Transannular, decarboxylative Claisen rearrangement reactions for the synthesis of sulfur-substituted vinylcyclopropanes

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1. General Experimental:

All reactions were performed under nitrogen unless otherwise stated. Melting points were determined using Stuart Scientific SMP1 melting point apparatus and are uncorrected. Infrared spectra were recorded on Mattson 5000 FTIR and Perkin-Elmer Spectrum RX FT-IR System spectrometers. Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded in CDCl3 unless otherwise stated on a Jeol GX-270, Brüker DRX-300, Brüker AV-400 or Brüker AV-500 spectrometer. Chemical shifts are in parts per million (ppm) and are referenced relative to the residual proton-containing solvent (^{1}H NMR: 7.26 ppm for CDCl3; ^{13}C NMR: 77.0 ppm for CDCl3). Mass spectra (CI, EI and FAB) were recorded using Micromass AutoSpec-Q, Micromass Platform II or Micromass AutoSpec Premier instruments. Elemental analyses were performed at the microanalytical laboratories of the London Metropolitan University. Optical rotations were measured on an Optical Activity Ltd. instrument. Analytical thin layer chromatography (TLC) was performed on pre-coated Aluminium-backed Merck Kieselgel 60 F_{254} plates. Visualisation was effected with ultraviolet light, potassium permanganate or vanillin as appropriate. Flash chromatography was performed using BDH (40–63 μm) silica gel unless otherwise stated. Standard solvents were distilled under nitrogen prior to use; Et_2O and THF from sodium-benzophenone ketyl, CH_2Cl_2 from CaH_2 and toluene from sodium. All other solvents were reagent grade. Petrol refers to petroleum ether of the fraction bp 40–60 °C. All liquid reagents were distilled prior to use. BSA was purchased from Alfa Aesar Lancaster and distilled prior to use. Potassium acetate was oven-dried at 120 °C for several days prior to use. Microwave reactions were performed in a Biotage initiator.

2. General Procedures

General Procedure A: preparation of cyclic orthoesters from1,4-diols

To a solution of the diol (1.0 equiv.) in CH_2Cl_2 was added CSA (1 mol%) and trimethylorthoformate (2.0 equiv.). The reaction mixture was stirred at rt for 1 h before addition of NEt_3. The mixture was concentrated under reduced pressure and purified by chromatography to give the desired orthoester.

General Procedure B: preparation of allylic alcohols from cyclic orthoesters

To a solution of the orthoester (1.0 equiv.) in PhMe at –78 °C was added DIBAL-H (1.3 equiv.) dropwise. The reaction mixture was allowed to warm to rt and stirred for 16 h. The reaction mixture was again cooled to 0 °C, carefully quenched with sat. Na/K tartrate soln. and the mixture stirred for a further 1 h. The aqueous layer was then extracted with EtOAc and the combined organic layers washed with sat. aq. NaCl (×2) and H_2O, dried ($MgSO_4$) and concentrated under reduced pressure. Purification by chromatography gave the desired alkene.

General Procedure C: preparation of mesylates from allylic alcohols

To a solution of alcohol (1.0 equiv.) in CH_2Cl_2 at 0 °C was added NEt_3 (3.0 equiv.). The reaction mixture was stirred at 0 °C for 15 min, and methanesulfonyl chloride (2.0 equiv.) was added dropwise. The reaction was stirred at 0 °C for 30 min, washed with 2 M aq. HCl (×2) and sat. aq. $NaHCO_3$ (×2). The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure to give the desired methane sulfonate

General Procedure D: alkylation of sulfone- and sulfoximine-substituted acetates

To a suspension of sodium hydride (60% dispersion in mineral oil, washed with hexane; 1.1 equiv.) in THF or DMF at 0 °C, was added dropwise a solution of the ester (1.0 equiv.) in THF or DMF. The reaction mixture was stirred at 0 °C for 30 min and a solution of the methane sulfonate or iodide (1.0 equiv.) in THF or DMF was added dropwise. The reaction mixture was stirred at 0 °C for a further 30 min, then at rt for 16 h. The solution was concentrated under reduced pressure and the crude product suspended in EtOAc, washed with sat. aq. NH_4Cl, H_2O and sat. aq. NH_4Cl

The organic phase was dried ($MgSO_4$), concentrated under reduced pressure and purified by chromatography to give the desired alkylated ester.

General Procedure E: hydrolysis of MOM ethers/*tert*-butyl esters

To a solution of the ester (1.0 equiv.) in MeCN was added 2 M aq. HCl The reaction mixture was heated under reflux for 2 h, cooled, and partitioned between CH_2Cl_2 and H_2O. The aqueous phase washed with CH_2Cl_2 (×5). The combined organic washings were dried ($MgSO_4$), concentrated under reduced pressure, and purified by chromatography to give the desired alcohol/hydroxyacid.

General Procedure F: hydrolysis of methyl esters

To a solution of the ester (1.0 equiv.) in THF was added 2 M aq. LiOH (5.0 equiv.). The reaction was stirred at rt for 1 h, then partitioned between Et_2O and H_2O and the aqueous layer acidified to pH 1 with 2 M aq. HCl. The aqueous layer was then extracted with Et_2O (×3) and the organic layers combined, dried ($MgSO_4$) and concentrated under reduced pressure to give, without further purification, the desired acid.

General Procedure G: cyclisation of hydroxyacids to give unsaturated ε-lactones

To a solution of the hydroxyacid (1.0 equiv.) in CH_2Cl_2 at 0 °C was added EDCI (1.1 equiv.) portionwise. The reaction mixture was allowed to warm to rt and left to stir for 16 h. The reaction mixture was partitioned between H_2O and CH_2Cl_2, the organic layer washed with sat. aq. NH_4Cl and H_2O, dried ($MgSO_4$) and concentrated under reduced pressure. The product was purified by chromatography to give the desired lactone.

General Procedure H: dCr reaction of unsaturated ε-lactones

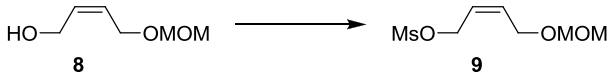
A solution of lactone (1.0 equiv.), BSA (1.0 equiv.) and KOAc (0.1 equiv.) in DMF was subjected to microwave irradiation at 160 °C for 10 min. The reaction mixture was diluted with EtOAc, washed with sat. aq. NaCl (×3) and H_2O, dried ($MgSO_4$) and concentrated under reduced pressure to give the desired cyclopropane.

General Procedure I: preparation of 1,4-diols from furan-2(5*H*)-ones

To a solution of furan-2(5*H*)-one (1.0 equiv.) in PhMe at −78 °C was added DIBAL-H (2.2 equiv.) dropwise. The reaction mixture was allowed to stir at –78 °C for 2 h, then warmed to rt and stirred for a further 2 h. The reaction mixture was again cooled to 0 °C and carefully quenched with sat. Na/K tartrate soln. and the mixture stirred for a further 1 h. The aqueous layer was then extracted with EtOAc and the combined organic layers washed with sat. aq. NaCl (×2) and H_2O, dried (Na_2SO_4) and concentrated under reduced pressure. Purification by chromatography gave the desired 1,4-diol.

3. Synthesis and reactions of lactone 13

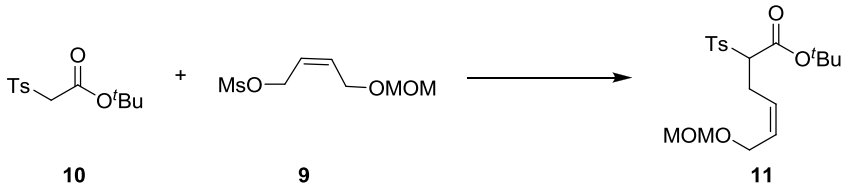
*Methanesulfonic acid (*Z*)-4-(methoxymethoxy)but-2-enyl ester* **9**



8 **9**

According to general procedure **C**, alcohol **8**[1] (1.72 g, 13.0 mmol, 1.0 equiv.) in CH_2Cl_2 (65 mL) was reacted with NEt_3 (5.44 mL, 39.0 mmol, 3.0 equiv.) and methanesulfonyl chloride (2.01 mL, 26.0 mmol, 2.0 equiv.) to give methanesulfonic acid (*Z*)-4-(methoxymethoxy)but-2-enyl ester **9** as an orange oil, which was used crude in the next step; R_f 0.17 (50% EtOAc–petrol); δ_H (270 MHz, $CDCl_3$) [5.94–5.85, 5.82–5.71] (2H, 2 × m, CH=CH), 4.84 (2H, d, *J* 6.5 Hz, CHC*H*$_2$OS), 4.62 (2H, s, OCH_2O), 4.17 (2H, d, *J* 6.5 Hz, CHC*H*$_2$OMOM), 3.37 (3H, s, OCH_3), 3.01 (3H, s, SCH_3); δ_C (67.5 MHz, $CDCl_3$) 132.6 (*C*HCH$_2$OMOM), 124.9 (*C*HCH$_2$OMs), 95.8 (OCH_2O), 65.3 (CH_2OS), 62.7 (=CH-*C*H$_2$O), 55.5 (OCH_3), 38.1 (SCH_3).

*(*Z*)-*tert*-Butyl 6-(methoxymethoxy)-2-tosylhex-4-enoate* **11**

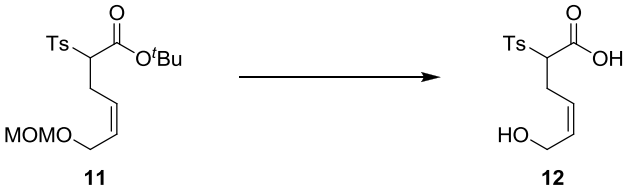


10 **9** **11**

According to general procedure **D**, a suspension of sodium hydride (766 mg, 31.9 mmol, 1.1 equiv.) in THF (50 mL) was treated with a solution of ester **10**[2] (7.84 g, 29.0 mmol, 1.0 equiv.) in THF (50 mL) followed by a solution of methanesulfonic acid (*Z*)-4-(methoxymethoxy)but-2-enyl ester **9** (29.0 mmol, 1.0 equiv.) in THF (40 mL). Purification by chromatography (20% EtOAc–petrol) gave (*Z*)-*tert*-butyl 6-(methoxymethoxy)-2-tosylhex-4-enoate **11** (6.95 g, 57% over two steps) as a yellow oil; R_f 0.32 (35% EtOAc–petrol); ν_{max} (film) 1732, 1699, 1597, 1456, 1396, 1369, 1327, 1306, 1292, 1246, 1213, 1147, 1105, 1086, 1047, 993, 947, 920, 883, 837, 816, 760, 714, 667 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.74 (2H, d, *J* 8.5 Hz, *o*-SO_2Ar), 7.33 (2H, d, *J* 8.5 Hz, *m*-SO_2Ar), [5.68-5.63, 5.44-5.39] (2H, m, -C*H*=C*H*-), 4.58 (2H, s, -OCH_2O-), [4.10, 4.01] (2× 1H, dd, *J* 12.5, 6.5 Hz, =CH-C*H*$_2$O-), 3.84 (1H, dd, *J* 10.5, 4.5 Hz, Ts-CH<), 3.32 (3H, s, -OCH_3), 2.75-2.70 (2H, m, Ts-CH-C*H*$_2$-CH=), 2.43 (3H, s, Ts-CH_3), 1.31 (9H, s, -$C(CH_3)_3$); δ_C (75 MHz, $CDCl_3$) 164.4 (C=O), 145.3

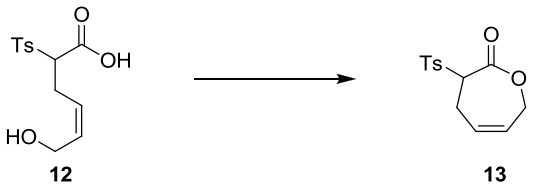
(4°), 134.4 (4°), 130.2 (3°), 129.6 (3°), 129.4 (3°), 126.2 (3°), 95.8 (-OCH_2O-), 83.3 (-*C*$(CH_3)_3$), 70.6 (Ts-*C*H-COO-), 62.8 (-O*C*H_2-CH=), 55.3 (-OCH_3), 27.6 (-C(*C*$H_3)_3$), 25.3 (Ts-CH-*C*H_2-CH=), 21.7 (Ts-CH_3); *m/z* (CI) 402 $[M+NH_4]^+$, 358 $[M+NH_4-CH_2OCH_3]^+$, 346, 323, 314, 302, 288, 284, 232, 197, 192, 174, 139 (Found: $[M+NH_4]^+$, 402.1948. $C_{19}H_{28}O_6S$ requires $[M+NH_4]^+$, 402.1950) (Found: C, 59.21; H, 7.37. $C_{19}H_{28}O_6S$ requires C, 59.35; H, 7.34%).

(Z)-6-Hydroxy-2-tosylhex-4-enoic acid **12**



According to general procedure **E**, ester **11** (882 mg, 2.29 mmol, 1.0 equiv.) was heated under reflux in MeCN (25 mL) and 2 M aq. HCl (5 mL). Purification by recrystallisation from $CHCl_3$–petrol gave (*Z*)-6-hydroxy-2-tosylhex-4-enoic acid **12** (577 mg, 81%) as a colourless crystalline solid; mp 124–126 °C; ν_{max} (film) 3480, 3029, 1732, 1597, 1444, 1401, 1383, 1319, 1303, 1292, 1246, 1146, 1084, 1016, 815, 711, 663 cm^{-1}; δ_H (300 MHz, DMSO-d_6) 7.75 (2H, d, *J* 7.0 Hz, *o*-SO_2Ar), 7.47 (2H, d, *J* 7.0 Hz, *m*-SO_2Ar), [5.60-5.53, 5.30-5.22] (2H, m, -C*H*=C*H*-), 4.20 (1H, dd, *J* 7.5, 3.5 Hz, Ts-CH<), 3.99-3.83 (2H, m, HO-C*H*$_2$-), 2.56-2.50 (2H, m, Ts-CH-C*H*$_2$-CH=), 2.42 (3H, s, Ts-CH_3); δ_C (75 MHz, DMSO-d_6) 166.8 (C=O), 145.5, 134.8, 134.6, 130.2, 129.4, 123.9, 69.6, 57.2, 25.4, 21.6; *m/z* (CI) 284 $[M+NH_4-H_2O]^+$, 258, 240, 223, 174, 156, 139, 130 (Found: $[M+NH_4-H_2O]^+$, 284.0968. $C_{13}H_{16}O_5S$ requires $[M+NH_4-H_2O]^+$, 284.0957) (Found: C, 54.76; H, 5.49. $C_{13}H_{16}O_5S$ requires C, 54.92; H, 5.67%).

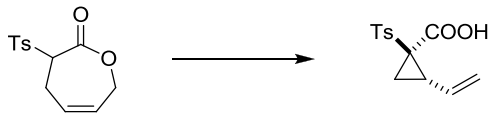
*3-Tosyl-3,4-dihydrooxepin-2(7*H*)-one* **13**



According to general procedure **G**, (*Z*)-6-hydroxy-2-tosylhex-4-enoic acid **12** (2.50 g, 8.80 mmol, 1.0 equiv.) in CH_2Cl_2 (150 mL) was treated with *N*,*N*'diisopropylcarbodiimide (1.51 mL, 9.67 mmol, 1.1 equiv.). Purification by chromatography (30% EtOAc–petrol) gave 3-tosyl-4,7-dihydrooxepin-2(3*H*)-one **13**

(1.83 g, 78%) as a colourless powder; mp 144–146 °C; R_f 0.56 (50% EtOAc–petrol); ν_{max} (film) 3041, 1745, 1597, 1471, 1435, 1400, 1387, 1352, 1321, 1257, 1225, 1176, 1146, 1084, 1049, 1016, 943, 912, 879, 816, 800, 766, 729, 706, 660 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.98 (2H, d, *J* 8.0 Hz, *o*-SO_2Ar), 7.38 (2H, d, *J* 8.0 Hz, *m*-SO_2Ar), [5.92-5.88, 5.86-5.82] (2H, m, -C*H*=C*H*-), [4.91 (app d quint, *J* 15.5, 3.0 Hz), 4.46 (ddd, *J* 15.0, 7.0, 1.0 Hz)], (2H, -OCH_2-), 4.70 (1H, dd, *J* 13.0, 4.0 Hz, Ts-CH<), [3.16-3.10, 2.69-2.61], (2H, m, Ts-CH-CH_2-CH=), 2.45 (3H, s, Ts-CH_3); δ_C (67.5 MHz, $CDCl_3$) 166.7 (C=O), 145.7 (4°), 133.6, (4°), 130.6 (3°), 129.7 (3°), 129.5 (3°), 124.3, (3°), 64.3 (Ts-CH<), 64.0 (-OCH_2-), 27.1 (Ts-CH-*C*H_2-CH=), 21.8 (Ts-CH_3); *m/z* (CI) 284 $[M+NH_4]^+$, 189, 174, 130, 77 (Found: $[M+NH_4]^+$, 284.0957. $C_{13}H_{14}O_4S$ requires $[M+NH_4]^+$, 284.0957) (Found: C, 58.51; H, 5.47. $C_{13}H_{14}O_4S$ requires C, 58.63; H, 5.30%).

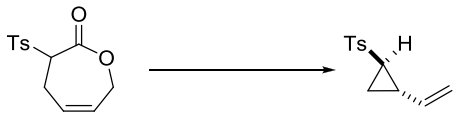
*(1*R**,2*S**)-1-Tosyl-2-vinylcyclopropanecarboxylic acid* **14**



13 **14**

A solution of lactone **13** (150 mg, 560 μmol, 1.0 equiv.) in CH_2Cl_2 (6 mL) was treated with KOAc (5.5 mg, 56.0 μmol, 0.1 equiv.) and BSA (140 μl, 560 μmol, 1.0 equiv.). The reaction mixture was stirred at rt for 16 h, then diluted with CH_2Cl_2, washed with 2 M aq. HCl and H_2O, dried ($MgSO_4$) and concentrated under reduced pressure to give (1*R**,2*S**)-1-tosyl-2-vinylcyclopropanecarboxylic acid **14** (150 mg, 100%) as a colourless solid; mp 118–120 °C; ν_{max} (nujol) 3339, 2717, 2590, 1694, 1596, 1318, 1289, 1145, 1084, 929, 817, 726, 665 cm^{-1}; δ_H (270 MHz, DMSO-d_6) 7.78 (2H, d, *J* 8.0 Hz, *o*-SO_2Ar), 7.33 (2H, d, *J* 8.0 Hz, *m*-SO_2Ar), 5.58 (1H, ddd, *J* 17.0, 10.0, 8.5 Hz, C*H*=CH_2), 5.39 (1H, dd, *J* 17.0, 1.5 Hz, CH=CH_2 *cis*), 5.22 (1H, dd, *J* 10.0, 1.5 Hz, CH=CH_2 *trans*), 3.02 (1H, m, SCCH), 2.44 (3H, s, $ArCH_3$), 2.16 (1H, dd, *J* 10.0, 5.5 Hz, $SCCH_2$), 1.96 (1H, dd, *J* 8.5, 5.5 Hz, $SCCH_2$); δ_C (100 MHz, DMSO-d_6) 168.0 (C=O), 145.2, 136.0 (4°), 130.6, 129.8, 128.8 (3°), 121.2 (CH=*C*H_2), 50.5 (SC), 33.0 (SC*C*H), 21.7 ($ArCH_3$), 20.3 (SC*C*H_2); *m/z* (CI) 284 $[M+NH_4]^+$, 242, 240, 174, 162, 145, 102, 85 (Found: $[M+NH_4]^+$, 284.0964. $C_{13}H_{14}O_4S$ requires $[M+NH_4]^+$, 284.0957).

p-*Tolyl (1*R**,2*S**)-2-vinylcyclopropyl sulfone* **15**

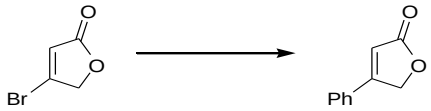


13 **15**

According to general procedure **H**, lactone **13** (150 mg, 560 μmol, 1.0 equiv.) in DMF (mL) was treated with BSA (140 μl, 560 μmol, 1.0 equiv.) and KOAc (5.53 mg, 56.0 μmol, 0.1 equiv.) to give *p*-tolyl (1*R**,2*S**)-2-vinylcyclopropyl sulfone **15** (110 mg, 88%) as a yellow oil; R_f 0.59 (50% EtOAc–petrol); ν_{max} (film) 3086, 3041, 2925, 1639, 1598, 1495, 1444, 1402, 1343, 1313, 1147, 1089, 942, 914, 858, 816, 743, 666, 646 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 7.76 (2H, d, *J* 8.0 Hz, *o*-SO_2Ar), 7.44 (2H, d, *J* 8.0 Hz, *m*-SO_2Ar), 5.38 (1H, ddd, *J* 17.0, 10.0, 8.5 Hz, C*H*=CH_2), 5.22 (1H, d, *J* 17.0 Hz, CH=CH_2 *cis*), 4.97 (1H, d, *J* 10.0 Hz, CH=CH_2 *trans*), 2.95 (1H, m, SCH), 2.40 (3H, s, $ArCH_3$), 2.24 (1H, m, SCHC*H*), [1.44, 1.17] (2H, 2 × m, SCHCH_2); δ_C (100 MHz, DMSO-d_6) 144.0, 137.6 (4°), 136.1, 129.9, 127.1 (3°), 116.1 (CH=*C*H_2), 38.7 (SCH), 22.3 (SCH*C*H), 21.0 ($ArCH_3$), 12.3 (SCH*C*H_2); *m/z* (CI) 240 $[M+NH_4]^+$, 223, 84, 67 (Found $[M+NH_4]^+$, 240.1067. $C_{12}H_{14}O_2S$ requires $[M+NH_4]^+$, 240.1058).

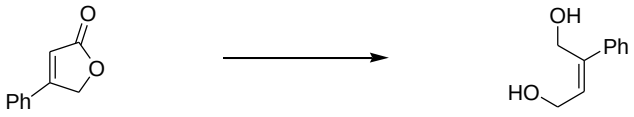
4. Synthesis of aryl-substituted substrate precursors

*4-Phenylfuran-2(*5H*)-one*



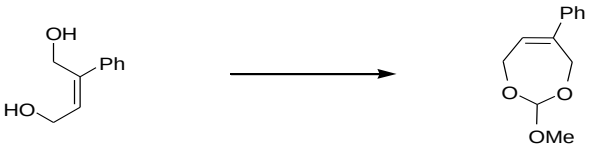
Phenylboronic acid (76 mg, 0.62 mmol, 1.0 equiv.), 4-bromofuran-2(5*H*)-one[3] (100 mg, 0.62 mmol, 1.0 equiv.) and $PdCl_2(PPh_3)_2$ (8.7 mg, 2.0 mol%) in 2 M aq. KF (2 mL) and THF (2 mL) were heated under reflux for 5 h. After cooling to rt the layers were separated and the aqueous layer further extracted with EtOAc (×3). The combined organic extracts were washed with sat. aq. NaCl, dried ($MgSO_4$) and concentrated under reduced pressure to give 4-phenylfuran-2(5*H*)-one as a colourless solid; R_f 0.57 (1% AcOH–EtOAc); ν_{max} (film) 3111, 2929, 1793, 1734, 1621, 1450, 1331, 1167, 1048, 894, 862, 771, 684 cm^{-1}; δ_H (400 MHz) 7.50 (5H, m, Ph), 6.38 (1H, t, *J* 1.5 Hz, CH), 5.23 (2H, d, *J* 1.5 Hz, CH_2); δ_C (100 MHz) 173.9 (C=O), 163.9, 131.8 (4°), 129.7, 129.3, 126.4 (3°), 113.1 (CH), 71.0 (CH_2); *m/z* (CI) 178 $[M+NH_4]^+$; data were in accordance with those previously reported.[4]

*(*Z*)-2-Phenylbut-2-ene-1,4-diol*



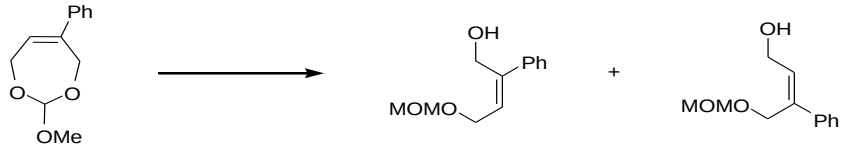
According to general procedure **I**, a solution of 4-phenylfuran-2(5*H*)-one (950 mg, 5.93 mmol, 1.0 equiv.) in PhMe (10 mL) was treated with DIBAL-H (1.7 M in PhMe; 7.68 mL, 13.0 mmol, 2.2 equiv.). Purification by chromatography (50–70% EtOAc–petrol) gave (*Z*)-2-phenylbut-2-ene-1,4-diol (793 mg, 81%) as a colourless oil; R_f 0.08 (50% EtOAc–petrol); ν_{max} (film) 3298, 2885, 1685, 1598, 1493, 1445, 1000, 758, 697 cm^{-1}; δ_H (300 MHz) 7.45 (2H, m, *m*-Ph), 7.35 (3H, m, *o*-/*p*–Ph), 6.12 (1H, t, *J* 7.0 Hz, CH), 4.59 (2H, s, CC*H*$_2$OH), 4.42 (2H, d, *J* 7.0 Hz, CHC*H*$_2$), 2.04 (2H, s, OH); δ_C (75 MHz) 142.9, 140.4 (4°), 129.8, 128.6, 127.8, 126.4 (3°), 60.4 (C*C*H_2OH), 59.0 (CH*C*H_2OH); *m/z* (CI) 182 $[M+NH_4]^+$, 164, 146, 118, 103, 91, 78; (Found $[M+NH_4]^+$, 182.1175. $C_{10}H_{12}O_2$ requires $[M+NH_4]^+$, 182.1176) (Found: C, 73.15; H, 7.37. $C_{10}H_{12}O_2$ requires C, 73.21; H, 7.40); data were in accordance with those previously reported.[5]

2-Methoxy-5-phenyl-4,7-dihydro-1,3-dioxepine



According to general procedure **A**, a solution of (*Z*)-2-phenylbut-2-ene-1,4-diol (3.67 g, 22.6 mmol, 1.0 equiv.) in CH_2Cl_2 (60 mL) was treated with CSA (52.5 mg, 0.23 mmol, 1 mol%) and trimethyl orthoformate (4.96 mL, 45.3 mmol, 2.0 equiv.). Purification by chromatography (20–40% EtOAc–petrol) gave 2-methoxy-5-phenyl-4,7-dihydro-1,3-dioxepine (3.64 g, 78%) as a colourless oil; R_f 0.59 (50% EtOAc–petrol); ν_{max} (film) 2940, 2869, 2842, 1599, 1494, 1446, 1344, 1279, 1209, 1133, 1102, 1088, 1034, 753, 701 cm^{-1}; δ_H (300 MHz) 7.29 (5H, m, Ph), 5.88 (1H, tt, *J* 4.0, 1.0 Hz, C*H*CH_2), 5.47 (1H, s, OCH), 4.88 (1H, dd, *J* 15.5, 2.0 Hz, CCH_2), 4.61 (1H, dddd *J* 16.0, 4.0, 2.0, 2.0 Hz, CHC*H*$_2$), 4.50 (1H, ddd, *J* 16.0, 3.5, 1.5 Hz, CCH_2), 4.28 (1H, dddd, *J* 16.0, 4.0, 2.0, 2.0 Hz, CHC*H*$_2$), 3.45 (3H, s, CH_3); δ_C (75 MHz) 141.1, 139.5 (4°), 128.5, 127.5, 126.3, 126.1 (3°), 113.8 (CHO), 64.0 (C*C*H_2O), 61.3 (CH*C*H_2O), 53.6 (CH_3); *m/z* (ESI) 229 $[M+Na]^+$, 206, 147, 129, 115, 91, 78 (Found $[M+Na]^+$, 229.0835. $C_{12}H_{14}O_3$ requires $[M+Na]^+$, 229.0835) (Found: C, 69.79; H, 6.90. $C_{12}H_{14}O_3$ requires C, 69.88; H, 6.84).

