80-5.66 (2H, m), 4.94 (1H, dd, J 1.6 and 17.1), 4.89 (1H, dd, J 1.2 and 10.9), 4.10 (2H, q, J 7.1), 3.53 (1H, m), 2.21-2.07 (2H, m), 2.06-1.94 (2H, m), 1.63-1.25 (8H, m), 1.22 (3H, t, J 7.1); δ_C (100 MHz, CDCl_3) 167, 149, 139, 122, 115, 72, 60, 37, 34, 32, 25, 24, 14; IR (thin film, ν/cm^{-1}) OH 3442 C=O 1718.

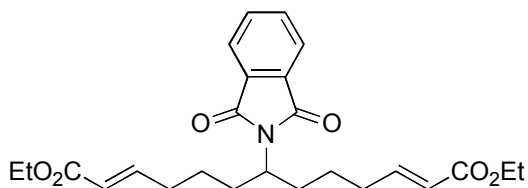
The disubstituted product was also obtained as a clear oil (0.083 mmol, 26 mg, 14%): HRMS calculated for $\text{C}_{17}\text{H}_{29}\text{O}_5$ ($\text{M}+\text{H}$) 313.2010, found 313.2007; δ_H (400 MHz, CDCl_3) 6.90 (2H, dt, J 15.6 and 7.0), 5.77 (2H, d, J 15.6), 4.12 (4H, t, J 7.1), 3.55 (1H, m), 2.18 (4H, d, J 6.8), 1.60-1.52 (4H, m), 1.42 (4H, m), 1.24 (6H, q, J 7.1); δ_C (100 MHz, CDCl_3) 167, 149, 122, 72, 60, 37, 32, 24, 14; IR (thin film, ν/cm^{-1}) OH 3483 C=O 1717

(2E,11E)-Diethyl 7-tert-butyldimethylsilyloxytrideca-2,11-dienedioate



To a solution of *tert*-butyldimethyl(undeca-1,10-dien-6-yloxy)silane (0.35 mmol, 100 mg, 1 eq) in dichloromethane (5 mL) under Ar, was added ethyl acrylate (2.12 mmol, 213 mg, 6 eq), followed by Hoveyda-Grubbs 2nd generation catalyst (0.009 mmol, 6 mg, 2.5 mol%) as a solid. The solution was stirred for 96 h, monitoring by TLC, after which time the reaction mixture was concentrated and purification by column chromatography (eluting with 9:1 H / EA) gave the product as a brown oil (0.23 mmol, 99 mg, 67%): HRMS calculated for C₂₃H₄₃O₅Si (M+H) 427.2874, found 427.2870; δ_{H} (400 MHz, CDCl₃) 6.92 (2H, dt, *J* 15.4 and 6.9) 5.78 (2H, dd, *J* 15.6 and 1.3), 4.15 (4H, q, *J* 7.1), 3.62 (1H, s), 2.16 (4H, m), 1.56-1.32 (8H, m), 1.26 (6H, t, *J* 7.1), 0.85 (9H, s), 0.03 (6H, s); δ_{C} (100 MHz, CDCl₃) 171, 153, 125, 76, 65, 41, 37, 30, 28, 23, 19, 0; IR (thin film, ν/cm^{-1}) C=O 1719.

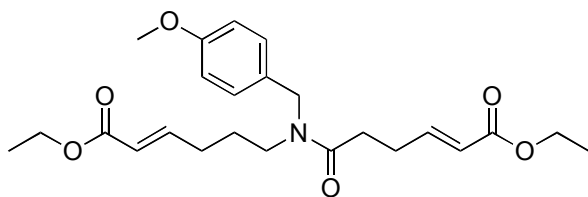
(2E,11E)-Diethyl 7-(1,3-dioxoisindolin-2-yl)trideca-2,11-dienedioate