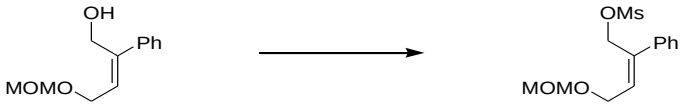
(Z)-4-Methoxymethoxy-2-phenylbut-2-en-1-ol and (Z)-4-methoxymethoxy-3-phenylbut-2-en-1-ol



According to general procedure **B**, a solution of 2-methoxy-5-phenyl-4,7-dihydro-1,3-dioxepine (4.64 g, 22.5 mmol, 1.0 equiv.) in PhMe (4.0 mL) was treated with DIBAL-H (1.2 M in PhMe; 41.2 mL, 49.5 mmol, 1.3 equiv.) Purification by chromatography (25% EtOAc–petrol) gave (*Z*)-4-methoxymethoxy-2-phenylbut-2-en-1-ol and (*Z*)-4-methoxymethoxy-3-phenylbut-2-en-1-ol (3.73 g, 80%; ratio 69:31; separable by chromatography) as colourless oils; (*Z*)-4-methoxymethoxy-2-phenylbut-2-en-1-ol: R_f 0.28 (50% EtOAc–heptane); ν_{max} (film) 3411, 2934, 2884, 1493, 1445, 1377, 1149, 1089, 1033, 1013, 945, 917, 766, 697 cm^{-1}; δ_H (300 MHz) 7.49 (2H, m, *m*-Ph), 7.39–

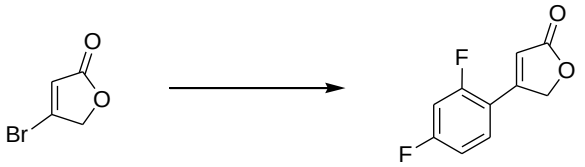
7.29 (3H, m, *o*-/*p*-Ph), 6.04 (1H, t, *J* 7.0 Hz, CH), 4.71 (2H, s, OCH_2O), 4.55 (2H, d, *J* 6.5 Hz, CCH_2OH), 4.35 (2H, d, *J* 7.0 Hz, $CHCH_2$), 3.42 (3H, s, CH_3), 2.37 (1H, t, *J* 6.5 Hz, OH); δ_C (75 MHz) 144.1, 140.5 (4°), 128.5, 127.8, 126.5, 126.4 (3°), 95.3 (OCH_2O), 63.2 (CH_2OH), 60.2 ($CHCH_2$), 55.4 (OCH_3); *m/z* (CI) 226 $[M+NH_4]^+$, 129 (Found $[M+NH_4]^+$, 226.1438. $C_{12}H_{16}O_3$ requires $[M+NH_4]^+$, 226.1438) (Found: C, 69.29; H, 7.72. $C_{12}H_{16}O_3$ requires C, 69.21; H, 7.74); (*Z*)-4-methoxymethoxy-3-phenylbut-2-en-1-ol: R_f 0.22 (50% EtOAc–heptane); ν_{max} (film) 3388, 2932, 2883, 1494, 1446, 1384, 1210, 1147, 1097, 1034, 945, 920, 757, 699 cm^{-1}; δ_H (300 MHz) 7.48 (2H, m, *m*-Ph), 7.32 (3H, m, *o*-/*p*-Ph), 6.27 (1H, t, *J* 7.0 Hz, CH), 4.66 (2H, s, OCH_2O), 4.56 (2H, s, CCH_2), 4.38 (2H, d, *J* 6.5 Hz, CH_2OH), 3.38 (3H, s, CH_3); δ_C (100 MHz) 140.5, 138.4 (4°), 131.8, 128.5, 127.7, 126.3 (3°), 95.1 (OCH_2O), 63.7 (CH_2OH), 58.9 ($CHCH_2$), 55.5 (OCH_3); *m/z* (CI) 226 $[M+NH_4]^+$, 191, 161, 159, 131, 129 (Found $[M+NH_4]^+$, 226.1438. $C_{12}H_{16}O_3$ requires $[M+NH_4]^+$, 226.1438) (Found: C, 69.27; H, 7.80. $C_{12}H_{16}O_3$ requires C, 69.21; H, 7.74).

Methanesulfonic acid (Z)-4-methoxymethoxy-2-phenylbut-2-enyl ester



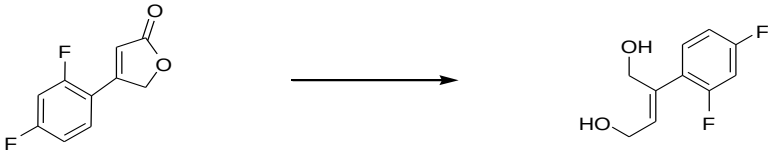
According to general procedure **C**, a solution of (*Z*)-4-methoxymethoxy-2-phenylbut-2-en-1-ol (122 mg, 0.59 mmol, 1.0 equiv.) in CH_2Cl_2 (2 mL) was treated with NEt_3 (245 μL, 1.76 mmol, 3.0 equiv.) and MsCl (90.7 μL, 1.17 mmol, 2.0 equiv.) to give methanesulfonic acid (*Z*)-4-methoxymethoxy-2-phenylbut-2-enyl ester (162 mg, 96%) as a colourless oil which was without further purification; R_f 0.34 (50% EtOAc–heptane); ν_{max} (film) 3025, 2937, 2888, 1447, 1354, 1174, 1150, 1103, 1037, 929, 845, 772, 699 cm^{-1}; δ_H (400 MHz) 7.43 (2H, m, *o*-Ph), 7.35 (3H, m, *m*-/*p*-Ph), 6.26 (1H, t, *J* 6.5 Hz, CH), 5.21 (2H, s, CCH_2), 4.70 (2H, s, OCH_2O), 4.39 (2H, d, *J* 6.5 Hz, $CHCH_2$), 3.41 (3H, s, OCH_3), 2.90 (3H, s, SCH_3); δ_C (100 MHz) 138.6, 135.6 (4°), 132.0, 128.6, 128.3, 126.3 (3°), 96.0 (OCH_2O), 65.8 (CH_2OS), 63.3 ($CHCH_2$), 55.5 (OCH_3), 38.2 (SO_2CH_3); *m/z* (CI) 304 $[M+NH_4]^+$ (Found $[M+NH_4]^+$, 304.1226. $C_{13}H_{18}O_5S$ requires $[M+NH_4]^+$, 304.1219).

*4-(2,4-Difluorophenyl)furan-2(5*H*)-one*



To 4-bromofuran-2(5*H*)-one (2.0 g, 12.3 mmol, 1.0 equiv.) and $PdCl_2(PPh_3)_2$ (172 mg, 0.25 mmol, 2 mol%) in 2 M aq. KF (40 mL) and THF (40 mL) was added 2,4-difluorophenylboronic acid (1.94 g, 12.3 mmol, 1.0 equiv.) and the mixture heated under reflux for 5 h. After cooling to rt the layers were separated and the aqueous layer extracted with EtOAc (×3). The combined organic phases were washed with sat. aq. NaCl, dried (Na_2SO_4) and concentrated under reduced pressure. Purification by chromatography (20–40% EtOAc–petrol) gave 4-(2,4-difluorophenyl)furan-2(5*H*)-one (2.39 g, 99%) as a colourless solid; R_f 0.40 (50% EtOAc–petrol); ν_{max} (film) 3118, 3059, 1799, 1735, 1618, 1609, 1585, 1508, 1490, 1456, 1425, 1333, 1266, 1163, 1148, 1106, 1049, 996, 961, 897, 888, 872, 809, 734 cm^{-1}; δ_H (300 MHz) 7.48 (1H, m, *o*-ArF), 6.99 (2H, m, *m*-ArF), 6.49 (1H, t, *J* 2.0 Hz, CH), 5.24 (2H, d, *J* 2.0 Hz, CH_2); δ_C (75 MHz) 173.4 (C=O), 166.5, 166.4, 163.3, 163.2, 163.1, 162.9, 159.9, 159.7, (CF), 157.3 (4°), 129.5, 129.4 (3°), 115.9, 115.9, 115.8, 115.8 (CFCH*C*H), 114.7, 114.6, 114.5 (*C*CF), 112.9, 112.8, 112.6, 112.6 (CF*C*HCH), 105.8, 105.4, 105.1 (CF*C*HCF) 71.7 (CH_2); *m/z* (EI) 214 $[M+NH_4]^+$, 197 (Found $[M+H]^+$, 197.0409. $C_{10}H_6F_2O_2$ requires $[M+H]^+$, 197.0409) (Found: C, 61.29; H, 3.06. $C_{10}H_6F_2O_2$ requires C, 61.23; H, 3.08); data were in accordance with those previously reported.[6]

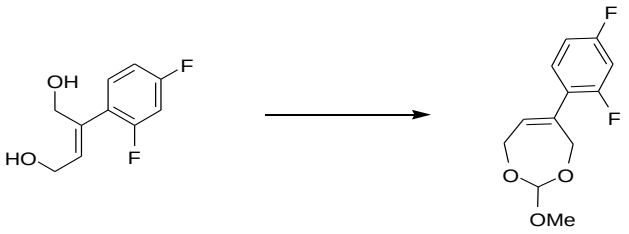
*(*Z*)-2-(2,4-Difluorophenyl)but-2-ene-1,4-diol*



According to general procedure **I**, a solution of 4-(2,4-difluorophenyl)furan-2(5*H*)-one (602 mg, 3.07 mmol, 1.0 equiv.) in PhMe (5 mL) was treated with DIBAL-H (1.7 M in PhMe; 3.97 mL, 6.75 mmol, 2.2 equiv.). Purification by chromatography (50–70% EtOAc–petrol) gave (*Z*)-2-(2,4-difluorophenyl)but-2-ene-1,4-diol (262 mg, 42%) as a colourless oil; R_f 0.10 (50% EtOAc–petrol); ν_{max} (film) 3305, 2884, 1613, 1592,

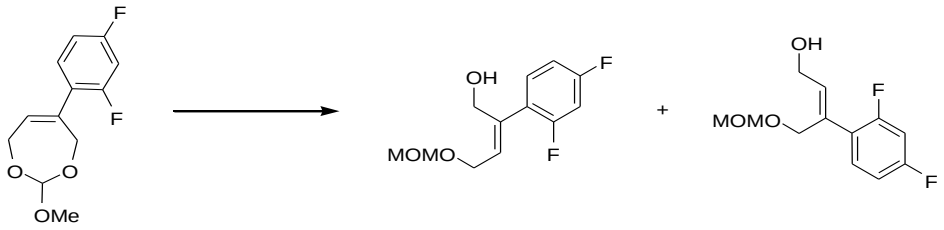
1500, 1421, 1265, 1138, 1095, 997, 965, 847, 811, 723 cm^{-1}; δ_H (400 MHz) 7.28 (1H, m, *o*-ArF), 6.84 (2H, m, *m*-ArF), 6.00 (1H, t, *J* 6.5 Hz, CH), 4.49 (2H, s, CC*H*$_2$OH), 4.40 (2H, d, *J* 6.5 Hz, CHC*H*$_2$), 2.22 (2H, br s, OH); δ_C (100 MHz) 163.7, 163.6, 161.2, 161.1, 160.9, 160.8, 158.7, 158.6 (CF), 138.2 (4°), 133.4 (3°), 131.1, 131.0 (CFCH*C*H), 128.6, 128.5 (*C*CF), 111.6, 111.5, 111.4, 111.3 (CF*C*HCH), 104.3, 104.1, 103.8 (CF*C*HCF), 61.1 (C*C*H$_2$), 58.8 (CH*C*H$_2$); *m/z* (CI) 218 $[M+NH_4]^+$, 182; (Found: C, 60.08; H, 5.00. $C_{10}H_{10}F_2O_2$ requires C, 60.00; H, 5.04).

5-(2,4-Difluorophenyl)-2-methoxy-4,7-dihydro-1,3-dioxepine



According to general procedure **A**, a solution of (*Z*)-2-(2,4-difluorophenyl)but-2-ene-1,4-diol (250 mg, 1.24 mmol, 1.0 equiv.) in CH_2Cl_2 (5 mL) was treated with CSA (14.5 mg, 0.062 mmol, 5 mol%) and trimethyl orthoformate (545 μL, 4.98 mmol, 4.0 equiv.). Purification by chromatography (20–50% EtOAc–petrol) gave 5-(2,4-difluorophenyl)-2-methoxy-4,7-dihydro-1,3-dioxepine (300 mg, 100%) as a colourless solid; mp 39–41°C; R_f 0.54 (50% EtOAc–heptane); ν_{max} (film) 2942, 2845, 1614, 1591, 1500, 1424, 1266, 1134, 1097, 1068, 1023, 966, 847, 798, 733 cm^{-1}; δ_H (300 MHz) 7.18 (1H, m, *o*-ArF), 6.80 (2H, m, *m*-ArF), 5.80 (1H, t, *J* 4.0 Hz, C*H*CH$_2$), 5.45 (1H, s, OCH), 4.74 (1H, ddd, *J* 15.5, 2.0, 2.0 Hz, CCH$_2$), 4.59 (1H, dddd *J* 16.5, 4.0, 2.0, 2.0 Hz, CHC*H*$_2$), 4.39 (1H, dddd, *J* 15.5, 3.5, 2.0, 2.0 Hz, CCH$_2$), 4.26 (1H, dddd, *J* 16.5, 4.0, 2.0, 2.0 Hz, CHC*H*$_2$), 3.43 (CH_3); δ_C (75 MHz) 164.1, 164.0, 161.5, 161.3, 160.8, 160.7, 158.2, 158.0 (CF), 136.5, (4°), 130.5, 130.3 (CFCH*C*H), 129.5, (3°), 124.0, 123.9, 123.8, 123.7 (*C*CF), 113.8 (CHO), 111.6, 111.5, 111.3, 111.2 (CF*C*HCH), 104.5, 104.1, 103.8 (CF*C*HCF), 63.9, 63.8 (C*C*H$_2$O), 61.1 (CH*C*H$_2$O), 53.7 (CH_3); *m/z* (ESI) 265 $[M+Na]^+$, 183, 165, 151, 127 (Found $[M+Na]^+$, 265.0646. $C_{12}H_{12}F_2O_3$ requires $[M+Na]^+$, 265.0647) (Found: C, 59.59; H, 4.89. $C_{12}H_{12}F_2O_3$ requires C, 59.50; H, 4.99).

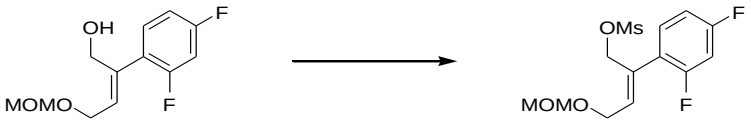
(Z)-2-(2,4-Difluorophenyl)-4-(methoxymethoxy)but-2-en-1-ol and *(Z)-3-(2,4-difluorophenyl)-4-(methoxymethoxy)but-2-en-1-ol*



According to general procedure **B**, to a solution of 5-(2,4-difluorophenyl)-2-methoxy-4,7-dihydro-1,3-dioxepine (781 mg, 3.22 mmol, 1.0 equiv.) in PhMe (8.3 mL) was treated with DIBAL-H (1.7 M in PhMe; 2.47 mL, 4.19 mmol, 1.3 equiv.). Purification by chromatography (20% EtOAc–petrol) gave (*Z*)-2-(2,4-difluorophenyl)-4-(methoxymethoxy)but-2-en-1-ol and (*Z*)-3-(2,4-difluorophenyl)-4-(methoxymethoxy)but-2-en-1-ol (739 mg, 94%; ratio 68:32; separable by chromatography) as colourless oils; (*Z*)-2-(2,4-difluorophenyl)-4-(methoxymethoxy)but-2-en-1-ol: R_f 0.25 (50% EtOAc–petrol); ν_{max} (film) 3394, 2939, 2886, 1616, 1592, 1501, 1422, 1266, 1139, 1097, 967, 850, 815 cm^{-1}; δ_H (300 MHz) 7.30 (1H, m, *o*-ArF), 6.83 (2H, m, *m*-ArF), 5.90 (1H, t, *J* 7.0 Hz, CH), 4.71 (2H, s, OCH_2O), 4.47 (2H, d, *J* 5.5 Hz, CCH_2OH), 4.34 (2H, d, *J* 7.0 Hz, $CHCH_2$), 3.41 (3H, s, CH_3), 2.22 (1H, t, *J* 6.0 Hz, OH); δ_C (100 MHz) 163.7, 163.5, 161.2, 161.1, 158.5, 158.6 (CF), 138.9 (4°), 131.1, 131.0 (CFCH*C*H), 130.2 (3°), 125.1, 124.9 (*C*CF), 111.5, 111.4, 111.3, 111.2 (CF*C*HCH), 104.3, 104.1, 103.8 (CF*C*HCF), 95.6 (OCH_2O), 63.0 (CH_2OH), 60.7, 60.6 ($CHCH_2O$), 55.4 (CH_3); *m/z* (CI) 262 $[M+NH_4]^+$, 227, 183 (Found $[M+NH_4]^+$, 262.1249. $C_{12}H_{14}F_2O_3$ requires $[M+NH_4]^+$, 262.1249) (Found: C, 58.92; H, 5.69. $C_{12}H_{14}F_2O_3$ requires C, 59.01; H, 5.78); (*Z*)-3-(2,4-difluorophenyl)-4-(methoxymethoxy)but-2-en-1-ol: R_f 0.19 (50% EtOAc–petrol); ν_{max} (film) 3404, 2945, 2887, 1616, 1593, 1501, 1422, 1266, 1140, 1097, 1039, 1007, 966, 919, 850, 815 cm^{-1}; δ_H (300 MHz) 7.29 (1H, m, *o*-ArF), 6.83 (2H, m, *m*-ArF), 6.07 (1H, t, *J* 7.0 Hz, CH), 4.62 (2H, s, OCH_2O), 4.47 (2H, s, CCH_2), 4.37 (2H, t, *J* 6.0 Hz, CH_2OH), 3.34 (3H, s, CH_3) 2.14 (1H, t, *J* 6.0 Hz, OH); δ_C (75 MHz) 164.0, 163.9, 161.7, 161.5, 160.7, 160.6, 158.4, 158.3 (CF), 134.9 (3°), 134.1(4°), 131.0, 130.9, 130.9, 130.8, (CFCH*C*H), 125.2, 125.1, 125.0, 124.9 (*C*CF), 111.4, 111.4, 111.2, 111.1 (CF*C*HCH), 104.4, 104.0, 103.7 (CF*C*HCF), 95.4 (OCH_2O), 64.4 (CH_2OH), 58.7 (CCH_2) 55.5 (CH_3); *m/z* (EI) 262 $[M+NH_4]^+$, 227, 197, 167 (Found $[M+NH_4]^+$,

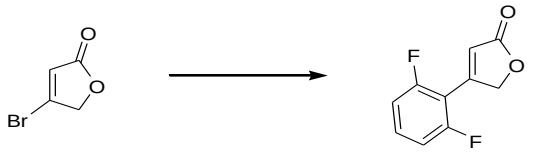
262.1249. $C_{12}H_{14}F_2O_3$ requires $[M+NH_4]^+$, 262.1249) (Found: C, 59.14; H, 5.67. $C_{12}H_{14}F_2O_3$ requires C, 59.01; H, 5.78).

*Methanesulfonic acid (*Z*)-2-(2,4-difluorophenyl)-4-(methoxymethoxy)but-2-enyl ester*



According to general procedure **C**, to a solution of (*Z*)-2-(2,4-difluorophenyl)-4-(methoxymethoxy)but-2-en-1-ol (68 mg, 0.28 mmol, 1.0 equiv.) in CH_2Cl_2 (1 mL) was treated with NEt_3 (116 μL, 0.84 mmol, 3.0 equiv.) and MsCl (43.1 μL, 0.56 mmol, 2.0 equiv.) to give methanesulfonic acid (*Z*)-2-(2,4-difluorophenyl)-4-(methoxymethoxy)but-2-enyl ester (84 mg, 93%) as a colourless oil, which was used without further purification; R_f 0.35 (50% EtOAc–petrol); ν_{max} (film) 2942, 1615, 1592, 1502, 1353, 1267, 1172, 1141, 1099, 1048, 1030, 920, 846, 807 cm^{-1}; δ_H (400 MHz) 7.28 (1H, m, *o*-ArF), 6.86 (2H, m, *m*-ArF), 6.07 (1H, t, *J* 6.5 Hz, CH), 5.13 (2H, s, CCH_2), 4.69 (2H, s, OCH_2O), 4.36 (2H, d, *J* 6.5 Hz, $CHC\mathit{H}_2$), 3.41 (3H, s, OCH_3), 2.92 (3H, s, SCH_3); δ_C (100 MHz) 164.0, 163.9, 161.5, 161.4, 161.2, 161.1, 158.7, 158.6 (CF), 134.8 (4°), 134.8 (3°), 131.3, 131.3, 131.2, 131.2 (CFCH*C*H), 123.1, 123.1, 123.0, 123.0 (*C*CF), 111.8, 111.8, 111.6, 111.5 (CF*C*HCH), 104.5, 104.2, 104.0 (CF*C*HCF), 96.0 (OCH_2O), 66.3, 66.3 ($CH\mathit{C}H_2$), 63.0 ($\mathit{C}CH_2$), 55.5 (OCH_3), 37.7 (SCH_3); *m/z* (CI) 340 $[M+NH_4]^+$, 165 (Found $[M+NH_4]^+$, 340.1025. $C_{11}H_{16}F_2O_5S$ requires $[M+NH_4]^+$, 340.1025).

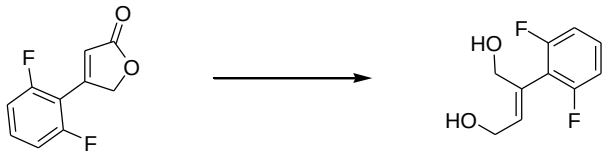
*4-(2,6-Difluorophenyl)furan-2(5*H*)-one*



To 4-bromofuran-2(5*H*)-one (4.25 g, 26.1 mmol, 1.0 equiv.) and $PdCl_2(PPh_3)_2$ (366 mg, 0.52 mmol, 2 mol%) in 2 M aq. KF (87 mL) and THF (87 mL) was added 2,6-difluorophenylboronic acid (4.12 g, 26.1 mmol, 1.0 equiv.) and the mixture heated under reflux for 5 h. After cooling to rt the layers were separated and the aqueous layer further extracted with EtOAc (×3). The combined organic phases were washed with sat. aq. NaCl, dried ($MgSO_4$) and concentrated under reduced pressure.

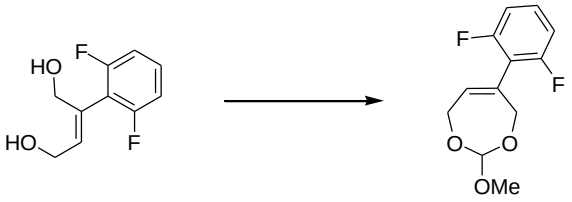
Purification by chromatography (30–50% EtOAc–petrol) gave 4-(2,6-difluorophenyl)furan-2(5*H*)-one (4.40 g, 86%) as a colourless solid; R_f 0.52 (50% EtOAc–petrol); ν_{max} (film) 3055, 2987, 1758, 1626, 1466, 1265, 1167, 1071, 1053, 1017, 896, 868, 791, 741, 704 cm^{-1}; δ_H (400 MHz) 7.45 (1H, tt, *J* 8.5, 6.5 Hz, *p*-ArF), 7.04 (2H, dd, *J* 9.5, 8.5 Hz, *m*-ArF), 6.68 (1H, s, CH), 5.29 (2H, s, CH_2); δ_C (100 MHz) 173.3 (C=O), 162.5, 162.4, 160.0, 159.9 (CF), 153.3 (*C*CH), 133.0, 132.9, 132.8 (CFCH*C*H), 119.4, 119.3, 119.2 (C*C*H), 112.7, 112.4 (*C*HCF), 108.5, 108.4, 108.2 (*C*CF), 73.1, 73.0 (CH_2); *m/z* (CI) 197 $[M+H]^+$, 410, 214 (Found $[M+H]^+$, 197.0421. $C_{10}H_6F_2O_2$ requires $[M+H]^+$, 197.0414) (Found: C, 61.18; H, 2.99. $C_{10}H_6F_2O_2$ requires C, 61.23; H, 3.08).

(Z)-2-(2,6-Difluorophenyl)but-2-ene-1,4-diol



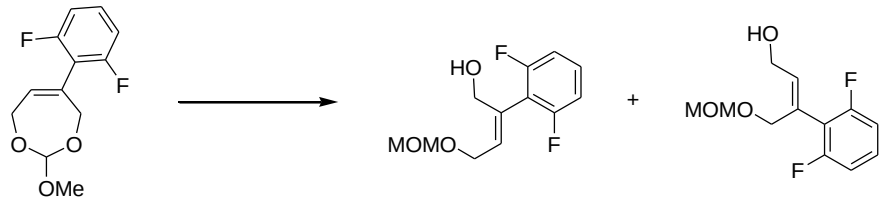
According to general procedure **I**, 4-(2,6-difluorophenyl)furan-2(5*H*)-one (4.32 g, 22.0 mmol, 1.0 equiv.) in PhMe (70 mL) was treated with DIBAL-H (1.2 M in PhMe; 40.4 mL, 48.5 mmol, 2.2 equiv.). Purification by chromatography (50% EtOAc–petrol) gave (*Z*)-2-(2,6-difluorophenyl)but-2-ene-1,4-diol (2.61 g, 60%) as a colourless oil; R_f 0.15 (50% EtOAc–petrol); ν_{max} (film) 3338, 2886, 1622, 1586, 1462, 1269, 1231, 1000, 788 cm^{-1}; δ_H (400 MHz) 7.22 (1H, tt, *J* 8.5, 6.5 Hz, *p*-ArF), 6.90 (2H, t, *J* 8.0 Hz, *m*-ArF), 6.00 (1H, t, *J* 6.5 Hz, CCH), 4.46 (2H, s, CCH_2), 4.45 (2H, d, *J* 7.0 Hz, CHCH_2), 2.14 (2H, br s, OH); δ_C (100 MHz) 161.6, 161.5, 159.1, 159.1 (CF) 136.0 (*C*HCH_2OH), 131.3 (*C*CH_2), 128.9, 128.8 (CFCH*C*H), 118.1 (*C*CF), 111.6, 111.5, 111.4, 111.3 (CF*C*H), 61.3 (C*C*H_2), 58.9 (CH*C*H_2); *m/z* (CI) 218 $[M+NH_4]^+$, 200 (Found $[M+NH_4]^+$, 218.0999. $C_{10}H_{10}F_2O_2$ requires $[M+NH_4]^+$, 218.0993) (Found: C, 59.97; H, 5.01. $C_{10}H_{10}F_2O_2$ requires C, 60.00; H, 5.04).

5-(2,6-Difluorophenyl)-2-methoxy-4,7-dihydro-1,3-dioxepine



According to general procedure **A**, (*Z*)-2-(2,6-difluorophenyl)but-2-ene-1,4-diol (1.60 g, 7.99 mmol, 1.0 equiv.) in CH_2Cl_2 (20 mL) was treated with CSA (18.6 mg, 0.08 mmol, 1 mol%) and trimethyl orthoformate (1.75 mL, 16.0 mmol, 2.0 equiv.). Purification by chromatography (20→50% EtOAc–petrol) gave 5-(2,6-difluorophenyl)-2-methoxy-4,7-dihydro-1,3-dioxepine (1.77 mg, 91%) as a yellow liquid; R_f 0.67 (50% EtOAc–petrol); ν_{max} (film) 2945, 2874, 2846, 1621, 1583, 1567, 1463, 1388, 1344, 1270, 1230, 1212, 1136, 1035, 998, 915, 814, 784, 722 cm^{-1}; δ_H (400 MHz) 7.22 (1H, tt, *J* 8.5, 6.5 Hz, *p*-ArF), 6.91 (2H, t, *J* 8.0 Hz, *m*-ArF), 5.92 (1H, t, *J* 3.5 Hz, C*H*CH_2), 5.49 (1H, s, OCH), 4.69 (2H, m, CCH_2), 4.38 (2H, m, CHC*H*$_2$), 3.47 (3H, s, CH_3); δ_C (100 MHz) 161.4, 161.3, 158.9, 158.8 (CF) 132.3 (*C*CH_2), 129.7 (*C*HCH_2), 128.9, 128.8, 128.7 (CFCH*C*H), 116.7 (*C*CF), 113.7 (CHO), 111.7, 111.6, 111.5, 111.4 (CF*C*H), 63.9 (C*C*H_2), 61.3 (CH*C*H_2), 53.7 (CH_3); *m/z* (CI) 143 $[M+H]^+$, 502, 260, 228, 211, 200, 182 (Found $[M+H]^+$, 243.0841. $C_{12}H_{12}F_2O_3$ requires $[M+H]^+$, 243.0833) (Found: C, 59.58; H, 5.05. $C_{12}H_{12}F_2O_3$ requires C, 59.50; H, 4.99).

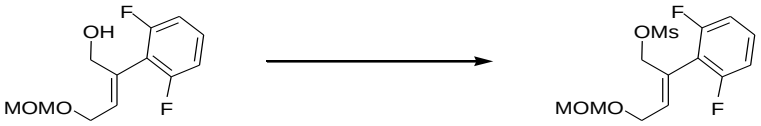
(Z)-2-(2,6–Difluorophenyl)-4-(methoxymethoxy)but-2-en-1-ol and *(Z)-3-(2,6-difluorophenyl)-4-(methoxymethoxy)but-2-en-1-ol*



According to general procedure **B**, 5-(2,6-difluorophenyl)-2-methoxy-4,7-dihydro-1,3-dioxepine (2.78 g, 11.48 mmol, 1.0 equiv.) in PhMe (36.4 mL) was treated with DIBAL-H (1.2 M in PhMe; 21.0 mL, 25.3 mmol, 2.2 equiv.). Purification by chromatography (5→10% Et_2O–CH_2Cl_2) gave (*Z*)-2-(2,6-difluorophenyl)-4-(methoxymethoxy)but-2-en-1-ol and (*Z*)-3-(2,6-difluorophenyl)-4-methoxymethoxy-but-2-en-1-ol (2.32 g, 82%; ratio 66:34; separable by chromatography) as colourless

oils; (*Z*)-2-(2,6-difluorophenyl)-4-(methoxymethoxy)but-2-en-1-ol: R_f 0.39 (20% Et_2O–CH_2Cl_2); ν_{max} (film) 3433, 2939, 1622, 1585, 1462, 1268, 1231, 1150, 1101, 1043, 996, 788 cm^{-1}; δ_H (400 MHz) 7.21 (1H, tt, *J* 8.5, 6.5 Hz, *p*-ArF), 6.90 (2H, t, *J* 8.0 Hz, *m*-ArF), 5.87 (1H, t, *J* 7.0 Hz, CH), 4.73 (2H, s, OCH_2O), 4.42 (2H, s, CCH_2OH), 4.37 (2H, d, *J* 7.0 Hz, $CHCH_2$), 3.42 (3H, s, CH_3), 2.16 (1H, br s, OH); δ_C (100 MHz) 161.7, 161.6, 159.2, 159.1 (CF), 132.9 (CCH_2), 132.4 ($CHCH_2$), 129.0, 128.9, 128.8 (CFCH*C*H), 118.3, 118.1, 117.9 (*C*CF), 111.5, 111.5, 111.4, 111.3 (CF*C*H), 95.3 (OCH_2O), 62.5 (CH_2OH), 60.8 ($CHCH_2$), 55.5 (CH_3); *m/z* (CI) 262 $[M+NH_4]^+$, 506, 230 (Found $[M+NH_4]^+$, 262.1265. $C_{12}H_{14}F_2O_3$ requires $[M+NH_4]^+$, 262.1255) (Found: C, 59.01; H, 5.78. $C_{12}H_{14}F_2O_3$ requires C, 59.06; H, 5.78); (*Z*)-3-(2,6-difluorophenyl)-4-(methoxymethoxy)but-2-en-1-ol: R_f 0.31 (20% Et_2O–CH_2Cl_2); ν_{max} (film) 3412, 2932, 1623, 1463, 1268, 1231, 1150, 1101, 1053, 995, 790 cm^{-1}; δ_H (400 MHz) 7.24 (1H, tt, *J* 8.5, 6.5 Hz, *p*-ArF), 6.92 (2H, t, *J* 8.0 Hz, *m*-ArF), 6.08 (1H, t, *J* 7.0 Hz, CH), 4.65 (2H, s, OCH_2O), 4.46 (2H, s, CCH_2), 4.42 (2H, d, *J* 7.0 Hz, CH_2OH), 3.35 (3H, s, CH_3) 2.11 (1H, br s, OH); δ_C (100 MHz) 161.7, 161.6, 159.2, 159.2 (CF) 137.2 ($CHCH_2$), 128.9, 128.8, 128.7 (CFCH*C*H), 127.8 (CCH_2), 118.2, 118.0, 117.8 (*C*CF), 111.5, 111.4, 111.3 (CF*C*H), 95.0 (OCH_2O), 64.1 (CH_2OH), 58.7 (CCH_2) 55.4 (CH_3); *m/z* (CI) 262 $[M+NH_4]^+$, 506, 230 (Found $[M+NH_4]^+$, 262.1263. $C_{12}H_{14}F_2O_3$ requires $[M+NH_4]^+$, 262.1255) (Found: C, 59.12; H, 5.69. $C_{12}H_{14}F_2O_3$ requires C, 59.01; H, 5.78).

Methanesulfonic acid (Z)-2-(2,6–difluorophenyl)-4-(methoxymethoxy)but-2-enyl ester

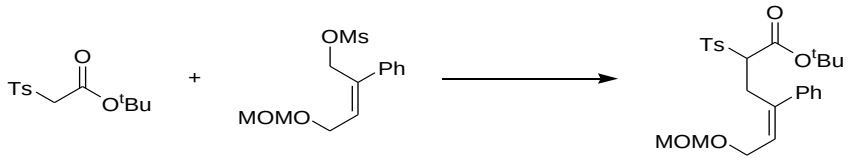


According to general procedure **C**, (*Z*)-2-(2,6-difluorophenyl)-4-(methoxymethoxy)but-2-en-1-ol (349 mg, 1.43 mmol, 1.0 equiv.) in CH_2Cl_2 (7.2 mL) was treated with NEt_3 (597 μL, 4.29 mmol, 3.0 equiv.) and MsCl (221 μL, 2.86 mmol, 2.0 equiv.) to give methanesulfonic acid (*Z*)-2-(2,6-difluorophenyl)-4-(methoxymethoxy)but-2-enyl ester as a colourless oil, used crude in the next step; R_f 0.64 (50% EtOAc–petrol); ν_{max} (film) 3436, 3004, 2934, 2887, 1622, 1586, 1464, 1360, 1329, 1271, 1254, 1196, 1151, 1104, 1047, 999, 789, 735 cm^{-1}; δ_H (400 MHz) 7.28 (1H, tt, *J* 8.5, 6.5 Hz, *o*-ArF), 6.93 (2H, t, *J* 8.0 Hz, *m*-ArF), 6.08 (1H, t, *J* 6.5 Hz,

CH), 5.11 (2H, s, CCH_2), 4.69 (2H, s, OCH_2O), 4.38 (2H, d, *J* 6.5 Hz, $CHCH_2$), 3.40 (3H, s, OCH_3), 2.93 (3H, s, SCH_3); δ_C (100 MHz) 161.6, 161.5, 159.1, 159.1 (CF), 137.3 (CCH_2), 129.8, 129.7, 129.6 ($CFCHCH$), 125.1 ($CHCH_2$), 116.2, 116.1, 115.9 (CCF), 111.7, 111.7, 111.5, 111.5 ($CFCHCH$), 95.9 (OCH_2O), 66.6 ($CHCH_2$), 62.8 (CCH_2), 55.5 (OCH_3), 37.9 (SCH_3); *m/z* (CI) 340 $[M+NH_4]^+$, 102 (Found $[M+NH_4]^+$, 340.1020. $C_{11}H_{16}F_2O_5S$ requires $[M+NH_4]^+$, 340.1030).

5. Synthesis and reactions of γ-aryl-substituted lactones 16a–c

tert-*Butyl (*E*)-6-Methoxymethoxy-4-phenyl-2-tosylhex-4-enoate*



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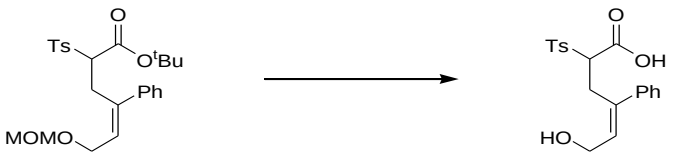
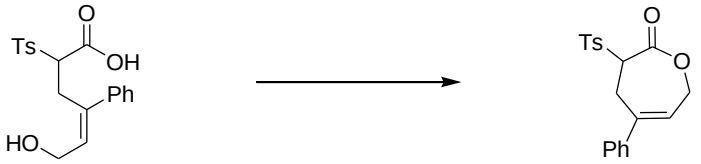
According to general procedure **D**, a suspension of sodium hydride (25 mg, 0.62 mmol, 1.1 equiv.) in THF (0.3 mL) at 0 °C was treated with *tert*-butyl 2-tosylacetate **10**[2] (153 mg, 0.57 mmol, 1.0 equiv.) in THF (0.4 mL) and methanesulfonic acid (*Z*)-4-methoxymethoxy-2-phenylbut-2-enyl ester (162 mg, 0.57 mmol, 1.0 equiv.) in THF (0.3 mL) to give *tert*-butyl (*E*)-6-methoxymethoxy-4-phenyl-2-tosylhex-4-enoate which was used without further purification; R_f 0.48 (50% EtOAc–heptane); ν_{max} (film) 2980, 2933, 1732, 1597, 1493, 1446, 1370, 1327, 1151, 1084, 1047, 919, 836, 816, 766, 714, 699, 566 cm^{-1}; δ_H (400 MHz) 7.77 (2H, d, *J* 8.0 Hz, *o*-SO_2Ar), 7.37 (2H, d, *J* 8.0 Hz, *m*-SO_2Ar), 7.29 (5H, m, Ph), 5.91 (1H, t, *J* 6.5 Hz, C*H*CH_2OH), 4.66 (2H, s, OCH_2O), 4.32 (1H, dd, *J* 13.0, 7.0 Hz, CHC*H*$_2$O), 4.18 (1H, dd, *J* 13.0, 6.0 Hz, CHC*H*$_2$O), 3.82 (1H, dd, *J* 4.5, 1.0 Hz, SCH), 3.39 (3H, s, OCH_3), 3.25 (2H, m, CHC*H*$_2$O), 2.48 (3H, s, $ArCH_3$), 1.23 (9H, s, $C(CH_3)_3$); δ_C (100 MHz) 164.3 (C=O), 145.3, 139.9, 137.6, 134.3 (4°), 129.6, 129.4, 128.7, 128.6, 127.9, 126.5 (3°), 95.9 (OCH_2O), 83.1 (*C*$(CH_3)_3$), 69.4 (SCH), 64.0 (O*C*H_2CH), 55.3 (OCH_3), 27.5 (C(*C*$H_3)_3$), 27.2 (SCH*C*H_2), 21.7 ($ArCH_3$); *m/z* (CI) 478 $[M+NH_4]^+$ (Found $[M+NH_4]^+$, 478.2260. $C_{25}H_{32}O_6S$ requires $[M+NH_4]^+$, 478.2263) (Found: C, 65.19; H, 7.00. $C_{25}H_{32}O_6S$ requires C, 65.17; H, 6.97).

*(*E*)-6-Hydroxy-4-phenyl-2-tosylhex-4-enoic acid*



According to general procedure **E**, a solution *tert*-butyl (*E*)-6-methoxymethoxy-4-phenyl-2-tosylhex-4-enoate (218 mg, 0.47 mmol, 1.0 equiv.) in MeCN (4.5 mL) was treated with 2 M aq. HCl (0.9 mL) to give (*E*)-6-hydroxy-4-phenyl-2-tosylhex-4-enoic acid, which was used without further purification.

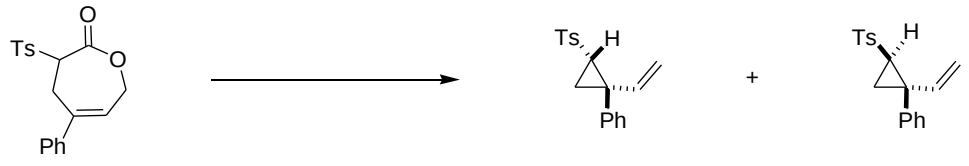
*5-Phenyl-3-tosyl-4,7-dihydrooxepin-2(3*H*)-one* **16a**



16a

According to general procedure **G**, a solution of (*E*)-6-hydroxy-4-phenyl-2-tosylhex-4-enoic acid, (109 mg, 0.30 mmol, 1.0 equiv.) in CH_2Cl_2 (0.75 mL) was treated with EDCI (63 mg, 0.33 mmol, 1.1 equiv.). Purification by chromatography (30% EtOAc–petrol) gave 5-phenyl-3-tosyl-4,7-dihydrooxepin-2(3*H*)-one **16a** (69 mg, 35% over three steps) as a colourless solid; R_f 0.40 (50% EtOAc–petrol); ν_{max} (film) 2925, 1739, 1596, 1324, 1269, 1158, 1143, 1087, 1056, 1019, 815, 746, 692, 662 cm^{-1}; δ_H (300 MHz) 7.99 (2H, d, *J* 8.5 Hz, *o*-SO_2Ar), 7.39–7.29 (7H, m, *m*-SO_2Ar and Ph), 6.07 (1H, m, C*H*CH_2O), [5.06, 5.00] (1H, 2 × dd, *J* 3.5, 3.5 Hz, SCH), [4.86, 4.82] (1H, 2 × d, *J* 4.0 Hz, OCH_2), [4.68, 4.62] (1H, 2 × d, *J* 7.5 Hz, OCH_2), [3.57, 3.51] (1H, 2 × m, SCHC*H*$_2$), 3.03 (1H, m, SCHC*H*$_2$), 2.45 (3H, s, CH_3); δ_C (75 MHz) 166.6 (C=O), 145.8, 141.4, 140.2, 133.5 (4°), 130.5, 129.7, 128.7, 125.9 (3°), 121.3 (*C*HCH_2O), 64.3 (SCH), 64.0 (OCH_2), 29.7, 29.5 (SCH*C*H_2), 21.8 ($ArCH_3$); *m/z* (CI) 360 $[M+NH_4]^+$, 187 (Found $[M+NH_4]^+$, 360.1263. $C_{19}H_{18}O_4S$ requires $[M+NH_4]^+$, 360.1264) (Found: C, 66.63; H, 5.30. $C_{19}H_{18}O_4S$ requires C, 66.65; H, 5.30).

*((1*R**,2*R**)-2-Phenyl-2-vinylcyclopropyl)* p-*tolyl sulfone* **17a** *and ((1*R**,2*S**)-2-phenyl-2-vinylcyclopropyl)* p-*tolyl sulfone* **18a**

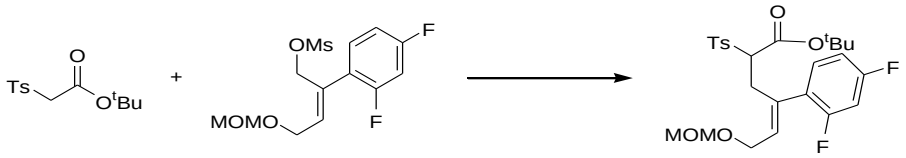


16a **17a** **18a**

According to general procedure **H**, a solution of lactone **16a** (27 mg, 0.08 mmol, 1.0 equiv.) in DMF (0.4 mL) was treated with KOAc (0.8 mg, 0.008 mmol, 0.1 equiv.) and BSA (19.1μL, 0.08 mmol, 1.0 equiv.) to give a diastereomeric mixture (3:2) of ((1*R**,2*R**)-2-phenyl-2-vinylcyclopropyl) *p*-tolyl sulfone **17a** and ((1*R**,2*S**)-2-phenyl-2-vinylcyclopropyl) *p*-tolyl sulfone **18a** (20 mg, 87%), which were separable by chromatography (20% EtOAc–petrol) as colourless oils; **17a**: R_f 0.57 (50% EtOAc–petrol); ν_{max} (film) 2924, 1633, 1598, 1446, 1403, 1318, 1266, 1148, 1088,

738, 701 cm^{-1}; δ_H (400 Hz) 7.86 (2H, d, *J* 8.0 Hz, *o*-SO_2Ar), 7.37 (2H, d, *J* 8.0 Hz, *m*-SO_2Ar), 7.24 (3H, m, *o*-/*p*-Ph), 7.04 (2H, dd, *J* 7.5, 1.5 Hz, *m*-Ph), 6.45 (1H, dd, *J* 17.0, 10.5 Hz, C*H*=CH_2), 5.18 (1H, dd, *J* 10.5, 1.0 Hz, CH=CH_2 *trans*), 4.57 (1H, dd, *J* 17.0, 1.0 Hz, CH=CH_2 *cis*), 2.89 (1H, dd, *J* 9.0, 6.0 Hz, SCH), 2.47 (3H, s, $ArCH_3$), 2.13 (1H, dd, *J* 6.0, 6.0 Hz, SCHCH_2), 1.83 (1H, dd, *J* 9.0, 5.5 Hz, SCHCH_2); δ_C (100 Hz) 144.4, 140.0, 138.2, 137.2 (4°), 129.7, 129.5, 128.5, 127.6, 127.5 (3°), 118.3 (CH=*C*H_2), 46.9 (SCH), 38.6 (SCH*C*), 21.7 ($ArCH_3$), 19.4 (SCH*C*H_2); *m/z* (CI) 316 $[M+NH_4]^+$, 143 (Found $[M+NH_4]^+$, 316.1382. $C_{18}H_{18}O_2S$ requires $[M+NH_4]^+$, 316.1371); 1**8a**: R_f 0.50 (50% EtOAc–petrol); ν_{max} (film) 3059, 2925, 1633, 1598, 1495, 1446, 1323, 1298, 1266, 1149, 1087, 914, 737, 702 cm^{-1}; δ_H (400 Hz) 7.56 (2H, d, *J* 8.0 Hz, *o*-SO_2Ar), 7.33–7.26 (7H, m, *m*-SO_2Ar and Ph), 5.64 (1H, dd, *J* 17.0, 10.5 Hz, C*H*=CH_2), 5.02 (1H, dd, *J* 10.5, 0.5 Hz, CH=CH_2 *trans*), 4.75 (1H, dd, *J* 17.0, 0.5 Hz, CH=CH_2 *cis*), 2.84 (1H, dd, *J* 8.5, 6.0 Hz, SCH), 2.43 (3H, s, $ArCH_3$), 2.25 (1H, dd, *J* 6.0, 5.5 Hz, SCHCH_2), 1.49 (1H, dd, *J* 8.5, 5.5 Hz, SCHCH_2); δ_C (100 Hz) 144.1, 141.7, 138.2, 134.8 (4°), 130.6, 129.6, 128.1, 127.7, 127.6 (3°), 115.3 (CH=*C*H_2), 45.8 (SCH), 38.3 (SCH*C*), 21.6 ($ArCH_3$), 18.0 (SCH*C*H_2); *m/z* (CI) 316 $[M+NH_4]^+$ (Found $[M+NH_4]^+$, 316.1380. $C_{18}H_{18}O_2S$ requires $[M+NH_4]^+$, 316.1371).

tert-*Butyl (*E*)-4-(2,4-Difluorophenyl)-6-methoxymethoxy-2-tosylhex-4-enoate*



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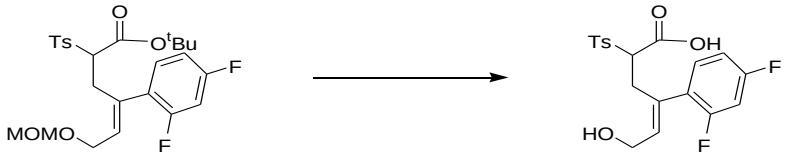
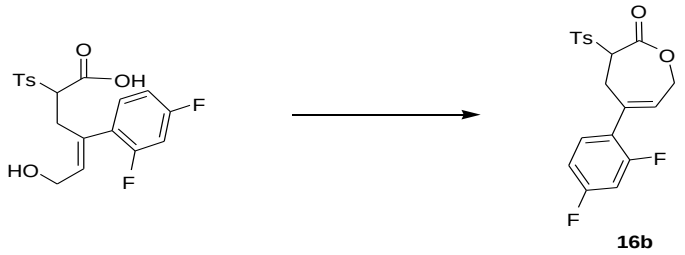
According to general procedure **D**, a suspension of sodium hydride (11.5 mg, 0.29 mmol, 1.1 equiv.) in THF (0.3 mL) was treated with *tert*-butyl 2-tosylacetate **10** (71 mg, 0.26 mmol, 1.0 equiv.) in THF (0.4 mL) followed by methanesulfonic acid (*Z*)-2-(2,4-difluorophenyl)-4-(methoxymethoxy)but-2-enyl ester (84 mg, 0.26 mmol, 1.0 equiv.) in THF (0.3 mL) to give *tert*-butyl (*E*)-4-(2,4-difluorophenyl)-6-methoxymethoxy-2-tosylhex-4-enoate, which was used without further purification; R_f 0.49 (50% EtOAc–heptane).

*(*E*)-4-(2,4-Difluorophenyl)-6-hydroxy-2-tosylhex-4-enoic acid*



According to general procedure **E**, a solution of *tert*-butyl (*E*)-4-(2,4-difluorophenyl)-6-methoxymethoxy-2-tosylhex-4-enoate (85 mg, 0.17 mmol, 1.0 equiv.) in MeCN (1.5 mL) was treated with 2 M aq. HCl (0.3 mL) to give (*E*)-4-(2,4-difluorophenyl)-6-hydroxy-2-tosylhex-4-enoic acid as a colourless gum, which was used without further purification.