To a stirring solution of 2-(undeca-1,10-dien-6-yl)isindoline-1,3-dione (0.168 mmol, 50 mg, 1 eq) in dichloromethane was added ethyl acrylate (1.02 mmol, 0.11 mL, 6 eq) followed by Hoveyda-Grubbs 2nd generation catalyst (0.0042 mmol, 3 mg, 2.5 mol%) as solid. The solution was stirred for at room temperature 96 h, monitoring by TLC, after which time another portion of catalyst (0.0042 mmol, 3 mg, 2.5 mol%) was added. The reaction mixture was stirred at room temperature for a further 24 h, at which point it was concentrated and subjected to purification by column chromatography (over SiO₂ eluting with 6:1 H/EA) yielding the product (0.149 mmol, 66 mg, 89%) as a clear yellow oil: R_f 0.6 in 2:1 H/EA; HRMS calculated for C₂₅H₃₂NO₆ (M+H) 442.2224, found 442.2220; δ_{H} (270 MHz, CDCl₃) 7.79-7.84 (2H, m, Ar-H), 7.69-7.74 (2H, m, Ar-H), 6.84 (2H, dd, *J* 15.70 and 7.02), 5.79 (2H, dt, *J* 15.70 and 1.45), 4.14 (4H, q, *J* 7.16), 2.03-2.25 (5H, m), 1.61-1.79 (4H, m), 1.33-1.46 (4H, m), 1.19-1.30 (6H, m); δ_{C} (270 MHz, CDCl₃) 166.7, 148.4, 134.1, 131.7, 123.4, 121.8, 60.3, 51.5, 32.0, 31.8, 25.1, 14.3; IR (thin film, ν/cm^{-1}) C=O 1706.

(2E)-Ethyl 6-((E)-ethyl enoyl)hex-2-enoate

5-(para-methoxybenzylcarbamoyl)pent-2-



To a solution of *N*-(para-methoxybenzyl)-*N*-(pent-4-enyl)pent-4-enamide (0.35 mmol, 100 mg, 1 eq) in dichloromethane (5 mL) under Ar, was added ethyl acrylate (2.09 mmol, 209 mg, 6 eq), followed by Hoveyda-Grubbs 2nd generation catalyst (0.009 mmol, 5 mg, 2.5 mol%) as a solid. The solution was stirred for 48 h, at which time another portion of catalyst (0.009 mmol, 0.005g, 2.5 mol%) was added. The solution stirred for a further 96 h, concentrated, and purification by column chromatography (eluting with 2:1 H / EA) gave the product as a brown oil (0.27 mmol, 118 mg, 79%): HRMS calculated for C₂₄H₃₄N₂O₆ (M+H) 432.2381, found 432.2382; δ_{H} (400 MHz, CDCl₃) 7.14-6.72 (6H, m), 5.85 and 5.78 (2H, dd, *J* 1.6 and 15.6, rotomers), 4.46 and 4.39 (2H, s, rotomers), 4.11 (4H, q, *J* 7.0), 3.78 and 3.77 (3H, s, rotomers), 3.31 and 3.11 (2H, t, *J* 7.8, rotomers), 2.62-2.33 (4H, m), 2.10 (2H, dt, *J* 6.7 and 15.1), 1.61 (2H, p, *J* 7.3), 1.28-1.13 (6H, m); δ_{C} (75 MHz, CDCl₃) 171.7, 171.1, 166.5, 159.3, 147.8, 147.5, 146.8, 129.4, 127.4, 122.5, 122.1, 121.8, 114.4, 114.0, 60.2, 60.0, 55.2, 55.1, 50.6, 47.7, 46.0, 45.8, 31.4, 31.2, 29.5, 29.1, 27.6, 27.4, 26.7, 25.8, 14.0; IR (thin film, ν/cm^{-1}) C=O 1711 1643.

References

1. E. Gomez-Sanchez and J. Marco-Contelles, *Tetrahedron*, 2005, **61**, 1207.