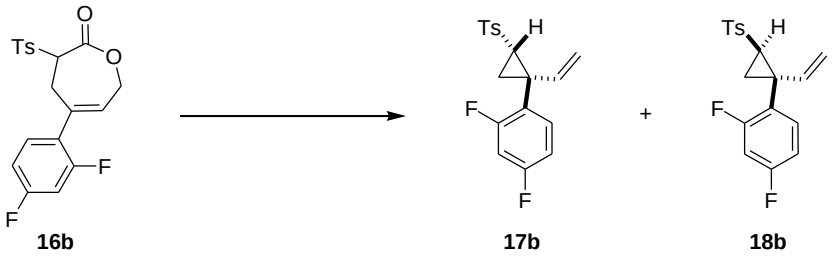
*5-(2,4-Difluorophenyl)-3-tosyl-4,7-dihydro-3*H*-oxepin-2-one* **16b**



16b

According to general procedure **G**, a solution of (*E*)-4-(2,4-difluorophenyl)-6-hydroxy-2-tosylhex-4-enoic acid (77 mg, 0.19 mmol, 1.0 equiv.) in CH_2Cl_2 (0.5 mL) was treated with EDCI (41 mg, 0.21 mmol, 1.1 equiv.). Purification by chromatography (40% EtOAc–petrol) gave 5-(2,4-difluorophenyl)-3-tosyl-4,7-dihydrooxepin-2(3*H*)-one **16b** (73 mg, 74% over three steps) as a colourless solid; R_f 0.36 (50% EtOAc–petrol); ν_{max} (film) 1745, 1594, 1501, 1321, 1305, 1291, 1265, 1139, 1084, 972, 850, 813, 670 cm^{-1}; δ_H (400 MHz) 7.95 (2H, d, *J* 8.5 Hz, *o*-SO_2Ar), 7.36 (2H, d *J* 8.0 Hz, *m*-SO_2Ar), 7.17 (1H, td, *J* 8.5, 6.5 Hz, *o*-ArF), 6.90–6.79 (2H, m, *m*-ArF), 5.95 (1H, m, *C*HCH_2O), [5.04, 4.99] (1H, 2 × dd, *J* 6.5, 3.5 Hz, SCH), [4.86, 4.81] (1H, 2 × d, *J* 4.0 Hz, OCH_2), [4.67, 4.62] (1H, 2 × d, *J* 7.5 Hz, OCH_2), [3.43, 3.37] (1H, 2 × m, SCHCH_2), 3.01 (1H, m, SCHCH_2), 2.45 (3H, s, CH_3); δ_C (75 MHz) 166.3 (C=O), 164.6, 164.4, 161.3, 161.2, 161.2, 161.1, 158.1, 157.9 (CF), 145.8, 136.8, 133.6 (4°), 130.4, 130.3, 130.3, 129.9 (CFCH*C*H), 130.5, 129.7, 125.1, (3°), 124.8, 124.7, 124.6, 124.5 (*C*CF), 111.9, 111.8, 111.6, 111.6 (CF*C*HCH), 104.9, 104.5, 104.2 (CF*C*HCF), 64.4, 63.6 (OCH_2), 63.7 (SCH), 30.0, 29.9 (SCH*C*H_2), 21.7 (CH_3); *m/z* (CI) 396 $[M+NH_4]^+$ (Found $[M+NH_4]^+$, 396.1075. $C_{19}H_{16}F_2O_4S$ requires $[M+NH_4]^+$, 396.1076).

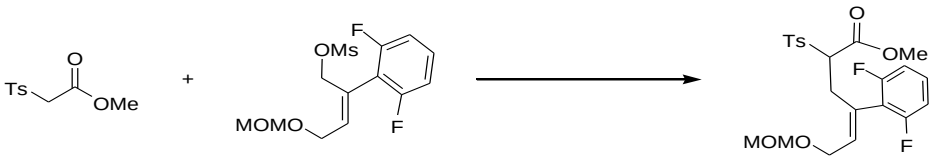
*((1*R**,2*R**)-2-(2,4-Difluorophenyl)-2-vinylcyclopropyl)* p-*tolyl sulfone* **17b** *and ((1*R**,2*S**)-2-(2,4-difluorophenyl)-2-vinylcyclopropyl)* p-*tolyl sulfone* **18b**



According to general procedure **H**, lactone **16b** (70.0 mg, 0.20 mmol, 1.0 equiv.) in DMF (1.0 mL) was treated with KOAc (pinch) and BSA (46.0 μL, 0.20 mmol, 1.0 equiv.) to give a diastereomeric mixture (3:2) of ((1*R**,2*R**)-2-(2,4-difluorophenyl)-2-vinylcyclopropyl) *p*-tolyl sulfone **17b** and ((1*R**,2*S**)-2-(2,4-difluorophenyl)-2-vinylcyclopropyl) *p*-tolyl sulfone **18b** (46 mg, 75%) as a colourless gum, separable by chromatography (10–20% EtOAc–petrol); **17b**: R_f 0.55 ν_{max} (film) 3056, 2926, 1618, 1508, 1426, 1266, 1148, 1090, 738 cm^{-1}; δ_H (500 MHz) 7.84 (2H, d, *J* 8.0 Hz, *o*-SO_2Ar), 7.36 (2H, d, *J* 8.0 Hz, *m*-SO_2Ar), 7.01 (1H, ddd, *J* 8.5, 8.5, 6.5 Hz, CFCHC*H*), 6.80 (1H, dddd, *J* 8.0, 8.0, 2.5, 1.0 Hz, CFC*H*CH), 6.72 (1H, ddd, *J* 10.0, 9.0, 2.5 Hz, CFCHCF), 6.39 (1H, dd, *J* 17.0, 10.5 Hz, C*H*=CH_2), 5.18 (1H, d, *J* 10.5 Hz, CH=CH_2 *trans*), 4.56 (1H, d, *J* 17.0 Hz, CH=CH_2 *cis*), 2.84 (1H, dd, *J* 9.0, 6.5 Hz, SCH), 2.47 (3H, s, $ArCH_3$), 2.19 (1H, dd, *J* 6.0, 6.0 Hz, SCHCH_2), 1.79 (1H, dd, *J* 9.0, 6.0 Hz, SCHCH_2); δ_C (100 MHz) 163.7, 163.6, 162.9, 162.8, 161.8, 161.7, 160.9, 160.8 (CF), 144.4, 138.0 (4°), 139.9 129.7, 127.6 (3°), 133.5 (*C*CF), 118.7 (CFCH*C*H), 115.4 (CH=*C*H_2), 111.2, 111.1, 111.0 (CF*C*HCH), 104.3, 104.1, 103.9 (CF*C*HCF), 45.4 (SCH), 29.7 (SCH*C*), 21.6 ($ArCH_3$), 18.7 (SCH*C*H_2); δ_F (376 MHz) –109.3 (1F, ddd, *J* 16.5, 8.0, 6.5 Hz, *p*-CF); *m/z* (CI) 352 $[M+NH_4]^+$, 316 (Found $[M+NH_4]^+$, 352.1198. $C_{18}H_{16}F_2O_2S$ requires $[M+NH_4]^+$, 352.1183); **18b**: R_f 0.59 (50% EtOAc–petrol); ν_{max} (film) 3923, 1598, 1505, 1425, 1321, 1290, 1148, 1088, 967, 851, 741, 659 cm^{-1}; δ_H (400 MHz) 7.66 (2H, d, *J* 8.0 Hz, *o*-SO_2Ar), 7.45 (1H, dd, *J* 15.0, 8.5 Hz, CFCHC*H*), 7.32 (2H, d, *J* 8.0 Hz, *m*-SO_2Ar), 6.90 (1H, dddd, *J* 9.0, 9.0, 2.5, 1.0 Hz, CFC*H*CH), 6.80 (1H, ddd, *J* 10.5, 9.0, 2.5 Hz, CFCHCF), 5.55 (1H, dd, *J* 17.0, 10.5 Hz, C*H*=CH_2), 5.04 (1H, d, *J* 10.5 Hz, CH=CH_2 *trans*), 4.74 (1H, d, *J* 17.0 Hz, CH=CH_2 *cis*), 2.82 (1H, dd, *J* 8.5, 6.5 Hz, SCH), 2.45 (3H, s, $ArCH_3$), 2.17 (1H, dd, *J* 6.0, 6.0 Hz, SCHCH_2), 1.64 (1H, dd, *J* 8.5, 6.0 Hz, SCHCH_2); δ_C (100 MHz) 163.8, 163.6, 162.6, 162.4, 161.3, 161.2, 160.2, 160.0 (CF), 144.5, 137.7 (4°),

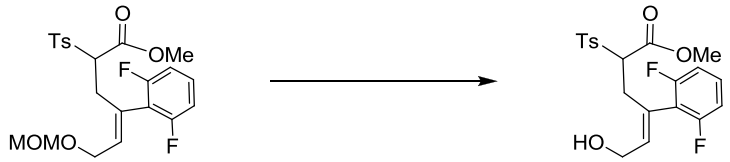
132.4, 132.3, 132.3, 132.2 (*C*CF), 135.5, 129.7, 127.6 (3°), 123.1, 123.0 (CFCH*C*H), 117.6 (CH=*C*H_2), 111.6, 111.6, 111.4, 111.4 (CF*C*HCH), 104.5, 104.2, 104.0 (CF*C*HCF), 46.7 (SCH), 29.7 (SCH*C*H), 21.7 (ArCH_3), 19.4 (SCH*C*H_2); δ_F (376 MHz) –108.8 (1F, ddd, *J* 16.5, 8.5, 6.5 Hz, *o*-CF), –109.4 (1F, dd, *J* 17.5, 8.5 Hz, *p*-CF); *m/z* (CI) 352 $[M+NH_4]^+$, 316, 298 (Found $[M+NH_4]^+$, 352.1198. $C_{18}H_{16}F_2O_2S$ requires $[M+NH_4]^+$, 352.1183);

*Methyl (*E*)-4-(2,6-difluorophenyl)-6-methoxymethoxy-2-tosylhex-4-enoate*



According to general procedure **D**, sodium hydride (40.2 mg, 1.00 mmol, 1.2 equiv.) in DMF (1.5 mL) was treated with methyl 2-tosylacetate[Error! Bookmark not defined.] (191 mg, 0.84 mmol, 1.0 equiv.) in DMF (1.5 mL) and methanesulfonic acid (*Z*)-2-(2,6-difluorophenyl)-4-(methoxymethoxy)but-2-enyl ester (0.84 mmol, 1.0 equiv.) in THF (1.2 mL) to give methyl (*E*)-4-(2,6-difluorophenyl)-6-methoxymethoxy-2-tosylhex-4-enoate, which was used without further purification; R_f 0.64 (50% EtOAc–petrol).

*(*E*)-Methyl 4-(2,6-difluorophenyl)-6-hydroxy-2-tosylhex-4-enoate*

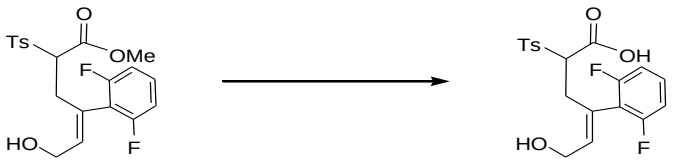


51 **52**

According to general procedure **E**, methyl (*E*)-4-(2,6-difluorophenyl)-6-methoxymethoxy-2-tosylhex-4-enoate (0.84 mmol, 1.0 equiv.) in MeCN (8.4 mL) was treated with 2 M aq. HCl (1.68 mL). Purification by chromatography (20→40% EtOAc–petrol) gave (*E*)-methyl 4-(2,6-difluorophenyl)-6-hydroxy-2-tosylhex-4-enoate (277 mg, 80% over three steps) as a colourless gum; R_f 0.33 (50% EtOAc–petrol); ν_{max} (film) 3055, 2986, 1741, 1620, 1463, 1423, 1265, 1149, 1085, 895, 738 cm^{-1}; δ_H (400 MHz) 7.70 (2H, d, *J* 8.0 Hz, *o*-SO_2Ar), 7.35 (2H, d, *J* 8.0 Hz, *m*-SO_2Ar), 7.23 (1H, tt, *J* 8.5, 6.5 Hz, *p*-ArF), 6.87 (2H, t, *J* 8.0 Hz, *m*-ArF), 5.83 (1H, t, *J* 7.0 Hz, C*H*CH_2OH), 4.36 (1H, dd, *J* 13.5, 7.5 Hz, C*H*$_2$OH), 4.18 (1H, dd, *J* 13.5, 6.5 Hz, C*H*$_2$OH), 3.84 (1H, dd, *J* 12.0, 3.5 Hz, SCH), 3.59 (3H, s, OCH_3), 3.29 (1H,

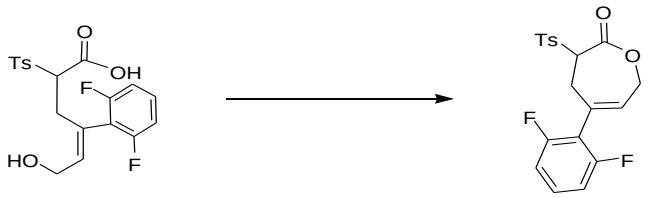
dd, *J* 14.0, 12.0 Hz, SCHC*H*$_2$), 3.02 (1H, dd, *J* 14.0, 2.5 Hz, SCHC*H*$_2$), 2.47 (3H, s, ArCH_3); δ_C (100 MHz) 166.3 (C=O), 161.5, 161.4, 159.0, 158.9 (CF), 145.7, 136.9, 133.6 (4°), 129.8, 129.2 (3°), 129.6, 129.5, 129.4 (CFCH*C*H), 125.0 (*C*HCH$_2$OH), 117.2 (*C*CF), 111.7, 111.6, 111.5, 111.4 (CF*C*H), 69.0 (SCH), 58.6 (CH$_2$OH), 53.1 (OCH_3), 28.0 (SCH*C*H$_2$), 21.7 (ArCH_3); *m/z* (CI) 428 $[M+NH_4]^+$, 410, 393, 272, 174; (Found $[M+NH_4]^+$, 428.1325. $C_{20}H_{20}F_2O_5S$ requires $[M+NH_4]^+$, 428.1343).

*(*E*)-4-(2,6-Difluorophenyl)-6-hydroxy-2-tosylhex-4-enoic acid*



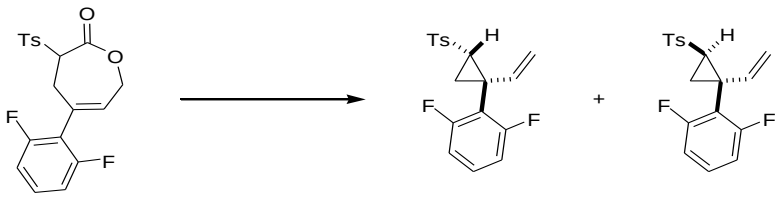
According to general procedure **F**, (*E*)-methyl 4-(2,6-difluorophenyl)-6-hydroxy-2-tosylhex-4-enoate (270 mg, 0.66 mmol, 1.0 equiv.) in THF (1.65 mL) was treated with 2 M aq. LiOH (1.65 mL) to give (*E*)-4-(2,6-difluorophenyl)-6-hydroxy-2-tosylhex-4-enoic acid (214 mg, 82%), which was used without further purification; ν_{max} (film) 3416, 3055, 2986, 1731, 1622, 1464, 1324, 1265, 1232, 1149, 1084, 1001, 815, 789, 738, 704 cm^{-1}; δ_H (400 MHz) 7.71 (2H, d, *J* 8.5 Hz, *o*-SO_2Ar), 7.33 (2H, d, *J* 8.5, 0.5 Hz, *m*-SO_2Ar), 7.23 (1H, tt, *J* 8.5, 6.5 Hz, *p*-ArF), 6.83 (2H, dd, *J* 8.5, 7.5 Hz, *m*-ArF), 5.82 (1H, dd, *J* 7.5, 6.5 Hz, C*H*CH$_2$OH), 4.42 (1H, dd, *J* 13.0, 8.5 Hz, C*H*$_2$OH), 4.12 (1H, dd, *J* 13.0, 6.0 Hz, C*H*$_2$OH), 3.81 (1H, dd, *J* 12.0, 3.0 Hz, SCH), 3.30 (1H, dd, *J* 14.0, 12.0 Hz, SCHC*H*$_2$), 2.96 (1H, dd, *J* 14.0, 2.0 Hz, SCHC*H*$_2$), 2.44 (3H, s, ArCH_3); δ_C (100 MHz) 168.2 (C=O), 161.5, 161.4, 159.0, 159.0 (CF), 145.8, 135.9, 133.5 (4°), 129.9, 129.3 (3°), 129.8, 129.6, 129.5 (CFCH*C*H), 125.9 (*C*HCH$_2$OH), 117.3, 117.1, 116.9 (*C*CF), 111.8, 111.7, 111.6, 111.5 (CF*C*H), 68.7 (SCH), 58.4 (CH$_2$OH), 28.2 (SCH*C*H$_2$), 21.8 (ArCH_3); *m/z* (CI) 370 $[M-CO_2+NH_4]^+$, 412, 396, 352, 335, 174 (Found $[M+NH_4]^+$, 414.1185. $C_{19}H_{18}F_2O_5S$ requires $[M+NH_4]^+$, 414.1187) (Found: C, 57.62; H, 4.49. $C_{19}H_{18}F_2O_5S$ requires C, 57.57; H, 4.58).

*5-(2,6-Difluorophenyl)-3-tosyl-4,7-dihydrooxepin-2(3*H*)-one* **16c**



According to general procedure **G**, (*E*)-4-(2,6-difluorophenyl)-6-hydroxy-2-tosylhex-4-enoic acid (98 mg, 0.25 mmol, 1.0 equiv.) in CH_2Cl_2 (1.25 mL) was treated with EDCI (52.7 mg, 0.28 mmol, 1.1 equiv.). Purification by chromatography (30% EtOAc–petrol) gave 5-(2,6-difluorophenyl)-3-tosyl-4,7-dihydrooxepin-2(3*H*)-one **16c** (73 mg, 74% over three steps) as a colourless solid; R_f 0.60 (50% EtOAc–petrol); ν_{max} (film) 3139, 1748, 1622, 1463, 1398, 1321, 1267, 1231, 1144, 1084, 1002, 781, 735, 666 cm^{-1}; δ_H (400 MHz) 7.95 (2H, d, *J* 8.5 Hz, *o*-SO_2Ar), 7.36 (2H, d *J* 8.0 Hz, *m*-SO_2Ar), 7.28 (1H, td, *J* 8.5, 6.5 Hz, *o*-ArF), 6.92 (2H, dd, *J* 8.0, 8.0 Hz, *m*-ArF), 5.96 (1H, m, *C*HCH$_2$O), [5.06, 5.02] (1H, 2 × dd, *J* 3.5, 3.5 Hz, SCH), [4.87, 4.83] (1H, 2 × d, *J* 4.0 Hz, OCH$_2$), [4.68, 4.64] (1H, 2 × d, *J* 7.5 Hz, OCH$_2$), 3.29 (1H, d, *J* 17.5 Hz, SCHC*H*$_2$), 3.02 (1H, m, SCHC*H*$_2$), 2.45 (3H, s, CH_3); δ_C (100 MHz) 166.2 (C=O), 161.0, 160.9, 158.5, 158.4 (CF), 145.7, 133.6, 130.6 (4°), 130.4, 129.6, (3°), 130.0, 129.9, 129.8 (CFCH*C*H), 127.5 (*C*HCH$_2$OH), 117.6 (*C*CF), 111.9, 111.8, 111.7, 111.6 (CF*C*HCH), 64.4 (OCH$_2$), 63.6 (SCH), 29.8 (SCH*C*H$_2$), 21.7 (CH_3); *m/z* (CI) 396 $[M+NH_4]^+$, 254, 242, 174 (Found $[M+NH_4]^+$, 396.1085. $C_{19}H_{16}F_2O_4S$ requires $[M+NH_4]^+$, 396.1081) (Found: C, 60.38; H, 4.19. $C_{19}H_{16}F_2O_4S$ requires C, 60.31; H, 4.26).

*((1*R**,2*R**)-2-(2,6-Difluorophenyl)-2-vinylcyclopropyl)* p-*tolyl sulfone* **17c** *and ((1*R**,2*S**)-2-(2,6-difluorophenyl)-2-vinylcyclopropyl)* p-*tolyl sulfone* **18c**



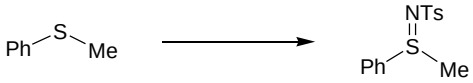
16c **17c** **18c**

According to general procedure **I**, lactone **16c** (63 mg, 0.17 mmol, 1.0 equiv.) in DMF (0.85 mL) was treated with KOAc (0.85 mg, 0.017 mmol, 0.1 equiv.) and BSA (41 μL, 0.17 mmol, 1.0 equiv.) to give a diastereomeric mixture (2:3) of ((1*R**,2*R**)-2-(2,6-difluorophenyl)-2-vinylcyclopropyl) *p*-tolyl sulfone **17c** and ((1*R**,2*S**)-2-(2,6-

difluorophenyl)-2-vinylcyclopropyl) *p*-tolyl sulfone **18c** (47 mg, 82%) as a colourless oil, separable by chromatography (10% Et_2O–petrol); **17c**: R_f 0.34 (50% Et_2O–petrol); ν_{max} (film) 3054, 1625, 1467, 1321, 1265, 1151, 1090, 1008, 790, 738, 704, 653 cm^{-1}; δ_H (400 MHz) 7.84 (2H, d, *J* 8.0 Hz, *o*-SO_2Ar), 7.34 (2H, d, *J* 8.0 Hz, *m*-SO_2Ar), 7.21 (1H, tt, *J* 8.5, 6.5 Hz, *p*-ArF), 6.80 (2H, t, *J* 8.0 Hz, *m*-ArF), 6.35 (1H, dd, *J* 17.0, 10.5 Hz, C*H*=CH_2), 5.17 (1H, d, *J* 10.5 Hz, CH=CH_2 *trans*), 4.62 (1H, d, *J* 17.0 Hz, CH=CH_2 *cis*), 2.91 (1H, dd, *J* 9.0, 6.5 Hz, SCHCH_2), 2.46 (3H, s, ArCH_3), 2.30 (1H, dd, *J* 6.5, 6.5 Hz, SCHCH_2), 1.8 (1H, dd, *J* 9.0, 6.0 Hz, SCHCH_2); δ_C (100 MHz) 162.9, 162.8, 160.4, 160.3 (CF), 144.4, 137.5 (4°), 134.5 (*C*H=CH_2), 129.9, 129.8, 129.7 (CFCH*C*H), 129.5, 128.1 (3°), 117.2 (CH=*C*H_2), 111.8, 111.5 (CF*C*H), 46.6 (SCH), 27.9 (SCH*C*), 21.7 (ArCH_3), 19.8 (CH_2); *m/z* (CI) 352 $[M+NH_4]^+$ (Found $[M+NH_4]^+$, 352.1183. $C_{18}H_{16}F_2O_2S$ requires $[M+NH_4]^+$, 352.1183) (Found: C, 64.69; H, 4.75. $C_{18}H_{16}F_2O_2S$ requires C, 64.65; H, 4.82); **18c**: R_f 0.27 (50% Et_2O–petrol); ν_{max} (film) 1628, 1466, 1325, 1298, 1234, 1150, 1088, 1004, 910, 734 cm^{-1}; δ_H (400 MHz) 7.68 (2H, d, *J* 8.0 Hz, *o*-SO_2Ar), 7.32 (2H, d, *J* 8.0 Hz, *m*-SO_2Ar), 7.30 (1H, tt, *J* 8.5, 6.5 Hz, *p*-ArF), 6.92 (2H, dd, *J* 17.0, 8.5 Hz, *m*-ArF), 5.56 (1H, dd, *J* 17.0, 10.5 Hz, C*H*=CH_2), 5.06 (1H, d, *J* 10.5 Hz, CH=CH_2 *trans*), 4.82 (1H, d, *J* 17.0 Hz, CH=CH_2 *cis*), 2.85 (1H, ddd, *J* 8.5, 6.5, 2.0 Hz, SCHCH_2), 2.44 (3H, s, ArCH_3), 2.23 (1H, ddd, *J* 6.5, 6.5, 2.5 Hz, SCHCH_2), 1.71 (1H, dd, *J* 9.0, 6.0 Hz, SCHCH_2); δ_C (125 MHz) 163.5, 163.5, 162.8, 162.7, 161.5, 161.5, 160.8, 160.8 (CF), 144.3, 138.6, 138.1 (4°), 134.5 (*C*H=CH_2), 129.5, 129.6, 129.7 (CFCH*C*H), 129.7, 127.7 (3°), 115.2 (CH=*C*H_2), 112.4, 112.2, 112.2, 112.1 (CF*C*HCF), 111.8, 111.8, 111.7, 111.6, 111.4, 111.4, 111.3, 111.2 (CF*C*H), 44.9 (SCH), 29.1 (SCH*C*), 21.6 (ArCH_3), 18.9 (CH_2); *m/z* (CI) 352 $[M+NH_4]^+$ (Found $[M+NH_4]^+$, 352.1197. $C_{18}H_{16}F_2O_2S$ requires $[M+NH_4]^+$, 352.1183) (Found: C, 64.77; H, 4.73. $C_{18}H_{16}F_2O_2S$ requires C, 64.65; H, 4.82).

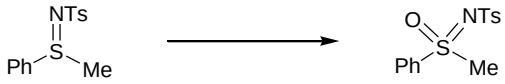
6. Synthesis and reactions of sulfoximinyl lactones 19 and 20

(±)-S-*Methyl*-S-*phenyl*-N-*tosylsulfilimine*



Thioanisole (5.87 mL, 50.0 mmol, 1.0 equiv.) and tetrabutylammonium bromide (0.81 g, 2.50 mmol, 5.0 mol%) were dissolved in CH_2Cl_2 (100 mL). Solid chloramine-T trihydrate (dried under vacuum over P_2O_5; 15.5 g, 55.0 mmol, 1.1 equiv.) was slowly added with stirring and cooling in a water bath. After addition was complete the water bath was removed and stirring continued for 2 h. The reaction mixture was washed with cold 5% aq. NaOH and H_2O (×2), the organic layer dried ($MgSO_4$) and concentrated under reduced pressure. The crude sulfilimine was recrystallised from methanol–water (9:1) to give (±)-*S*-methyl-*S*-phenyl-*N*-tosylsulfilimine (13.9 g, 95%) as colourless needles; mp 130 °C; R_f 0.07 (20% EtOAc–petrol); ν_{max} (nujol) 1593, 1295, 1279, 1142, 1086, 1021, 989, 932, 826, 766, 746, 689, 652 cm^{-1}; δ_H (270 MHz) 7.68 (4H, m, *o*-Ph, *o*-SO_2Ar), 7.49 (3H, m, *m*-/*p*-Ph), 7.14 (2H, d, *J* 8.0 Hz, *m*-SO_2Ar), 2.82 (3H, s, SCH_3), 2.33 (3H, s, $ArCH_3$); δ_C (100 MHz) 141.7, 141.2, 136.1 (4°), 132.4, 129.9, 129.2, 126.2, 125.8 (3°), 39.1 (SCH_3), 21.3 ($ArCH_3$); *m/z* (CI) 294 $[M+H]^+$, 206, 189; data were in accordance with those previously reported.[7]

(±)-S-*Methyl*-S-*phenyl*-N-*tosylsulfoximine*

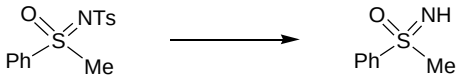


54

To a solution of the (±)-*S*-methyl-*S*-phenyl-*N*-tosylsulfilimine (13.5 g, 46.0 mmol, 1.0 equiv.) in CCl_4 (100 mL) and MeCN (100 mL) was added $RuO_2.xH_2O$ (12.2 mg, 0.92 mmol, 2.0 mol%). A solution of $NaIO_4$ (19.7 g, 92.0 mmol, 2.0 equiv.) in H_2O (200 mL) was then added slowly (~30 min) and the reaction stirred for 90 min. The phases were separated and the aqueous layer extracted with CH_2Cl_2. The organic layers were combined and *i*PrOH (4.5 mL) added and the reaction mixture stirred for a further 1 h, then filtered over celite, dried ($MgSO_4$), and concentrated under reduced pressure. The yellow/green crystals were washed with EtOH to give the (±)-*S*-methyl-*S*-phenyl-*N*-tosylsulfoximine (11.8 g, 83%) as colourless crystals; mp 102 °C; ν_{max} (nujol) 1597, 1580, 1327, 1314, 1230, 1146, 1090, 1067, 982, 811, 754, 740, 689, 653 cm^{-1}; δ_H (270

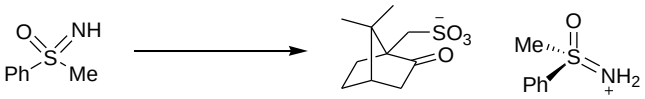
MHz) 8.00 (2H, d, *J* 7.5 Hz, *o*-Ph), 7.84 (2H, d, *J* 8.5 Hz, *o*-SO_2Ar), 7.72–7.56 (3H, m, *m*-/*p*-Ph), 7.24 (2H, d, *J* 8.5 Hz, *m*-SO_2Ar), 3.41 (3H, s, SCH_3), 2.38 (3H, s, $ArCH_3$); δ_C (67.5 MHz) 142.9, 140.7, 138.6 (4°), 134.5, 129.8, 129.4, 127.6, 126.7 (3°), 46.7 (SCH_3), 21.6 ($ArCH_3$); *m/z* (CI) 327 $[M+NH_4]^+$, 294, 189, 52; data were in accordance with those previously reported.[8]

(±)-S-*Methyl*-S-*phenylsulfoximine*



A solution of (±)-*S*-methyl-*S*-phenyl-*N*-tosylsulfoximine (11.8 g, 38.1 mmol, 1.0 equiv.) was heated in conc. H_2SO_4 (20 mL) for 25 min at 120 °C. The reaction was cooled to rt, then poured into ice and neutralised using 2 M aq. NaOH. The reaction mixture was extracted with CH_2Cl_2 (×2), and the organic layer dried ($MgSO_4$) and concentrated under reduced pressure to give (±)-*S*-methyl-*S*-phenylsulfoximine (5.83 g, 99%) as a colourless oil; ν_{max} (film) 3268, 3191, 3091, 3062, 3018, 1446, 1409, 1320, 1222, 1097, 1070, 1029, 1010, 950, 769, 742, 690 cm^{-1}; δ_H (270 MHz) 7.99 (2H, d, *J* 8.0 Hz, *o*-Ph), 7.64–7.50 (3H, m, *m*-/*p*-Ph), 3.07 (3H, s, SCH_3); δ_C (67.5 MHz) 143.4 (4°), 133.2, 129.4, 127.8 (3°), 46.2 (SCH_3); *m/z* (CI) 156 $[M+H]^+$; data were in accordance with those previously reported.[9]

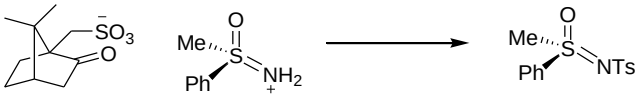
(–)-(R_S*)*-S-*Methyl*-S-*phenylsulfoximine-(–)-camphorsulfonic acid*



A solution of (–)-(*R*)-camphorsulfonic acid (4.28 g, 18.4 mmol, 0.5 equiv.) in dry acetone (distilled over P_2O_5; 30 mL) was added to a solution of (±)-*S*-methyl-*S*-phenylsulfoximine (5.72 g, 36.9 mmol, 1.0 equiv.) in dry acetone (20 mL) at rt and stirred for 16 h. The precipitate was then filtered and washed with dry acetone (×3) to give (–)-(R_S)-*S*-methyl-*S*-phenylsulfoximine-(–)-camphorsulfonic acid (5.40 g, 40% from a possible 50%) as a colourless powder; mp 172–174 °C; ν_{max} (nujol) 1728, 1580 1415, 1253, 1231, 1190, 1140, 1038, 669, 748 cm^{-1}; δ_H (270 MHz) 8.17 (2H, d, *J* 8.0 Hz, *o*-Ph), 7.82–7.67 (3H, m, *m*-/*p*-Ph), 3.84 (3H, s, SCH_3), [3.11 and 2.62] (2H, 2 × d, *J* 15.0 Hz, SCH_2), [2.42, 2.24] (2H, 2 × m, SCH_2CCH_2), 1.96 (1H, dd, *J* 4.0, 4.0

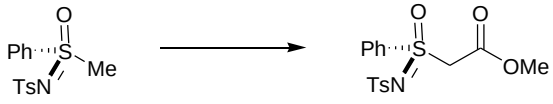
Hz, C*H*CH_2CO), 1.89 (1H, dd, *J* 8.0, 4.0 Hz, CHC*H*$_2$CO), 1.80 (1H, d, *J* 18.5 Hz, CHC*H*$_2$CO), 1.48 (1H, ddd, *J* 13.0, 9.5, 4.0 Hz, CHC*H*$_2$$CH_2$), 1.28 (1H, ddd, *J* 13.0, 9.5, 4.0 Hz, CHC*H*$_2$$CH_2$), [0.95, 0.73] (6H, 2 × s, CSA$^-$$CH_3$); δ_C (125 MHz, DMSO-d_6) 215.9 (C=O), 137.9 (4°), 130.2, 128.2, 125.5 (3°), 58.0 (SO_2CH_2*C*), 47.1 (*C*CH_3)$_2$), 46.9 (SO_2CH_2), 43.5 (SCH_3), 42.2 (*C*H_2CO), 42.1 (*C*HCO), 26.3 (SO_2CH_2C*C*H_2), 24.1 (*C*H_2CCO), 19.9, 19.5 (C(*C*H_3)$_2$); *m/z* (CI) 156; data were in accordance with those previously reported.[10]

(–)-(R_S*)*-S-*Methyl*-S-*phenyl*-N-*tosylsulfoximine*



(–)-(*R*$_S$)-*S*-Methyl-*S*-phenylsulfoximine-(–)-camphorsulfonic acid (8.2 g, 22.2 mmol, 1.0 equiv.) was dissolved in dry pyridine (15 mL). Tosyl chloride (4.23 g, 22.2 mmol, 1.0 equiv.) was added slowly and the reaction was stirred for 16 h. The reaction mixture was then poured onto H_2O and extracted with CH_2Cl_2. The organic layers were combined, washed with 2 M aq. HCl (×2) and H_2O, dried ($MgSO_4$) and concentrated under reduced pressure to give (–)-(*R*$_S$)-*S*-methyl-*S*-phenyl-*N*-tosylsulfoximine (6.07 g, 88%) as a colourless crystalline solid; mp 106–107 °C; $[\alpha]_D^{22}$ −40.0 (*c* 5.0, CH_2Cl_2); ν_{max} (nujol) 2361, 1735, 1312, 1239, 1061, 965, 805, 685, 651 cm^{-1}; δ_H (270 MHz) 7.99 (2H, d, *J* 8.0 Hz, *o*-Ph), 7.82 (2H, d, *J* 8.0 Hz, *o*-SO_2Ar), 7.72–7.55 (3H, m, *m*-/*p*-Ph), 7.23 (2H, d, *J* 8.0 Hz, *m*-SO_2Ar), 3.41 (3H, s, SCH_3), 2.38 (3H, s, ArCH_3); δ_C (67.5 MHz) 143.0, 140.7, 138.6 (4°), 134.5, 129.8, 129.4, 127.6, 126.7 (3°), 46.7 (SCH_3), 21.6 (ArCH_3); data were in accordance with those previously reported.[11]

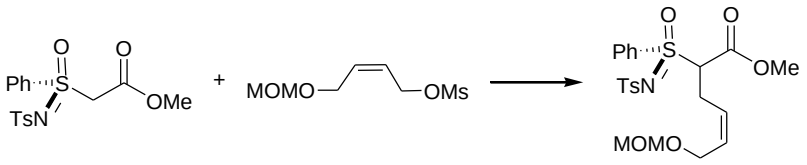
Methyl (R_S*)-2-(*N-*tosylphenylsulfonimidoyl)acetate*



To a suspension of sodium hydride (60% dispersion in mineral oil, washed in hexane; 430 mg, 10.7 mmol, 2.2 equiv.) in THF (10 mL) was added dimethyl carbonate (8.50 mL, >20 equiv.) and the reaction mixture stirred at reflux whilst a solution of (–)-(*R*$_S$)-*S*-methyl-*S*-phenyl-*N*-tosylsulfoximine (1.50 g, 4.85 mmol, 1.0 equiv.) in THF (15 mL) was added dropwise. The stirred reaction mixture was heated under reflux

overnight, cooled on ice and then quenched with MeOH–AcOH (2:1, 15 mL). The solution was poured onto H_2O and the product extracted with Et_2O (×5). The combined organic layers were washed with sat. aq. $NaHCO_3$ and H_2O, dried ($MgSO_4$) and concentrated under reduced pressure. The yellow oil was then treated with EtOH to give methyl (R_S)-2-(*N*-tosylphenylsulfonimidoyl)acetate (1.39 g, 78%) as a colourless solid; mp 76–77 °C; $[\alpha]_D^{22}$ −32.2 (*c* 5.0, CH_2Cl_2); R_f 0.43 (50% EtOAc–petrol); ν_{max} (film) 1742, 1643, 1496, 1447, 1318, 1153, 814, 666 cm^{-1}; δ_H (270 MHz) 7.99 (2H, d, *J* 7.5 Hz, *o*-Ph), 7.86 (2H, d, *J* 8.5 Hz, *o*-SO_2Ar), 7.70 (1H, m, *p*-Ph), 7.58 (2H, m, *m*-Ph), 7.25 (2H, d, *J* 8.5 Hz, *m*-SO_2Ar), [4.79, 4.58] (2H, AB doublet, *J* 14.5 Hz, CH_2), 3.64 (3H, s, OCH_3), 2.38 (3H, s, $ArCH_3$); δ_C (67.5 MHz) 162.2 (C=O), 143.3, 140.4, 135.9 (4°), 135.0, 129.5, 129.4, 128.7, 126.8 (3°), 61.4 (CH_2), 53.4 (OCH_3), 21.6 ($ArCH_3$); *m/z* (CI) 385 $[M+NH_4]^+$, 279, 208, 189; data were in accordance with those previously reported.[12]

Methyl (R_S*,Z)-6-(methoxymethoxy)-2-(*N*-tosylphenylsulfonimidoyl)hex-4-enoate*

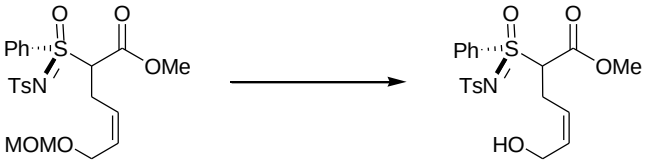


9

According to general procedure **D**, a suspension of sodium hydride (0.42 g, 10.5 mmol, 1.1 equiv.) in THF (10 mL) was treated with methyl (R_S)-2-(*N*-tosylphenylsulfon-imidoyl)acetate (3.49 g, 9.5 mmol, 1.0 equiv.) in THF (25 mL), followed by mesylate **9** (2.00 g, 9.50 mmol, 1.0 equiv.) in THF (15 mL). Purification by chromatography (20→40% EtOAc–petrol) gave a diastereomeric mixture (1:1) of methyl (R_S,*Z*)-6-(methoxymethoxy)-2-(*N*-tosylphenylsulfonimidoyl)hex-4-enoate (3.68 g, 80%) as a colourless gum; R_f 0.42 (50% EtOAc–petrol); ν_{max} (film) 2952, 1746, 1598, 1447, 1321, 1245, 1152, 1087, 1061, 1018, 997, 815, 765, 685, 666 cm^{-1}; δ_H (500 MHz) 7.96 (2H, m, *o*-Ph), 7.88 (2H, m, *o*-SO_2Ar), 7.76 (1H, m, *p*-Ph), 7.63 (2H, m, *m*-Ph), 7.28 (2H, m, *m*-SO_2Ar), 5.71 (1H, dt, *J* 11.0, 6.5 Hz, OCH_2CH), 5.40 (1H, m, $SCHCH_2CH$), [4.89, 4.64] (1H, dd, *J* 11.0, 3.5 Hz, SCH), [4.59, 4.57] (2H, 2 × s, OCH_2O), 4.08–3.98 (2H, m, $CHCH_2O$), [3.74, 3.69] (3H, 2 × s, CO_2CH_3), [3.35, 3.33] (3H, 2 × s, CH_2OCH_3), [2.91–2.84, 2.72–2.54] (2H, 2 × m, $SCHCH_2$), 2.42 (3H, s, $ArCH_3$); δ_C (125 MHz) 165.2, 164.0 (C=O), 143.1, 143.0, 140.7, 140.5, 134.4, 133.8 (4°), 135.0, 135.0, 131.3, 131.2, 129.8, 129.7, 129.3, 126.7, 126.7, 124.7 (3°),

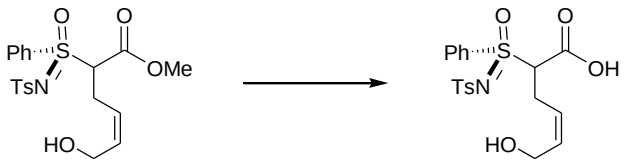
95.8 (OCH_2O), 71.1, 70.4 (SCH), 62.6 (OCH_2CH), 55.3 (CH_2OCH_3), 53.4, 53.3 (CO_2CH_3), 26.4, 25.1 ($SCHCH_2$), 21.6 ($ArCH_3$); *m/z* (CI) 499 $[M+NH_4]^+$, 455, 450, 420, 385, 313, 189 (Found $[M+NH_4]^+$, 499.1591. $C_{22}H_{27}NO_7S_2$ requires $[M+NH_4]^+$, 499.1573) (Found: C, 54.89; H, 5.63; N, 2.92. $C_{22}H_{27}NO_7S_2$ requires C, 54.87; H, 5.65; N, 2.91).

Methyl (R_S*,Z)-6-hydroxy-2-(*N*-tosylphenylsulfonimidoyl)hex-4-enoate*



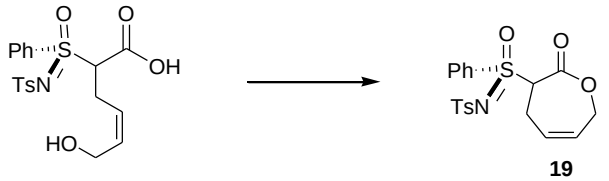
According to general procedure **E**, methyl (R_S,*Z*)-6-(methoxymethoxy)-2-(*N*-tosylphenylsulfonimidoyl)hex-4-enoate (1.40 g, 2.90 mmol, 1.0 equiv.) was heated under reflux in MeCN (30 mL) and 2 M aq. HCl (6 mL) to give methyl (R_S,*Z*)-6-hydroxy-2-(*N*-tosylphenylsulfonimidoyl)hex-4-enoate (1.13 g, 89%) as a viscous, colourless oil; R_f 0.13 (50% EtOAc–petrol); ν_{max} (film) 3525, 2954, 1744, 1598, 1447, 1318, 1242, 1153, 1088, 1062, 998, 815, 754, 685. 665 cm^{-1}; δ_H (400 MHz) 7.94 (2H, d, *J* 8.5 Hz, *o*-Ph), 7.87 (2H, m, *o*-SO_2Ar), 7.76 (1H, m, *p*-Ph), 7.62 (2H, m, *m*-Ph), 7.28 (2H, m, *m*-SO_2Ar), 5.77 (1H, m, C*H*CH_2OH), 5.35 (1H, m, $SCHCH_2CH$), [4.99, 4.67] (1H, dd, *J* 11.5, 3.5 Hz, SCH), 4.16–4.05 (2H, m, CH_2OH), [3.76, 3.61] (3H, 2 × s, OCH_3), 2.96–2.84 (1H, m, $SCHCH_2$), [2.77, 2.69] (1H, m, $SCHCH_2$), 2.41 (3H, s, $ArCH_3$); δ_C (100 MHz) 165.6, 165.3 (C=O), 143.2, 143.0, 140.6, 140.4, 134.4, 133.3 (4°), 135.2, 135.0, 133.9, 133.8, 129.8, 129.6, 129.4, 129.3, 124.0, 123.8 (3°), 71.2, 70.5 (SCH), 58.1, 58.0 (CH_2OH), 53.5, 53.4 (OCH_3), 26.4, 25.0 ($SCHCH_2$), 21.6 ($ArCH_3$); *m/z* (CI) 455 $[M+NH_4]^+$, 300, 189, 160 (Found $[M+NH_4]^+$, 455.1295. $C_{20}H_{23}NO_6S_2$ requires $[M+NH_4]^+$, 455.1311) (Found: C, 55.02; H, 5.27; N, 3.09. $C_{20}H_{23}NO_6S_2$ requires C, 54.90; H, 5.30; N, 3.20).

(R_S*,Z)-6-Hydroxy-2-(*N*-tosylphenylsulfonimidoyl)hex-4-enoic acid*



According to procedure **F**, methyl (R_S,*Z*)-6-hydroxy-2-(*N*-tosylphenylsulfonimidoyl)hex-4-enoate (1.10 g, 2.51 mmol, 1.0 equiv.) in THF (6.3 mL) was treated with 2 M aq. LiOH (6.3 mL, 2.00 mmol, 5.0 equiv.) to give (R_S,*Z*)-6-hydroxy-2-(*N*-tosylphenylsulfonimidoyl)hex-4-enoic acid (860 mg, 81%) as a colourless solid, which was used without further purification; mp 149–151 °C; δ_H (400 MHz, DMSO-d_6); 7.91–7.88 (2H, m, *o*-Ph), 7.85–7.79 (1H, m, *p*-Ph), 7.72–7.63 (4H, m, *o*-SO_2Ar and *m*-Ph), 7.35–7.31 (2H, m, *m*-SO_2Ar), 5.82–5.75 (1H, m, C*H*CH_2OH), 5.48–5.41 (1H, m, SCHCH_2C*H*), 4.90 (1H, dd, *J* 11.5, 3.0 Hz, SCH), 4.10 (2H, ddd, *J* 19.0, 13.0, 7.0 Hz, CH_2OH), [2.82–2.80, 2.69–2.61] (2H, 2 × m, SCHCH_2), 2.41 (3H, s, ArCH_3); δ_C (100 MHz, DMSO-d_6) 165.6, 165.5 (C=O), 143.1, 143.0, 142.9, 141.1, 136.6, 135.1 (4°), 135.4, 135.2, 134.9, 133.6, 130.1, 130.0, 129.8, 129.8, 129.8, 128.5, 126.4, 125.0, 122.9, 122.4 (3°) 70.3, 70.1 (SCH), 57.1, 57.1 (CH_2OH), 25.4, 24.7 (SCH*C*H_2), 21.4 (ArCH_3); *m/z* (FAB$^+$) 424 $[M+H]^+$, 406, 392, 296, 167, 125, 89, 77 (Found $[M+H]^+$, 424.0887. $C_{19}H_{21}NO_6S_2$ requires $[M+H]^+$, 424.0889) (Found: C, 53.91; H, 4.94; N, 3.24. $C_{19}H_{21}NO_6S_2$ requires C, 53.88; H, 5.00; N, 3.31).

(R_S*)-3-(*N*-Tosylphenylsulfonimidoyl)-4,7-dihydrooxepin-2(*3H*)-one* **19**

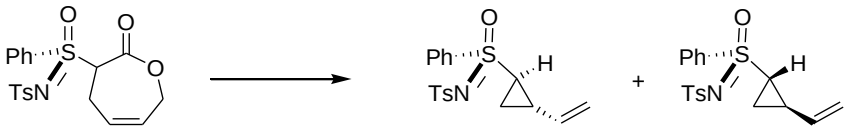


19

According to general procedure **G**, (R_S,*Z*)-6-hydroxy-2-(*N*-tosylphenylsulfonimidoyl)hex-4-enoic acid (0.84 g, 1.99 mmol, 1.0 equiv.) in CH_2Cl_2 (5 mL) was treated with EDCI (0.42 g, 2.19 mmol, 1.1 equiv.). The product was purified by chromatography (20→50% EtOAc–petrol) to give (R_S)-3-(*N*-tosylphenylsulfonimidoyl)-4,7-dihydrooxepin-2(3*H*)-one **19** (0.68 g, 84%) as a colourless crystalline solid; mp 74–76 °C; R_f 0.26 (50% EtOAc–petrol); ν_{max} (film)

3441 (br), 3056, 1748, 1598, 1448, 1386, 1316, 1265, 1151, 1087, 736 cm^{-1}; δ_H (500 MHz) 8.14 (2H, d, *J* 7.5 Hz, *o*-Ph), 7.87 (2H, d, *J* 8.5 Hz, *o*-SO_2Ar), 7.70 (1H, m, *p*-Ph), 7.58 (2H, dt, *J* 7.5, 7.5 Hz, *m*-Ph), 7.28 (2H, m, *m*-SO_2Ar), [6.03, 5.78] (1H, dd, *J* 13.0, 4.0 Hz, SCH), 5.88 (2H, d, *J* 4.0 Hz, HC=CH), [5.11, 4.51] (2H, m, OCH_2), [3.31, 3.15] (1H, dd, *J* 17.5, 3.5 Hz, SCHCH_2), 2.45–2.36 (1H, m, SCHCH_2), 2.40 (3H, s, $ArCH_3$); δ_C (125 MHz) 166.4 (C=O), 143.2, 143.2, 140.40, 140.2, 133.0, 132.8, (4°), 134.9, 131.1, 131.0, 129.3, 129.0, 128.9, 128.6, 126.7, 126.7, 124.9, 124.5, (3°), 65.4, 65.3 (SCH), 64.2, 64.1 (OCH_2), 28.9, 27.5 (SCHCH_2), 21.5 ($ArCH_3$); *m/z* (CI) 423 $[M+NH_4]^+$, 379, 189, 128 (Found $[M+NH_4]^+$, 423.1055. $C_{19}H_{19}NO_5S_2$ requires $[M+NH_4]^+$, 423.1048) (Found: C, 56.21; H, 4.80; N, 3.52. $C_{19}H_{19}NO_5S_2$ requires C, 56.28; H, 4.72; N, 3.45).

($R_{S,}$*1*R,*2*S)-S-*Phenyl*-S-*(2-vinylcyclopropyl)*-N-*tosylsulfoximine and* ($R_{S,}$*1*S,*2*R)-S-*Phenyl*-S-*(2-vinylcyclopropyl)*-N-*tosylsulfoximine* **21**

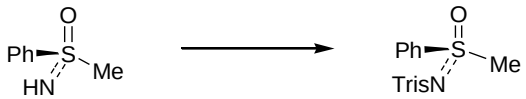


19 **21** (3:2 ratio: unassigned)

According to general procedure **H**, lactone **19** (50.0 mg, 120 μmol, 1.0 equiv.), was treated with BSA (30.5 μl, 120 μmol, 1.0 equiv.) and KOAc (1.2 mg, 12.0 μmol, 0.1 equiv.) in DMF (0.6 mL) to give a diastereomeric mixture (3:2, unassigned) of (*R*$_{S,}$1*R*,2*S*)-*S*-phenyl-*S*-(2-vinylcyclopropyl)-*N*-tosylsulfoximine and (*R*$_{S,}$1*S*,2*R*)-*S*-phenyl-*S*-(2-vinylcyclopropyl)-*N*-tosylsulfoximine **21** (28.0 mg, 65%) as a colourless oil; R_f 0.50 (50% EtOAc–petrol); ν_{max} (film) 3052, 2985, 2923, 2852, 1640, 1598, 1447, 1421, 1316, 1264, 1151, 1070 cm^{-1}; δ_H (400 MHz) 7.96 (2H, m, *o*-Ph), 7.83 (2H, d, *J* 8.0 Hz, *o*-SO_2Ar), 7.70 (1H, t, *J* 7.5 Hz, *p*-Ph), 7.60 (2H, t, *J* 7.5 Hz, *m*-Ph), 7.26 (2H, d, *J* 8.0 Hz, *m*-SO_2Ar), 5.55 (1H, ddd, *J* 17.5, 10.0, 7.5 Hz, C*H*=CH_2 minor), 5.35 (1H, ddd, *J* 17.5, 10.0, 7.5 Hz, C*H*=CH_2 major), 5.28 (1H, d, *J* 17.5 Hz, CH=CH_2 *cis* minor), 5.15 (1H, d, *J* 10.0 Hz, CH=CH_2 *trans* minor), 5.07 (1H, d, *J* 17.0 Hz, CH=CH_2 *cis* major), 5.01 (1H, d, *J* 10.0 Hz, CH=CH_2 *trans* major), 2.70 (1H, m, SCH major and minor), 2.63 (1H, m, SCH*C*H minor), 2.42 (3H, s, $ArCH_3$), 2.23 (1H, m, SCHC*H* major), 1.95 (1H, dt, *J* 10.0, 5.5 Hz, SCHCH_2 major), 1.42 (1H, dt, *J* 8.0, 6.5 Hz, SCHCH_2 major), 1.53 (1H, dt, *J* 10.0, 5.5 Hz, SCHCH_2 minor), 1.16 (1H, dt, *J* 8.0, 6.5 Hz, SCHCH_2 minor); δ_C (100 MHz) 142.8, 140.8, 138.7 (4°), 134.2,

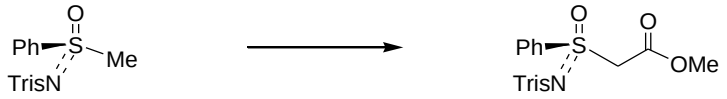
134.1, 134.0, 129.6, 129.2, 127.7, 127.6, 126.6 (3°), 117.7, 117.4 (CH=*C*H_2), 41.7, 41.6 (SCH), 24.1, 23.3 (SCH*C*H), 21.5 (ArCH_3), 14.4, 12.7 (SCH*C*H_2); *m/z* (CI) 362 $[M+H]^+$, 379, 189, 52 (Found $[M+H]^+$, 362.0888. $C_{18}H_{19}NO_3S_2$ requires $[M+H]^+$, 362.0885) (Found: C, 59.81; H, 5.26; N, 3.89. $C_{18}H_{19}NO_3S_2$ requires C, 59.81; H, 5.30; N, 3.87).

(+)-(S_S*)*-S-*Methyl*-S-*phenyl*-N-*(2,4,6-triisopropylphenylsulfonyl)sulfoximine*



To a solution of (+)-(S_S)-*S*-methyl-*S*-phenylsulfoximine (8.40 g, 54.0 mmol, 1.0 equiv.) in pyridine (45 mL) at –5 °C, was added DMAP (30 mg) and 2,4,6-triisopropylphenylsulfonyl chloride (16.4 g, 54.0 mmol, 1.0 equiv.) to give a yellow solution. The reaction was heated at 60 °C for 2 h. The reaction was cooled to rt, poured into cold H_2O and 2 M aq. HCl added. The organic layer was extracted with CH_2Cl_2, and then washed with 2 M aq. HCl and H_2O, until pH 8 was achieved. The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The orange oil was treated with EtOH to give (+)-(S_S)-*S*-methyl-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (14.15 g, 59%) as a colourless solid; R_f 0.60 (50% EtOAc–petrol); mp 139–141 °C; $[\alpha]_D^{20}$ +20.0 (*c* 5.0, CH_2Cl_2); ν_{max} (film) 3055, 2963, 2870, 1599, 1463, 1448, 1423, 1312, 1294, 1265, 1238, 1148, 1100, 1069, 741, 704 cm^{-1}; δ_H (400 MHz) 8.02 (2H, d, *J* 8.0 Hz, *o*-Ph) 7.71 (1H, t, *J* 7.5 Hz, *p*-Ph) 7.61 (2H, t, *J* 8.0 Hz, *m*-Ph), 7.14 (2H, s, *m*-SO_2Ar), 4.40 (2H, sept, *J* 6.5 Hz, *o*-ArCH), 3.44 (3H, s, SCH_3), 2.90 (1H, sept, *J* 7.0 Hz, *p*-ArCH), 1.29–1.24 (18H, m, CH(CH_3)$_2$); δ_C (100 MHz) 152.0, 149.0, 138.8, 137.2 (4°), 134.3, 129.6, 127.5, 123.4 (3°), 47.0 (SCH_3), 34.1 (*p*-ArCH), 29.3 (*o*-ArCH), 24.7, 24.6 (*o*-ArCH(*C*H_3)$_2$), 23.7 (*p*-ArCH(*C*H_3)$_2$); *m/z* (CI) 439 $[M+NH_4]^+$, 422, 299, 208, 156, 141, 80; data were in accordance with those previously reported.[13]

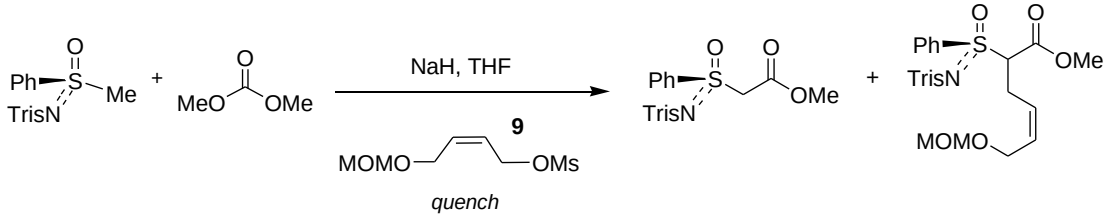
(+)-Methyl (S_S*)-2-(*N-*(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)acetate*



To sodium hydride (60% dispersion in mineral oil, washed with hexane; 68.0 mg, 2.82 mmol, 2.5 equiv.) suspended in THF (2 mL) was added dimethyl carbonate (2

mL) and the reaction mixture stirred at reflux whilst a solution of (+)-(S_S)-*S*-methyl-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (500 mg, 1.13 mmol, 1.0 equiv.) in THF (3 mL) was added dropwise. The stirred reaction was heated under reflux for 16 h, cooled on ice and quenched with MeOH–AcOH (2:1; 2 mL). The solution was poured on to H_2O and the product extracted with Et_2O (×5). The combined organic layers were washed with sat. aq. $NaHCO_3$ and H_2O, dried ($MgSO_4$) and concentrated under reduced pressure. The yellow oil was then crystallised from EtOH to give (+)-methyl (S_S)-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)acetate (0.29 g, 75%) as a colourless solid; mp 111–112 °C; R_f 0.40 (100% CH_2Cl_2); $[\alpha]_D^{20}$ +11.0 (*c* 5.0, CH_2Cl_2); ν_{max} (film) 3055, 2960, 1749, 1599, 1265, 1149, 1095, 1065, 738, 704 cm^{-1}; δ_H (400 MHz) 8.04 (2H, d, *J* 7.5 Hz, *o*-Ph), 7.74 (1H, t, *J* 7.5 Hz, *p*-Ph) 7.62 (2H, t, *J* 8.0 Hz, *m*-Ph), 7.14 (2H, s, *m*-SO_2Ar), [4.76, 4.62] (2H, AB doublet, *J* 14.5 Hz, CH_2), 4.40 (2H, sept, *J* 6.5 Hz, *o*-ArCH), 3.68 (3H, s, OCH_3), 2.90 (1H, sept, *J* 7.0 Hz, *p*-ArCH), 1.29–1.21 (18H, m, $CH(CH_3)_2$); δ_C (100 MHz) 162.2, (C=O), 152.2, 149.1, 137.0, 136.5 (4°), 134.8, 129.4, 128.6, 123.5 (3°), 61.8 (OCH_3), 53.2 (CH_2), 34.1 (*p*-ArCH), 29.3 (*o*-ArCH), 24.7, 24.6 (*o*-ArCH(CH_3)$_2$), 23.6 (*p*-ArCH(CH_3)$_2$); *m/z* (CI) 497 $[M+NH_4]^+$, 301, 208 (Found $[M+NH_4]^+$, 497.2141. $C_{24}H_{33}NO_5S_2$ requires $[M+NH_4]^+$, 497.2144).

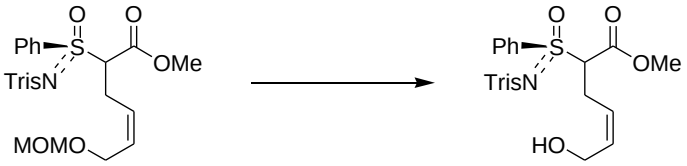
Methyl (S_S*,*Z*)-6-(methoxymethoxy)-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoate*



To a suspension of sodium hydride (60% dispersion in mineral oil, washed with hexane; 1.19 g, 29.7 mmol, 2.5 equiv.) in THF (30 mL) was added dimethyl carbonate (20 mL) and the reaction mixture was stirred at reflux whilst a solution of (+)-methyl (S_S)-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)acetate (5.00 g, 11.9 mmol, 1.0 equiv.) in THF (30 mL) was added dropwise. The stirred reaction was heated under reflux overnight, cooled in ice and quenched with mesylate **9** (2.49 g, 11.9 mmol, 1.0 equiv.), followed by MeOH–AcOH (2:1; 10 mL) The solution was poured on to water and the product extracted with Et_2O (×5). The combined organic

layers were washed with sat. aq. $NaHCO_3$ and H_2O, dried ($MgSO_4$) and concentrated under reduced pressure. The yellow oil was purified by chromatography (100% CH_2Cl_2) to give recovered (+)-methyl (S_S)-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)acetate (2.06 g, 36%) as a colourless solid, and methyl (S_S,*Z*)-6-(methoxymethoxy)-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoate (3.01 g, 47%) as a yellow oil; R_f 0.17 (100% CH_2Cl_2); ν_{max} (film) 2958, 1747, 1600, 1448, 1362, 1317, 1244, 1196, 1150, 1094, 1048, 998, 940, 922, 844, 768, 749, 685, 665 cm^{-1}; δ_H (400 MHz) 7.95 (2H, d, *J* 8.0 Hz, *o*-Ph), 7.73 (1H, tt, *J* 7.5, 1.0 Hz, *p*-Ph), 7.59 (2H, td, *J* 8.0, 3.0 Hz, *m*-Ph), 7.13 (2H, s, *m*-SO_2Ar), 5.70 (1H, dt, *J* 11.0, 6.5 Hz, OCH_2CH), 5.39 (1H, dd, *J* 11.0, 7.0 Hz, $SCHCH_2CH$), [4.57, 4.56] (2H, 2 × s, CH_2OCH_3), 4.06–3.95, (2H, m, *o*-ArCH), [3.72, 3.62] (3H, 2 × s, CO_2CH_3), [3.32, 3.31] (3H, 2 × s, CH_2OCH_3), 2.88 (1H, sept, *J* 7.0 Hz, *p*-ArCH), 1.28–1.19 (18H, m, $CH(CH_3)_2$); δ_C (100 MHz) 165.3, 165.1 (C=O), 152.2, 152.1, 149.2, 149.1, 137.3, 137.0, 134.2, 132.3, 131.1, 124.9 (4°), 134.9, 134.8, 132.6, 131.2, 129.8, 129.2, 124.9, 123.5 (3°), 95.8 (OCH_2O), 71.4, 70.7 (SCH), 62.6, 62.6 (OCH_2OCH_2), 55.4, 55.3 (CH_2OCH_3), 53.3, 53.2 (CO_2CH_3), 34.1, (*p*-ArCH), 29.3, 29.3 (*o*-ArCH), 26.5, 25.2 ($SCHCH_2$), 24.7, 24.6 (*o*-ArCH(CH_3)$_2$), 23.6, (*p*-ArCH(CH_3)$_2$); *m/z* (CI) 611 $[M+NH_4]^+$, 567, 532, 497, 425, 301 (Found $[M+NH_4]^+$, 611.2388. $C_{30}H_{43}NO_7S_2$ requires $[M+NH_4]^+$, 611.2825) (Found: C, 60.59; H, 7.18; N, 2.26. $C_{30}H_{43}NO_7S_2$ requires C, 60.68; H, 7.30; N, 2.36).

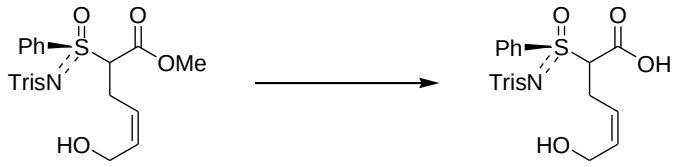
Methyl (S_S,Z*)-6-hydroxy-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoate*



According to general procedure **E**, a solution of methyl (S_S,*Z*)-6-(methoxymethoxy)-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoate (2.50 mg, 4.20 mmol) in MeCN (42 mL) was treated with 2 M aq. HCl (8.5 mL) to give methyl (S_S,*Z*)-6-hydroxy-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoate (2.14 g, 93%) as a yellow oil; R_f 0.24 (50% EtOAc–petrol); ν_{max} (film) 3425, 2960, 1743, 1643, 1600, 1448, 1314, 1245, 1149, 1093, 1054 cm^{-1}; δ_H (400 MHz) 7.95 (2H, d, *J* 8.0 Hz, *o*-Ph), 7.76 (1H, dt, *J* 7.5, 7.5 Hz, *p*-Ph), 7.62 (2H, dt, *J* 8.0, 7.5

Hz, *m*-Ph), 7.14 (2H, s, *m*-SO_2Ar), 5.79 (1H, dt, *J* 13.0, 6.5 Hz, C*H*CH_2OH), 5.37 (1H, dt, *J* 18.0, 8.0 Hz, SCHCH_2C*H*), [4.99, 4.59] (1H, 2 × dd, *J* 11.5, 3.5 Hz, SCH), 4.37 (2H, 2 × sept, *J* 6.5 Hz, *o*-ArCH), 4.18–4.06 (2H, m, CH_2OH), [3.77, 3.63] (3H, 2 × s, OCH_3), 3.00–2.87 (2H, m, *p*-ArCH and 1 × SCHCH_2), [2.80–2.71, 2.59–2.51] (1H, 2 × m, 1 × SCHCH_2), 1.30–1.18 (18H, m, CH(CH_3)$_2$); δ_C (100 MHz) 165.8, 165.5 (C=O), 152.3, 152.1, 149.2, 149.1, 137.9, 137.2, 136.9, 134.9, 133.8, 128.2, 124.0 (4°), 135.0, 133.8, 129.7, 129.7, 129.2, 129.1, 125.3, 124.7, 123.5, 123.5 (3°), 71.5, 70.8 (SCH), 58.1, 58.0 (CH_2OH), 53.4, 53.3 (CO_2CH_3), 34.1, (*p*-ArCH), 29.4, 29.3 (*o*-ArCH), 26.4, 25.1 (SCHCH_2), 24.7, 24.6 (*o*-ArCH(CH_3)$_2$), 23.6, (*p*-ArCH(CH_3)$_2$); *m/z* (CI) 567 $[M+NH_4]^+$, 425, 301, 284, 194 (Found $[M+NH_4]^+$, 567.2579. $C_{28}H_{39}NO_6S_2$ requires $[M+NH_4]^+$, 567.2563).

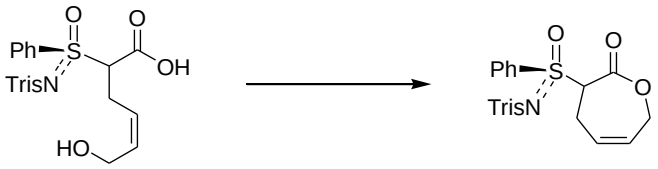
(S_S*,Z)-6-Hydroxy-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoic acid*



According to general procedure **F**, a solution of methyl (S_S,*Z*)-6-hydroxy-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoate (2.14 g, 3.89 mmol, 1.0 equiv.) in THF (10 mL) was treated with 2 M aq. LiOH (10.0 mL, 20.0 mmol, 5.0 equiv.) to give (S_S,*Z*)-6-hydroxy-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoic acid (1.84 g, 88%) as a colourless crystalline solid; mp 58–60 °C; ν_{max} (film) 3445 (br), 2963, 1645, 1600, 1448, 1265, 1147, 1094, 1063, 738 cm^{-1}; δ_H (400 MHz) 7.95, (2H, d, *J* 7.5 Hz, *o*-Ph), 7.73 (1H, m, *p*-Ph), 7.59 (2H, dt, *J* 7.5, 7.5 Hz, *m*-Ph), 7.13 (2H, s, *m*-SO_2Ar), 5.76 (1H, dd, *J* 17.5, 7.0 Hz, C*H*CH_2OH), 5.58 (1H, br s, CO_2H), 5.42 (1H, dd, *J* 16.0, 10.0 Hz, SCHCH_2C*H*), [4.83, 4.58] (1H, 2 × dd, *J* 11.5, 3.0 Hz, SCH), 4.32 (2H, sept, *J* 6.5 Hz, *o*-ArCH), [4.12, 4.01] (2H, 2 × d, *J* 6.5 Hz, CH_2OH), 2.95–2.56 (3H, m, *p*-ArCH and SCHCH_2), 1.29–1.20 (18H, m, CH(CH_3)$_2$); δ_C (100 MHz) 166.7, 166.2 (C=O), 152.4, 149.2, 136.8, 134.3, 133.9, 124.2 (4°), 135.0, 133.0, 132.8, 129.7, 129.3, 124.9, 124.7, 123.5 (3°), 71.4, 70.9 (SCH), 58.5, 57.8 (CH_2OH), 34.2 (*p*-ArCH), 29.3 (*o*-ArCH), 26.2, 25.1 (SCHCH_2), 24.7, 24.7, 24.6, 24.6 (*o*-ArCH(CH_3)$_2$), 23.6 (*p*-ArCH(CH_3)$_2$); *m/z* (FAB) 536 $[M+NH_4]^+$, 538, 518, 446, 282, 267, 203, 125, 93 (Found $[M+NH_4]^+$, 536.2122.

$C_{27}H_{37}NO_6S_2$ requires $[M+NH_4]^+$, 536.2141) (Found: C, 60.55; H, 6.91; N, 2.63. $C_{27}H_{37}NO_6S_2$ requires C, 60.53; H, 6.96; N, 2.61).

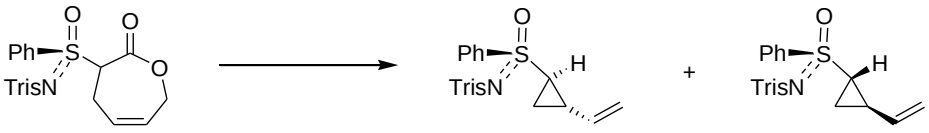
*(S$_S$)-3-(*N*-(2,4,6-Triisopropylphenylsulfonyl)phenylsulfonimidoyl)-4,7-dihydrooxepin-2(3*H*)-one* **20**



20

According to general procedure **G**, a solution of (*S*$_S$,*Z*)-6-hydroxy-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoic acid (1.00 g, 1.87 mmol, 1.0 equiv.) in CH_2Cl_2 (10 mL) was treated with EDCI (0.39 g, 2.05 mmol, 1.1 equiv.) and purified by chromatography (50% EtOAc–petrol) to give (*S*$_S$)-3-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)-4,7-dihydrooxepin-2(3*H*)-one **20** (0.87 g, 90%) as a colourless crystalline solid; mp 77–79 °C; R_f 0.63 (50% EtOAc–petrol); ν_{max} (film) 3442 (br), 3055, 1752, 1638, 1600, 1422, 1265, 1148, 1093, 1054, 895, 735 cm^{-1}; δ_H (500 MHz) 8.14 (2H, 2 × dt, *J* 7.0, 1.5 Hz, *o*-Ph), 7.69 (1H, m, *p*-Ph), 7.57 (2H, m, *m*-Ph), [7.11, 7.10] (2H, 2 × s, *m*-SO_2Ar), [6.00, 5.73] (1H, dd, *J* 13.0, 3.5Hz, SCH), 5.88 (2H, br d, *J* 3.5 Hz, HC=CH), [5.12, 4.51] (2H, m, OCH_2), 4.37 (2H, sept, *o*-ArCH), [3.40, 3.21] (1H, dd, *J* 17.5, 3.0 Hz, SCHCH_2), 2.87 (1H, sept, *p*-ArCH), 2.41 (1H, td, *J* 16.0, 2.5 Hz, SCHCH_2), 1.27–1.14 (18H, m, CH(CH_3)$_2$); δ_C (125 MHz) 166.3 (C=O), 152.2, 149.2, 149.0, 137.0, 136.7, 133.5, 133.1 (4°), 134.8, 134.8, 131.1, 130.9, 128.8, 128.7, 124.8, 124.4, 123.5, 123.4 (3°), 66.0, 65.8 (SCH), 64.2, 64.0 (OCH_2), 34.1 (*p*-ArCH), 29.3, 29.2 (*o*-ArCH), 28.9, 27.6 (SCHCH_2), 24.7, 24.7, 24.6, 24.5 (*o*-ArCH(*C*H_3)$_2$), 23.6 (*p*-ArCH(*C*H_3)$_2$); *m/z* (CI) 535 $[M+NH_4]^+$, 491, 425, 301 (Found $[M+NH_4]^+$, 535.2300. $C_{27}H_{35}NO_5S_2$ requires $[M+NH_4]^+$, 535.2300) (Found: C, 62.54; H, 6.71; N, 2.87. $C_{27}H_{35}NO_5S_2$ requires C, 62.64; H, 6.81; N, 2.71).

($S_{S,}$*1*R,*2*S)-S-*Phenyl*-S-*(2-vinylcyclopropyl)*-N-*tosylsulfoximine and* ($S_{S,}$*1*S,*2*R)-S-*Phenyl*-S-*(2-vinylcyclopropyl)*-N-*tosylsulfoximine* **22**

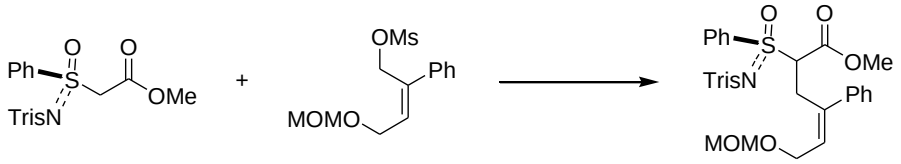


20 **22** (3:2 ratio: unassigned)

According to general procedure **H**, a solution of lactone **20** (50.0 mg, 97.0 μmol, 1.0 equiv.) was treated with BSA (23.9 μl, 97.0 μmol, 1.0 equiv.) and KOAc (1.0 mg, 9.70 μmol, 0.1 equiv.) in DMF (1 mL) to give a diastereomeric mixture (3:2, unassigned) of ($S_{S,}$1*R*,2*S*)-*S*-phenyl-*S*-(2-vinylcyclopropyl)-*N*-tosylsulfoximine and ($S_{S,}$1*S*,2*R*)-*S*-phenyl-*S*-(2-vinylcyclopropyl)-*N*-tosylsulfoximine **22** (32 mg, 69%) as a brown oil; R_f 0.80 (50% EtOAc–petrol); ν_{max} (film) 3449 (br), 3057, 1639, 1421, 1264, 1148, 1100, 895, 737 cm^{-1}; δ_H (500 MHz) 7.94 (2H, dt, *J* 8.0, 1.5 Hz, *o*-Ph), 7.66 (1H, m, *p*-Ph), 7.56 (2H, td, *J* 8.0, 1.5 Hz, *m*-Ph), 7.11 (1H, s, *m*-SO_2Ar major), 7.10 (1H, s, *m*-SO_2Ar minor), 5.50 (1H, ddd, *J* 17.0, 10.0, 7.5 Hz, C*H*=CH_2 minor), 5.32 (1H, ddd, *J* 17.0, 10.0, 7.5 Hz, C*H*=CH_2 major), 5.23 (1H, d, *J* 17.0 Hz, CH=CH_2 *cis* minor), 5.11 (1H, d, *J* 10.0 Hz, CH=CH_2 *trans* minor), 5.04 (1H, d, *J* 17.0 Hz, CH=CH_2 *cis* major), 4.98 (1H, d, *J* 10.0 Hz, CH=CH_2 *trans* major), 4.35 (2H, 2 × sept, *J* 7.0 Hz, *o*-ArCH), 2.88 (1H, sept, *J* 7.0 Hz, *p*-ArCH), 2.67 (1H, m, SCH major), 2.65 (1H, m, SCH minor), 2.61 (1H, m, SCHC*H* minor), 2.23 (1H, m, SCHC*H* major), [1.92, 1.37] (2H, 2 × m, SCHCH_2 major), [1.50, 1.10] (2H, 2 × m, SCHCH_2 minor), 1.28–1.20 (18H, m, CH(CH_3)$_2$); δ_C (125 MHz) 151.9, 151.8, 149.1, 139.2, 139.2, 137.3 (4°), 134.3, 133.9, 129.4, 127.7, 127.6, 123.3 (3°), 134.2, 133.8 (*C*H=CH_2), 117.5, 117.2 (CH=*C*H_2), 42.0 (SCH), 34.1 (*p*-ArCH), 29.2, 29.2 (*o*-ArCH), 24.7, 24.7, 24.6, 24.6 (*o*-ArCH(*C*H_3)$_2$), 23.7, 23.2 (SCH*C*H), 23.6 (*p*-ArCH(*C*H_3)$_2$), 14.2, 12.4 (SCH*C*H_2); *m/z* (CI) 491 $[M+NH_4]^+$, 474 $[M+H]^+$, 301, 52 (Found $[M+H]^+$, 474.2157. $C_{26}H_{35}NO_3S_2$ requires $[M+H]^+$, 474.2137) (Found: C, 66.00; H, 7.44; N, 2.80. $C_{26}H_{35}NO_3S_2$ requires C, 65.92; H, 7.45; N, 2.96).

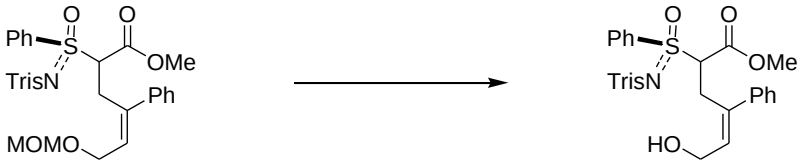
7. Synthesis and reactions of sulfoximinyl γ-aryl lactones 23a–c

*(±)-Methyl (Z)-6-methoxymethoxy-4-phenyl-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)-phenylsulfonimidoyl)hex-4-enoate*



According to general procedure **D**, a suspension of sodium hydride (13.7 mg, 0.57 mmol, 1.2 equiv.) in THF (0.75 mL) was treated with (±)-methyl 2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)acetate (228 mg, 0.48 mmol, 1.0 equiv.) in THF (1.0 mL) and methanesulfonic acid (*Z*)-4-methoxymethoxy-2-phenylbut-2-enyl ester (136 mg, 0.48 mmol, 1.0 equiv.) in THF (0.75 mL) to give (±)-methyl (*Z*)-6-methoxymethoxy-4-phenyl-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoate, which was used without further purification; R_f 0.40 (50% EtOAc–petrol).

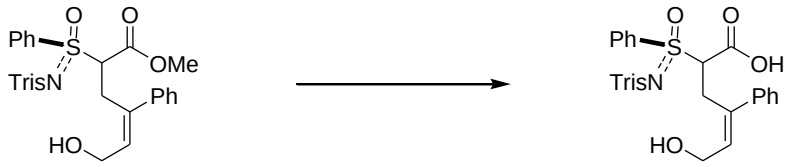
*(±)-Methyl (Z)-6-hydroxy-4-phenyl-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)-phenylsulfonimidoyl)hex-4-enoate*



According to general procedure **E**, a solution of (*Z*)-6-methoxymethoxy-4-phenyl-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoate (276 mg, 0.41 mmol, 1.0 equiv.) in MeCN (4 mL) was treated with 2 M aq. HCl (0.8 mL). Purification by chromatography (20→50% EtOAc–petrol) gave (±)-methyl (*Z*)-6-hydroxy-4-phenyl-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoate as a colourless oil; R_f 0.16 (50% EtOAc–petrol); ν_{max} (film) 2957, 2869, 1743, 1599, 1447, 1313, 1296, 1243, 1195, 1147, 1091, 1048, 1021, 997, 764, 683 cm^{-1}; δ_H (400 MHz) 7.93 (2H, dd, *J* 8.0, 8.0 Hz, *o*-SPh), 7.74 (1H, m, *p*-SPh), 7.59 (2H, m, *m*-SPh), 7.32–7.17 (5H, m, Ph), 7.10 (2H, s, *m*-SO_2Ar), 5.97 (1H, 2 × t, *J* 6.5 Hz, C*H*CH_2OH), [4.63, 4.41] (1H, 2 × dd, *J* 11.5, 3.5 Hz, SCH), 4.30 (2H, sept, *J* 7.0 Hz, *o*-ArCH), 4.20 (2H, m, CH_2OH), [3.48, 3.41] (3H, 2 × s, OCH_3), 3.17 (2H, m, SCHCH_2), 2.87 (1H, 2 × sept, *J* 7.0 Hz, *p*-ArCH), [2.04, 1.84] (1H, 2 × dd, *J* 7.0, 5.0

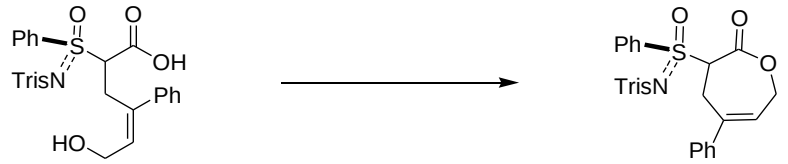
Hz, SCHCH_2), 1.27–1.18 (18H, m, CH(CH_3)$_2$); δ_C (100 MHz) 165.5, 165.4 (C=O), 152.2, 152.1, 149.2, 149.1, 139.4, 139.3, 137.1, 137.0, 134.8, 134.6, (4°), 136.1, 135.8, 135.2, 134.9, 129.7, 129.6, 129.2, 128.8, 128.6, 128.2, 128.1, 126.6, 126.4 (3°), 123.4, 123.4 (*m*-SO_2Ar), 70.6, 70.4 (SCH), 58.9, 58.8 (CH_2OH), 53.1, 53.1 (OCH_3), 34.1 (*p*-ArCH), 29.3 (*o*-ArCH), 27.8, 26.7, (SCH*C*H_2), 24.7, 24.6 (*o*-ArCH(*C*H_3)$_2$), 23.6 (*p*-ArCH(*C*H_3)$_2$); *m/z* (CI) 643 $[M+NH_4]^+$ (Found $[M+NH_4]^+$, 643.2873. $C_{34}H_{43}NO_6S_2$ requires $[M+NH_4]^+$, 643.2870) (Found: C, 65.29; H, 6.93; N, 2.24. $C_{34}H_{43}NO_6S_2$ requires C, 65.25; H, 6.93; N, 2.24.).

*(±)-(Z)-6-Hydroxy-4-phenyl-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoic acid*



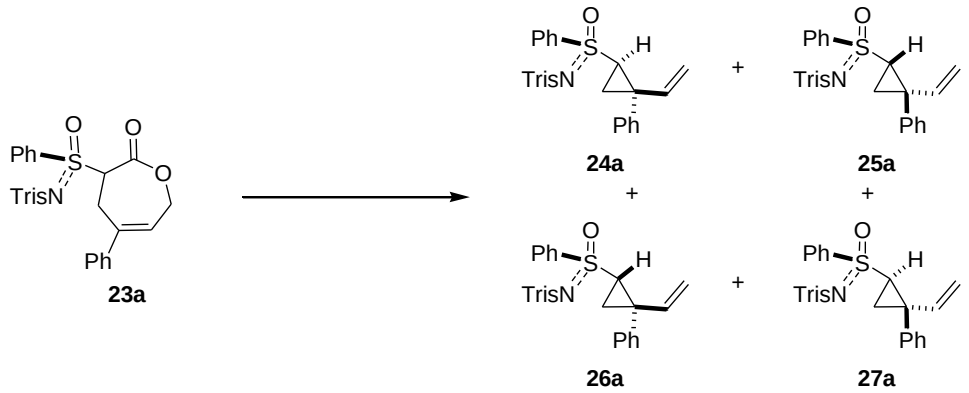
According to general procedure **F**, a solution of (±)-methyl (*Z*)-6-hydroxy-4-phenyl-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoate (117 mg, 0.19 mmol, 1.0 equiv.) in THF (0.5 mL) was treated with 2 M aq. LiOH (0.5 mL) to give (±)-(*Z*)-6-hydroxy-4-phenyl-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoic acid as a colourless foam, which was used without further purification; ν_{max} (film) 3420, 2959, 1738, 1599, 1447, 1311, 1295, 1244, 1147, 1092, 1049, 1021, 997, 764, 753, 743, 684 cm^{-1}; δ_H (300 MHz; CD_3OD) 7.87 (2H, d, *J* 8.0 Hz, *o*-SPh), 7.79 (1H, 2 × t, *J* 7.5 Hz, *p*-SPh), 7.61 (2H, 2 × t, *J* 8.0 Hz, *m*-SPh), 7.31 (2H, s, *m*-SO_2Ar), 7.25–7.09 (5H, m, Ph), [5.93, 5.87] (1H, 2 × t, *J* 6.5 Hz, C*H*CH_2OH), 4.20 (2H, 2 × sept, *J* 6.5 Hz, *o*-ArCH), 4.29–4.04 (3H, m, SCH and CH_2OH), 3.40–3.06 (2H, m, SCHCH_2), 2.90 (1H, 2 × sept, *J* 6.5 Hz, *p*-ArCH), 1.26–1.12 (18H, m, CH(CH_3)$_2$); δ_C (75 MHz; CD_3OD) 166.7, 166.6 (C=O), 153.8, 153.8, 150.6, 150.6, 141.2, 141.0, 138.5, 138.5, 136.2, 136.1, 133.4, 133.3 (4°), 136.5, 136.4, 130.9, 130.9, 130.6, 130.4, 129.8, 129.7 129.1, 129.1, 127.7, 127.6, 124.6 (3°), 72.0, 71.5 (SCH), 59.7, 59.7 (CH_2OH), 35.4 (*p*-ArCH), 30.5, 30.5 (*o*-ArCH), 28.6, 28.0 (SCH*C*H_2), 25.1, 25.1 (*o*-ArCH(*C*H_3)$_2$), 24.1 (*p*-ArCH(*C*H_3)$_2$); *m/z* (CI) 629 $[M+NH_4]^+$, 594, 550 (Found $[M+NH_4]^+$, 629.2717. $C_{33}H_{41}NO_6S_2$ requires $[M+NH_4]^+$, 629.2714).

*(±)-5-Phenyl-3-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)-4,7-dihydrooxepin-2(3*H*)-one* **23a**



According to general procedure **G**, a solution of (±)-(*Z*)-6-hydroxy-4-phenyl-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoic acid (109 mg, 0.18 mmol, 1.0 equiv.) in CH_2Cl_2 (1.0 mL) was treated with EDCI (41 mg, 0.21 mmol, 1.2 equiv.). Purification by chromatography (30% EtOAc–petrol) gave (±)-5-phenyl-3-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)-4,7-dihydro-oxepin-2(3*H*)-one **23a** (103 mg, 36% over four steps) as a colourless solid; R_f 0.45 (50% EtOAc–petrol); ν_{max} (film) 2958, 1753, 1599, 1446, 1311, 1246, 1148, 1093, 1057 cm^{-1}; δ_H (400 MHz) 8.17 (2H, m, *o*-SPh), 7.70 (1H, td, *J* 7.5, 1.5 Hz, *p*-SPh), 7.58 (2H, m, *m*-SPh), 7.37–7.31 (4H, m, *o*-/*m*-Ph), 7.27 (1H, m, *p*-Ph), [7.12, 7.11] (2H, 2 × s, *m*-SO_2Ar), [6.15, 5.91] (1H, dd, *J* 13.0, 3.5 Hz, SCH), 6.05 (1H, ddtd, *J* 9.5, 5.5, 3.5, 2.0 Hz, OCH_2CH), 5.26 (1H, ddd, *J* 16.0, 12.5, 3.5 Hz, OCH_2), 4.67 (1H, dd, *J* 16.0, 7.5 Hz, OCH_2), 4.39 (2H, 2 × sept, *J* 7.0 Hz, *o*-ArCH), [3.82, 3.61] (1H, d, *J* 17.5 Hz, $SCHCH_2$), 2.87 (1H, 2 × sept, *J* 7.0 Hz, *p*-ArCH), 2.75 (1H, 2 × d, *J* 13.5 Hz, $SCHCH_2$), 1.28–1.20 (18H, m, $CH(CH_3)_2$); δ_C (100 MHz) 166.3 (C=O), 152.3, 149.3, 149.0, 141.0, 140.8, 140.4, 140.3, 137.0, 136.6, 133.6, 133.2 (4°), 134.9, 131.1, 131.0, 128.9, 128.8, 128.7, 128.7, 126.3, 126.0, 123.5, 123.5, 121.9, 121.6 (3°), 66.0, 65.7 (SCH), 64.4, 64.2 (OCH_2), 34.1 (*p*-ArCH), 31.9, 30.4 ($SCHCH_2$), 29.4, 29.3 (*o*-ArCH), 24.7, 24.7, 24.6, 24.5 (*o*-ArCH(CH_3)$_2$), 23.6 (*p*-ArCH(CH_3)$_2$); *m/z* (CI) 611 $[M+NH_4]^+$, 425, 301, 251, 206, 156, 132 (Found $[M+NH_4]^+$, 611.2623. $C_{33}H_{39}NO_5S_2$ requires $[M+NH_4]^+$, 611.2613) (Found: C, 66.66; H, 6.53; N, 2.27. $C_{33}H_{39}NO_5S_2$ requires C, 66.75; H, 6.62; N, 2.36.).

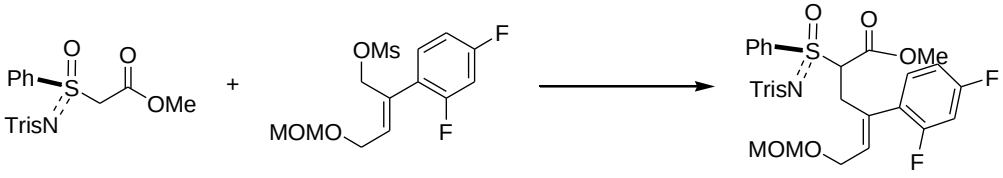
(S*$_S$,*1*R,*2*R)-S-*Phenyl*-S-*(2-phenyl-2-vinylcyclopropyl)*-N-*(2,4,6-triisopropylphenyl-sulfonyl)sulfoximine* **24a**, (S*$_S$,*1*S,*2*S)-S-*phenyl*-S-*(2-phenyl-2-vinylcyclopropyl)*-N-*(2,4,6-triisopropylphenylsulfonyl)sulfoximine* **25a**, (S*$_S$,*1*S,*2*R)-S-*phenyl*-S-*(2-phenyl-2-vinylcyclopropyl)*-N-*(2,4,6-triisopropylphenylsulfonyl)sulfoximine* **26a**, *and* (S*$_S$,*1*R,*2*S)-S-*phenyl*-S-*(2-phenyl-2-vinylcyclopropyl)*-N-*(2,4,6-triisopropylphenyl-sulfonyl)sulfoximine* **27a**



According to general procedure **H**, a solution of lactone **23a** (50 mg, 0.08 mmol, 1.0 equiv.) in DMF (0.4 mL) was treated with KOAc (0.8 mg, 0.008 mmol, 0.1 equiv.) and BSA (20.8 μL, 0.08 mmol, 1.0 equiv.) to give the sulfoximines **24a**–**27a** as a colourless gum (34 mg, 78%) as a mixture of diastereomers (ratio **24a**:**25a**:**26a**:**27a** = 44:22:26:7) which were separable by chromatography (10% EtOAc–petrol); **25a** (isolated as a single diastereoisomer): R_f 0.44 (50% EtOAc–petrol); ν_{max} (film) 2960, 1600, 1447, 1423, 1311, 1265, 1148, 1099, 1068, 998, 737, 702 cm^{-1}; δ_H (400 Hz) 8.03 (2H, d, *J* 7.5 Hz, *o*-Ph), 7.70 (1H, tt, *J* 7.5, 1.5 Hz, *p*-Ph), 7.60 (2H, t, *J* 7.5 Hz, *m*-Ph), 7.21 (3H, m, Ph), 7.11 (2H, s, *m*-SO_2Ar), 6.82 (2H, m, Ph), 6.12 (1H, dd, *J* 17.0, 10.5 Hz, C*H*=CH_2), 5.04 (1H, dd, *J* 10.5, 1.0 Hz, CH=CH_2 *trans*), 4.42 (1H, d, *J* 17.0 Hz, CH=CH_2 *cis*), 4.39 (2H, sept, *J* 7.0 Hz, *o*-ArCH), 3.33 (1H, dd, *J* 9.0, 6.0 Hz, SCH), 2.88 (1H, sept, *J* 7.0 Hz, *p*-ArCH), 2.30 (1H, dd, *J* 6.0, 6.0 Hz, SCHCH_2), 2.07 (1H, dd, *J* 9.0, 6.0 Hz, SCHCH_2), 1.24 (18H, m, CH_3); δ_C (100 MHz) 151.9, 149.1, 139.2, 139.1, 137.3 (4°), 138.8 (*C*H=CH_2), 134.0, 129.2, 128.6, 127.8, 127.7, 123.3 (3°), 119.0 (CH=*C*H_2), 48.4 (SCH), 39.4 (SCH*C*), 34.1 (*p*-ArCH), 29.2 (*o*-ArCH), 24.7, 24.6, 23.7, 23.6 (CH(*C*H_3)$_2$), 20.0 (SCH*C*H_2); *m/z* (CI) 550 $[M+H]^+$, 567, 425, 301 (Found $[M+H]^+$, 550.2457. $C_{32}H_{39}NO_3S_2$ requires $[M+H]^+$, 550.2450); **24a** (isolated as a single diastereoisomer): R_f 0.41 (50% EtOAc–petrol); ν_{max} (film) 2961, 2929, 1600, 1463, 1447, 1423, 1311, 1265, 1149, 1097, 1051, 739, 703 cm^{-1}; δ_H (400 Hz) 8.04 (2H, d, *J* 7.5 Hz, *o*-Ph), 7.68 (1H, t, *J* 7.5 Hz, *p*-Ph), 7.58 (2H, t, *J* 7.5 Hz, *m*-

Ph), 7.29 (5H, m, Ph), 7.12 (2H, s, *m*-SO_2Ar), 6.43 (1H, dd, *J* 17.0, 10.5 Hz, C*H*=CH_2), 5.12 (1H, d, *J* 10.5 Hz, CH=CH_2 *trans*), 4.65 (1H, dd, *J* 17.0, 0.5 Hz, CH=CH_2 *cis*), 4.39 (2H, sept, *J* 7.0 Hz, *o*-ArCH), 3.03 (1H, dd, *J* 8.5, 6.5 Hz, SCH), 2.90 (1H, sept, *J* 7.0 Hz, *p*-ArCH), 2.03 (1H, dd, *J* 6.0, 6.0 Hz, SCHCH_2), 1.75 (1H, dd, *J* 8.5, 6.0 Hz, SCHCH_2), 1.28 (18H, m, CH_3); δ_C (125 MHz) 151.8, 149.2, 140.3, 139.7, 137.5 (4°), 136.1, 133.8, 129.5, 129.4, 128.6, 127.9, 127.7, 123.2 (3°), 118.8 (CH=*C*H_2), 49.0 (SCH), 41.1 (SCH*C*), 34.1 (*p*-ArCH), 29.3 (*o*-ArCH), 24.8, 24.7, 23.7, 23.6 (CH(*C*H_3)$_2$), 19.1 (SCH*C*H_2); *m/z* (CI) 550 $[M+H]^+$, 567, 425, 301 (Found $[M+H]^+$, 550.2465. $C_{32}H_{39}NO_3S_2$ requires $[M+H]^+$, 550.2450); **26a** (isolated as a single diastereoisomer): R_f 0.38 (50% EtOAc–petrol); ν_{max} (film) 2960, 2928, 1600, 1463, 1448, 1311, 1295, 1265, 1244, 1148, 1098, 1068, 1030, 738, 702 cm^{-1}; δ_H (400 Hz) 7.61 (1H, m, Ph), 7.43 (4H, m, Ph), 7.21 (1H, m, Ph), 7.10 (2H, m, Ph), 7.08 (2H, s, *m*-SO_2Ar), 6.79 (2H, d, *J* 7.5 Hz, Ph), 5.72 (1H, dd, *J* 17.0, 10.5 Hz, C*H*=CH_2), 5.05 (1H, d, *J* 10.5 Hz, CH=CH_2 *trans*), 4.82 (1H, d, *J* 17.0 Hz, CH=CH_2 *cis*), 4.33 (2H, sept, *J* 6.5 Hz, *o*-ArCH), 3.51 (1H, dd, *J* 9.0, 5.5 Hz, SCH), 2.87 (1H, sept, *J* 7.0 Hz, *p*-ArCH), 2.63 (1H, dd, *J* 6.0, 6.0 Hz, SCHCH_2), 1.89 (1H, dd, *J* 9.0, 6.0 Hz, SCHCH_2), 1.25 (18H, m, CH_3); δ_C (100 MHz) 151.7, 149.0, 140.3, 137.8, 137.2 (4°), 133.5, 132.4, 130.3, 129.4, 128.7, 128.0, 127.6, 123.2 (3°), 115.6 (CH*C*H_2), 46.8 (SCH), 38.2 (SCH*C*), 34.1 (*p*-ArCH), 29.1 (*o*-ArCH), 24.7, 24.6, 23.7, 23.6 (CH(*C*H_3)$_2$), 17.4 (SCH*C*H_2); *m/z* (CI) 550 $[M+H]^+$, 567, 425, 301, 272, 254, 237 (Found $[M+H]^+$, 550.2435. $C_{32}H_{39}NO_3S_2$ requires $[M+H]^+$, 550.2450).

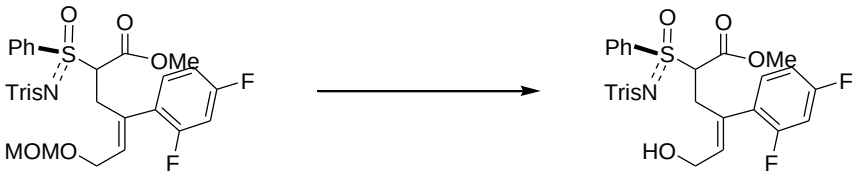
*(±)-Methyl (*E*)-4-(2,4-difluorophenyl)-6-(methoxymethoxy)-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoate*



According to general procedure **D**, a suspension of sodium hydride (54 mg, 1.35 mmol, 1.1 equiv.) in THF (1.5 mL) was treated with (±)-methyl 2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)acetate (589 mg, 1.23 mmol, 1.0 equiv.) in THF (2 mL) and methanesulfonic acid (*Z*)-2-(2,4-difluorophenyl)-4-(methoxymethoxy)but-2-enyl ester (396 mg, 1.23 mmol, 1.0 equiv.) in THF (1.5 mL) to give (±)-methyl (*E*)-4-(2,4-difluorophenyl)-6-(methoxymethoxy)-2-(*N*-(2,4,6-

triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoate as a colourless gum, which was used without further purification; R_f 0.44 (50% EtOAc–petrol); ν_{max} (film) 2955, 2925, 1744, 1599, 1501, 1315, 1243, 1148, 1091, 1039, 1022, 997, 961, 845, 684 cm^{-1}; δ_H (300 MHz) 7.92 (2H, d, *J* 7.5 Hz, *o*-Ph), 7.74 (1H, t, *J* 7.5 Hz, *p*-Ph), 7.59 (2H, t, *J* 8.0 Hz, *m*-Ph), 7.08 (2H, *m*-SO_2Ar), 7.13–7.03 (1H, m, ArF), 6.85–6.70 (2H, m, ArF), 5.76 (1H, t, *J* 6.5 Hz, C*H*CH_2O), 4.58 (2H, s, OCH_2O), 4.47 (1H, dd, *J* 12.0, 3.0 Hz, SCH), 4.27 (2H, sept, *J* 7.0 Hz, *o*-ArCH), 4.10 (2H, dd, *J* 6.5, 3.0 Hz, OC*H*$_2$CH), 3.54 (3H, s, CO_2CH_3), 3.34 (3H, s, CH_2OCH_3), [3.21, 3.17] (1H, 2 × m, SCHC*H*$_2$), 3.00 (1H, 2 × d, *J* 12.0 Hz, SCHC*H*$_2$), 2.86 (1H, sept, *J* 7.0 Hz, *p*-ArCH), 1.25–1.16 (18H, m, CH(C*H*$_3$)$_2$); δ_C (75 MHz) 164.8 (C=O), 164.3, 164.0, 161.6, 161.5, 161.0, 160.8, 158.3, 158.2 (CF), 152.1, 149.2, 137.0, 133.0 (4°),134.8, 134.7, 129.7, 129.2, 123.4 (3°), 131.3, 131.2, 131.2, 131.1 (CFCH*C*H), 124.0, 123.9, 123.8, 123.7 (*C*CF), 111.5, 111.5 111.3, 111.2 (CF*C*HCH), 104.6, 104.2, 103.9 (CF*C*HCF), 95.9 (OCH_2O), 70.1 (SCH), 63.3 (CH*C*H_2O), 55.4 (CH_2OCH_3), 53.1 (CO_2CH_3), 34.1 (*p*-ArCH), 29.7, 29.0 (SCH*C*H_2), 29.3 (*o*-ArCH), 24.7 (*o*-ArCH(*C*H_3)$_2$), 23.6 (*p*-ArCH(*C*H_3)$_2$); *m/z* (EI) 723 $[M+NH_4]^+$ (Found $[M+NH_4]^+$, 723.2943. $C_{36}H_{45}F_2NO_7S_2$ requires $[M+NH_4]^+$, 723.2944) (Found: C, 61.23; H, 6.42; N, 1.95. $C_{36}H_{45}F_2NO_7S_2$ requires C, 61.26; H, 6.43; N, 1.98.).

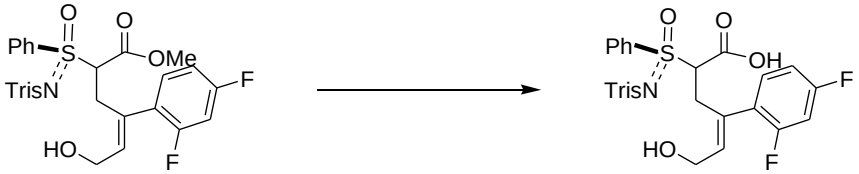
*(±)-Methyl (*E*)-4-(2,4-difluorophenyl)-6-hydroxy-2-(*N*-(2,4,6-triisopropyl-phenylsulfonyl)phenylsulfonimidoyl)hex-4-enoate*



According to general procedure **E**, (±)-methyl (*E*)-4-(2,4-difluorophenyl)-6-(methoxymethoxy)-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoate (433 mg, 0.61 mmol, 1.0 equiv.) in MeCN (6 mL) was treated with 2 M aq. HCl (1.2 mL). Purification by chromatography (20→40% EtOAc–petrol) gave (±)-methyl (*E*)-4-(2,4-difluorophenyl)-6-hydroxy-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoate (331 mg, 41% over two steps) as a colourless gum; R_f 0.21 (50% EtOAc–petrol); ν_{max} (film) 2958, 1743, 1599, 1501, 1447, 1423, 1312, 1295, 1242, 1147, 1091, 1048, 1021, 997, 966, 846, 769, 740, 684 cm^{-1}; δ_H (500 MHz) 7.90 (2H, m, *o*-Ph), 7.73 (1H, m, *p*-Ph), 7.58 (2H, m, *m*-Ph), 7.09

(1H, m, *o*-ArF), 7.09 (2H, s, *m*-SO_2Ar), 6.79 (2H, m, *m*-ArF), 5.84 (1H, 2 × t, *J* 6.5 Hz, C*H*CH_2OH), [4.69, 4.38] (1H, 2 × dd, *J* 11.5, 3.5 Hz, C*H*CH_2OH), 4.30 (2H, m, C*H*$_2$OH), 4.24 (2H, m, *o*-ArCH), [3.53, 3.46] (3H, 2 × s, OCH_3), [3.33, 3.25] (1H, 2 × dd, *J* 14.0, 3.5 Hz, SCHC*H*$_2$), [3.16, 2.97] (1H, 2 × dd, *J* 14.0, 11.5 Hz, SCHC*H*$_2$), 2.86 (1H, 2 × sept, *J* 7.0 Hz, *p*-ArCH), [2.14, 1.85] (1H, t, *J* 6.0 Hz, OH), 1.21 (18H, m, CH(C*H*$_3$)$_2$); δ_C (125 MHz) 165.6, 165.4 (C=O), 163.6, 163.5, 161.6, 161.5, 161.0, 160.9, 159.0, 158.9 (CF), 152.2, 152.2, 149.2, 149.1, 137.1, 136.9, 134.0, 130.8, 130.7 (4°), 124.1, 124.0, 124.0, 123.9 (*C*CF), 135.3, 135.1, 135.0, 134.9, 129.7, 129.6, 129.2, 123.5, 123.4 (3°), 131.3, 131.3, 131.2, 131.2, 131.1, 131.1, 131.0, 131.0 (CFCH*C*H), 111.7, 111.5, 111.3 (CF*C*HCH), 104.6, 104.4, 104.2, 104.0 (CF*C*HCF), 70.7, 70.3 (SCH), 58.7, 58.5 (CH_2OH), 53.2, 53.2 (OCH_3), 34.1 (*p*-ArCH), 29.3, 29.3 (*o*-ArCH), 28.9, 27.8 (SCH*C*H$_2$), 24.7, 24.6 (*o*-ArCH(*C*H$_3$)$_2$), 23.6 (*p*-ArCH(*C*H$_3$)$_2$; δ_F (376 MHz) [–108.8, –109.0] (1F, 2 × qd, *J* 8.0, 6.5 Hz, *o*-CF), –109.8 (1F, m, *p*-CF); *m/z* (EI) 679 $[M+NH_4]^+$, 644, 408 (Found $[M+NH_4]^+$, 679.2680. $C_{34}H_{41}F_2NO_6S_2$ requires $[M+NH_4]^+$, 679.2682) (Found: C, 61.80; H, 6.32; N, 2.18. $C_{34}H_{41}F_2NO_6S_2$ requires C, 61.70; H, 6.24; N, 2.12).

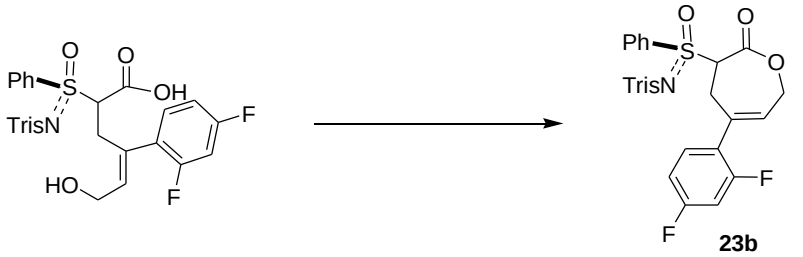
*(±)-(*E*)-4-(2,4-Difluorophenyl)-6-hydroxy-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)-phenylsulfonimidoyl)hex-4-enoic acid*



According to general procedure **F**, a solution of (±)-methyl (*E*)-4-(2,4-difluorophenyl)-6-hydroxy-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfon-imidoyl)hex-4-enoate (326 mg, 0.49 mmol, 1.0 equiv.) in THF (1.25 mL) was treated with 2 M aq. LiOH (1.25 mL) to give (±)-(*E*)-4-(2,4-difluorophenyl)-6-hydroxy-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoic acid (290 mg, 91%) as a colourless foam, which was used without further purification; ν_{max} (film) 2958, 2556, 1731, 1599, 1501, 1448, 1423, 1293, 1244, 1141, 1091, 1049, 1021, 997, 966, 848, 765, 741, 684 cm^{-1}; δ_H (300 MHz; CD_3OD) 7.86 (2H, d, *J* 8.0 Hz, *o*-Ph), 7.78 (1H, m, *p*-Ph), 7.60 (2H, m, *m*-Ph), 7.24–7.09 (1H, m, *o*-ArF), 7.15 (2H, s, *m*-SO_2Ar), 6.96–6.81 (2H, m, *m*-ArF), 5.77 (1H, 2 × t, *J* 6.5 Hz, C*H*CH_2OH), 4.29–4.03 (3H, m, SCH and C*H*$_2$OH), 4.17 (2H, 2 × sept, *J* 6.5 Hz, *o*-ArCH), 3.28–3.05 (2H, m,

SCHCH_2), 2.90 (1H, 2 × sept, *J* 7.0 Hz, *p*-ArCH), 1.26–1.12 (18H, m, CH(CH_3)$_2$); δ_C (75 MHz; CD_3OD) 166.0 (C=O), 165.9, 165.7, 163.2, 163.0, 162.6, 162.4, 159.9, 159.7 (CF), 153.8, 150.6, 150.6, 138.5, 138.4, 137.2, 137.0, 136.3, 136.2 (4°), 126.0, 126.0, 125.8, 125.6 (*C*CF), 133.2, 133.1, 133.0, 133.0, 131.5, 131.4, 124.5 (3°), 130.9, 130.8, 130.6, 130.4 (CFCH*C*H), 112.7, 112.4, 112.3 (CF*C*HCH), 105.4, 105.0, 104.7 (CF*C*HCF) 72.0, 71.4 (SCH), 59.3, 59.2 (CH_2OH), 35.4 (*p*-ArCH), 30.5 (*o*-ArCH), 29.7, 29.0 (SCH*C*H_2) 25.1, 25.1, 25.0 (*o*-ArCH(*C*H_3)$_2$), 24.1 (*p*-ArCH(*C*H_3)$_2$); *m/z* (EI) 665 $[M+NH_4]^+$, 630 (Found $[M+NH_4]^+$, 665.2524. $C_{33}H_{39}F_2NO_6S_2$ requires $[M+NH_4]^+$, 665.2525) (Found: C, 61.06; H, 5.99; N, 2.09. $C_{33}H_{39}F_2NO_6S_2$ requires C, 61.19; H, 6.07; N, 2.16).

*(±)-5-(2,4-Difluorophenyl)-3-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)-4,7-dihydrooxepin-2(3*H*)-one* **23b**

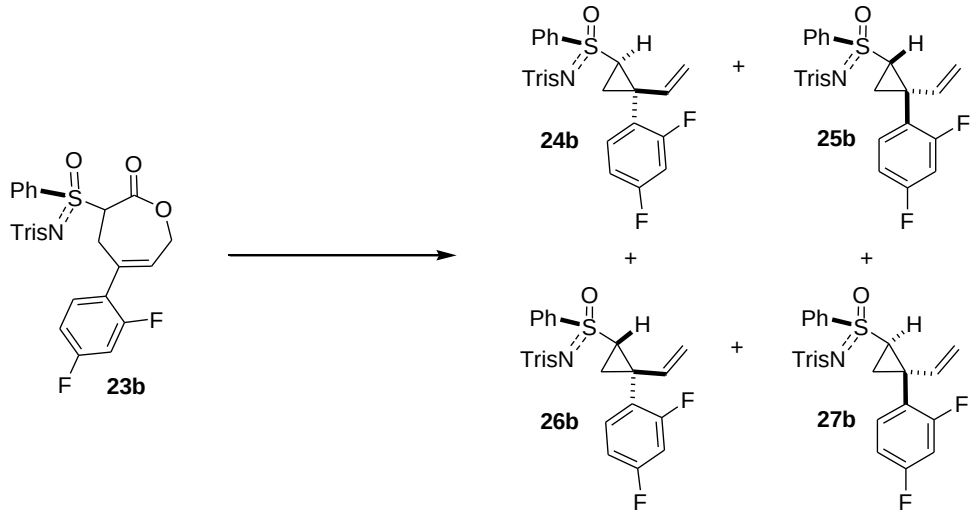


23b

According to general procedure **G**, (±)-(*E*)-4-(2,4-difluorophenyl)-6-hydroxy-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoic acid (260 mg, 0.40 mmol, 1.0 equiv.) in CH_2Cl_2 (1.0 mL) at 0 °C was treated with EDCI (85 mg, 0.44 mmol, 1.1 equiv.). Purification by chromatography (40% EtOAc–petrol) gave (±)-5-(2,4-difluorophenyl)-3-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)-4,7-dihydrooxepin-2(3*H*)-one **23b** (89 mg, 35%) as a colourless solid; mp 86–87 °C; R_f 0.48 (50% EtOAc–petrol); ν_{max} (film) 2959, 1754, 1502, 1231, 1141, 1090, 1048, 1022, 998, 972, 847, 733, 682 cm^{-1}; δ_H (400 MHz) 8.13 (2H, 2 × d, *J* 7.0 Hz, *o*-Ph), 7.70 (1H, t, *J* 7.5 Hz, *p*-Ph), 7.57 (2H, t, *J* 7.5 Hz, *m*-Ph), 7.30–7.12 (1H, m, *o*-ArF), [7.12, 7.10] (2H, 2 × s, *m*-SO_2Ar), 6.92–6.79 (2H, m, *m*-ArF), [6.08, 5.89] (1H, 2 × dd, *J* 13.0, 3.5 Hz, SCH), 5.96 (1H, m, C*H*CH_2O), 5.23 (1H, ddd, *J* 16.0, 13.0, 3.5 Hz, OCH_2), 4.68 (1H, ddd, *J* 16.0, 7.5, 4.0 Hz, OCH_2), 4.37 (2H, sept, *J* 6.5 Hz, *o*-ArCH), [3.66, 3.47] (1H, 2 × d, *J* 17.5 Hz, SCHCH_2), 2.88 (1H, sept, *J* 6.5 Hz, *p*-ArCH), 2.78 (1H, m, SCHCH_2) 1.27–1.12 (18H, m, CH(CH_3)$_2$); δ_C (125 MHz) 166.1, 166.0 (C=O), 163.8, 163.8, 161.9, 161.8, 160.6, 160.5, 158.6, 158.5 (CF),

152.3, 152.2, 149.2, 149.0, 136.9, 136.5, 135.9, 135.7, 134.9, 134.9, 133.5, 133.2 (4°), 131.0, 130.9, 128.9, 128.8, 125.5, 125.1, 123.5, 123.4 (3°), 130.6, 130.6, 130.5, 130.5, 130.4, 130.4, 130.3, 130.3 (CFCH*C*H), 124.7, 124.7, 124.6, 124.5 (*C*CF), 111.9, 111.8, 111.8, 111.8 111.7, 111.7, 111.6, 111.6 (CF*C*HCH), 104.7, 104.5, 104.3 (CF*C*HCF), 65.8, 65.4 (SCH), 64.0, 63.8 (OCH_2), 34.1, 34.1 (*p*-ArCH), 32.0, 30.6 (SCH*C*H_2), 29.3, 29.3 (*o*-ArCH), 24.7, 24.6, 24.4 (*o*-ArCH(*C*H_3)$_2$), 23.6 (*p*-ArCH(*C*H_3)$_2$); *m/z* (EI) 647 $[M+NH_4]^+$, 630 $[M+H]^+$ (Found $[M+H]^+$, 630.2156. $C_{33}H_{37}F_2NO_5S_2$ requires $[M+H]^+$, 630.2154) (Found: C, 63.07; H, 5.97; N, 2.18. $C_{33}H_{37}F_2NO_5S_2$ requires C, 62.94; H, 5.92; N, 2.22).

(S*$_S$,*1*R,*2*R)-S-*(2-(2,4-Difluorophenyl)-2-vinylcyclopropyl)*-S-*phenyl*-N-*(2,4,6-triisopropylphenylsulfonyl)sulfoximine* **24b**, (S*$_S$,*1*S,*2*S)-S-*(2-(2,4-difluorophenyl)-2-vinylcyclopropyl)*-S-*phenyl*-N-*(2,4,6-triisopropylphenylsulfonyl)sulfoximine* **25b**, (S*$_S$,*1*S,*2*R)-S-*(2-(2,4-difluorophenyl)-2-vinylcyclopropyl)*-S-*phenyl*-N-*(2,4,6-triisopropylphenylsulfonyl)sulfoximine* **26b**, *and* (S*$_S$,*1*R,*2*S)-S-*(2-(2,4-difluorophenyl)-2-vinylcyclopropyl)*-S-*phenyl*-N-*(2,4,6-triisopropylphenylsulfonyl)-sulfoximine* **27b**

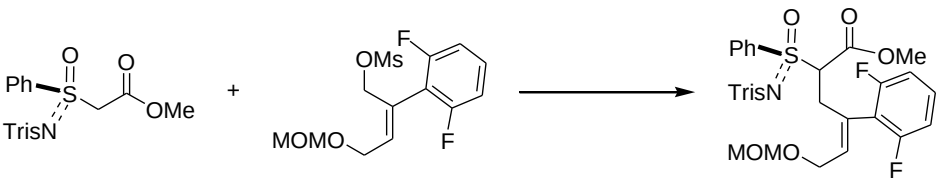


According to general procedure **H**, lactone **23b** (7.0 mg, 0.02 mmol, 1.0 equiv.) in DMF (0.1 mL) was treated with KOAc (pinch) and BSA (4.6 μL, 0.02 mmol, 1.0 equiv.) to give the sulfoximines **24b**–**27b** as a colourless gum (5 mg, 70%) as a mixture of diastereoisomers (ratio **24b**:**25b**:**26b**:**27b** = 44:16:33:7) which were partially separable by chromatography (10→40% EtOAc–petrol); **25b** (isolated as a single diastereoisomer): R_f 0.60 (50% EtOAc–petrol); ν_{max} (film) 2985, 1740, 1447, 1374, 1240, 1047, 938, 847, 737, 634, 608 cm^{-1}; δ_H (500 MHz) 8.00 (2H, dd, *J* 8.5,

1.0 Hz, *o*-Ph), 7.69 (1H, tt, *J* 7.5, 1.5 Hz, *p*-Ph), 7.57 (2H, t, *J* 8.0 Hz, *m*-Ph), 7.12 (2H, s, *m*-SO_2Ar), 6.89 (1H, dt, *J* 8.5, 6.5 Hz, CFCHC*H*) 6.78 (1H, t, *J* 8.0, Hz, CFC*H*CH) 6.67 (1H, ddd, *J* 10.0, 9.0, 2.5 Hz, CFCHCF) 6.11 (1H, dd, *J* 17.0, 10.5 Hz, C*H*=CH_2), 5.06 (1H, dd, *J* 10.5, 1.0 Hz, CH=CH_2 *trans*) 4.44 (1H, d, *J* 17.0 Hz, CH=CH_2 *cis*) 4.40 (2H, sept, *J* 7.0 Hz, *o*-ArCH) 3.29 (1H, dd, *J* 9.0, 6.0 Hz, SCH) 2.88 (1H, sept, *J* 7.0 Hz, *p*-ArCH) 2.39 (1H, dd, *J* 6.5, 6.5 Hz, SCHCH_2) 2.06 (1H, dd, *J* 9.0, 6.5 Hz, SCHCH_2), 1.22–1.25 (18H, m, CH(CH_3)$_2$); δ_C (125 MHz) 163.6, 163.5, 162.3, 162.2, 160.2, 160.1 (CF), 152.0, 149.1, 138.2, 137.1 (4°), 134.2 (*C*H=CH_2), 134.1 (*p*-Ph), 132.0, 131.9, 131.9 (CFCH*C*H), 129.0 (*m*-Ph), 128.1 (*o*-Ph), 123.3 (*m*-SO_2Ar), 122.3, 122.2 (*C*CF), 118.4 (CH=*C*H_2), 111.7, 111.6 (CF*C*HCH), 104.5, 104.3, 104.1 (CF*C*HCF), 48.0 (SCH), 34.1 (SCH*C*), 34.1 (*p*-ArCH), 29.2 (*o*-ArCH), 24.7, 24.6, 23.7, 23.6 (CH(*C*H_3)$_2$), 20.3 (SCH*C*H_2); *m/z* (CI) 603 $[M+NH_4]^+$, 586, 301 (Found $[M+H]^+$, 586.2257. requires $[M+H]^+$, 586.2261); **24b** and **26b** (isolated as a mixture of the two diastereoisomers): R_f 0.67 (50% EtOAc–petrol); ν_{max} (film) 2985, 1740, 1447, 1374, 1240, 1094, 1047, 938, 847, 737, 634, 608 cm^{-1}; δ_H (500 MHz) 8.03 (2H, dd, *J* 8.5, 1.0 Hz, *o*-Ph **24b**) 7.66 (2H, m, Ph) 7.57 (3H, m, Ph) 7.47 (2H, dd, *J* 8.5, 7.5 Hz, *m*-Ph minor) 7.32 (1H, dt, *J* 8.5, 6.5 Hz, *p*-Ph **24b**), 7.11 (2H, s, *m*-SO_2Ar **24b**), 7.06 (2H, s, *m*-SO_2Ar **26b**), 6.85 (1H, m, ArF), 6.74 (1H, m, ArF), 6.50 (1H, m, ArF), 6.36 (1H, dd, *J* 17.0, 10.5 Hz, C*H*=CH_2 **24b**), 5.60 (1H, dd, *J* 17.0, 10.5 Hz, C*H*=CH_2 **26b**), 5.11 (1H, dd, *J* 10.5, 1.0 Hz, CH=CH_2 *trans* **24b**), 5.02 (1H, d, *J* 10.5Hz, CH=CH_2 *trans* **26b**), 4.74 (1H, dd, *J* 17.0, 1.5 Hz, CH=CH_2 *cis* **26b**), 4.64 (1H, d, *J* 17.0Hz, CH=CH_2 *cis* **24b**), 4.35 (2H, sept, *J* 6.5 Hz, *o*-ArCH **24b**), 4.27 (2H, sept, *J* 6.5 Hz, *o*-ArCH **26b**), 3.43 (1H, dd, *J* 9.0, 5.5 Hz, SCH **26b**), 2.98 (1H, dd, *J* 9.0, 6.5 Hz, SCH **24b**), 2.88 (1H, sept, *J* 6.5 Hz, *p*-ArCH **24b**), 2.85 (1H, sept, *J* 6.5 Hz, *p*-ArCH **26b**), 2.61 (1H, dd, *J* 6.0, 6.0 Hz, SCHCH_2 **26b**), 2.13 (1H, dd, *J* 6.5 Hz, SCHCH_2 **24b**), 1.96 (1H, dd, *J* 9.0, 6.5 Hz, SCHCH_2 **26b**), 1.71 (1H, dd, *J* 9.0, 6.0 Hz, SCHCH_2 **24b**), 1.30–1.17 (18H, m, CH(CH_3)$_2$); δ_C (125 MHz) 163.7, 163.6, 163.5, 162.8, 162.1, 162.1, 161.7, 161.6, 161.5, 160.8, 160.7, 160.1, 160.0 (CF), 151.9, 149.2, 149.0, 137.6, 137.4, 137.0 (4°), 138.5, 134.5 (*C*H=CH_2), 134.0, 133.9, 129.4, 129.0, 128.0, 127.6 (3°), 132.9, 132.9, 132.8, 132.8 (CFCH*C*H), 123.3, 122.8, 122.8, 122.7, 122.6 (*C*CF), 118.3, 115.6 (CH=*C*H_2), 117.0, 117.0, 111.7, 111.7, 111.5, 111.5, 111.2, 111.0 (CF*C*HCH), 104.4, 104.2, 104.1, 104.0, 103.9, 103.7 (CF*C*HCF), 48.9, 46.7 (SCH), 35.5, 34.1, 33.9 (*p*-ArCH), 29.7, 29.3, 29.1 (*o*-ArCH), 24.8, 24.8, 24.6, 24.6, 23.7, 23.6, 23.6 (CH(*C*H_3)$_2$), 19.7, 17.7

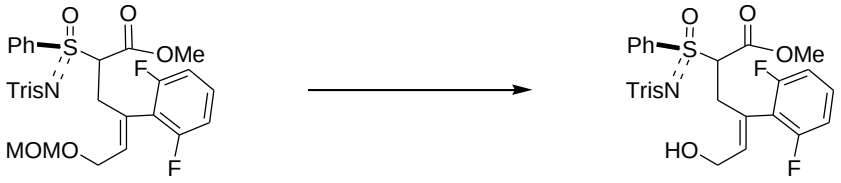
(SCH*C*H$_2$); *m/z* (CI) 603 [M+NH$_4$]$^+$, 586, 425 (Found [M+H]$^+$, 586.2258. requires [M+H]$^+$, 586.2261).

*(±)-Methyl (*E*)-4-(2,6-difluorophenyl)-6-(methoxymethoxy)-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoate*



According to general procedure **D**, sodium hydride (102 mg, 2.55 mmol, 1.2 equiv.) in DMF (3.5 mL) was treated with (±)-methyl 2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)acetate (1.02 g, 2.13 mmol, 1.0 equiv.) in DMF (3.5 mL) and methanesulfonic acid (*Z*)-2-(2,6-difluorophenyl)-4-(methoxymethoxy)but-2-enyl ester (2.13 mmol, 1.0 equiv.) in DMF (3.5 mL) to give (±)-methyl (*E*)-4-(2,6-difluorophenyl)-6-(methoxymethoxy)-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoate as a colourless gum, which was used without further purification; R_f 0.71 (50% EtOAc–heptane).

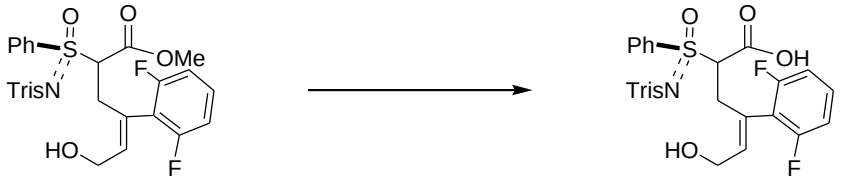
*(±)-Methyl (*E*)-4-(2,6-difluorophenyl)-6-hydroxy-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoate*



According to general procedure **E**, (±)-methyl (*E*)-4-(2,6-difluorophenyl)-6-(methoxymethoxy)-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoate (2.13 mmol, 1.0 equiv.) in MeCN (22 mL) was treated with 2 M aq. HCl (4.5 mL). Purification by chromatography (20→40% EtOAc–petrol) gave (±)-methyl (*E*)-4-(2,6-difluorophenyl)-6-hydroxy-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoate (491 mg, 33% over two steps) as a colourless gum; R_f 0.36 (50% EtOAc–heptane); ν_{max} (film) 2958, 1744, 1621, 1462, 1316, 1237, 1150, 1095, 1057 cm^{-1}; δ_H (400 MHz) 7.90 (2H, d, *J* 8.0 Hz, *o*-Ph), 7.72 (1H, m, *p*-Ph), 7.58 (2H, m, *m*-Ph), 7.22 (1H, m, *o*-ArF), 7.09 (2H, s, *m*-SO$_2$Ar), 6.86 (2H, 2 × t, *J* 8.0 Hz, *m*-ArF), 5.84 (1H, 2 × t, *J* 6.5 Hz, C*H*CH$_2$OH), 4.64 (1H, dd, *J* 12.0, 3.0 Hz, SC*H*), 4.37

(1H, dd, *J* 11.0, 4.5 Hz, SC*H*), 4.29 (2H, m, CH_2OH), 4.25 (2H, m, *o*-ArCH), [3.58, 3.47] (3H, 2 × s, OCH_3), [3.25, 3.18] (1H, 2 × dd, *J* 13.5, 2.0 Hz, SCHCH_2), [3.15, 3.00] (1H, 2 × d, *J* 12.0 Hz, SCHCH_2), 2.86 (1H, 2 × sept, *J* 7.0 Hz, *p*-ArCH), 2.05 (1H, br s, OH), 1.20 (18H, m, CH(CH_3)$_2$); δ_C (100 MHz) 165.5, 165.3 (C=O), 161.4, 158.9 (CF), 152.2, 152.1, 149.2, 149.1, 137.7, 137.5, 134.1, 129.4 (4°), 137.1, 136.9 (*C*HCH$_2$OH), 134.9, 134.8, 129.6, 129.5, 129.3, 129.2, 123.4 (3°), 124.1, 124.0 (CFCH*C*H), 117.1 (*C*CF), 111.7, 111.6, 111.5, 111.3 (CF*C*HCH), 70.4, 70.1 (SCH), 58.6, 58.5 (CH_2OH), 53.2, 53.1 (OCH_3), 34.1 (*p*-ArCH), 29.3 (*o*-ArCH), 29.0, 27.8 (SCH*C*H$_2$), 24.6, 24.6 (*o*-ArCH(*C*H$_3$)$_2$), 23.6 (*p*-ArCH(*C*H$_3$)$_2$); *m/z* (CI) 679 $[M+NH_4]^+$, 586, 425, 301, 272 (Found $[M+H]^+$, 662.2416. $C_{34}H_{41}F_2NO_6S_2$ requires $[M+H]^+$, 662.2422) (Found: C, 61.77; H, 6.18; N, 2.11. $C_{34}H_{41}F_2NO_6S_2$ requires C, 61.70; H, 6.24; N, 2.12).

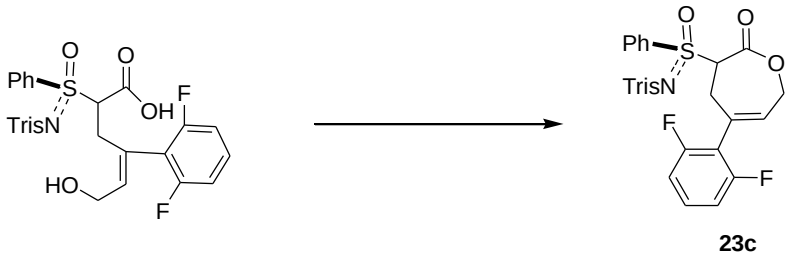
*(±)-(*E*)-4-(2,6-Difluorophenyl)-6-hydroxy-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)-phenylsulfonimidoyl)hex-4-enoic acid*



According to general procedure **F**, a solution of (±)-methyl (*E*)-4-(2,6-difluorophenyl)-6-hydroxy-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoate (491 mg, 0.74 mmol, 1.0 equiv.) in THF (1.85 mL) was treated with 2 M aq. LiOH (1.85 mL) to give (±)-(*E*)-4-(2,6-difluorophenyl)-6-hydroxy-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoic (402 mg, 84%) as a colourless foam, which was used without further purification; ν_{max} (film) 3427, 2961, 2929, 2870, 1707, 1622, 1599, 1463, 1398, 1265, 1232, 1146, 1095, 1064, 1021, 998, 738 cm^{-1}; δ_H (400 MHz; CD_3OD) 7.80 (2H, d, *J* 7.5 Hz, *o*-Ph), 7.71 (1H, 2 × t, *J* 7.5 Hz, *p*-Ph), 7.53 (2H, 2 × t, *J* 7.5 Hz, *m*-Ph), 7.31 (1H, m, *o*-ArF), [7.14, 7.13] (2H, 2 × s, *m*-SO_2Ar), 6.92 (2H, 2 × t, *J* 8.0 Hz, *m*-ArF), [5.80, 5.74] (1H, 2 × t, *J* 6.5 Hz, C*H*CH$_2$OH), [4.39, 4.29] (2H, 2 × dd, *J* 13.5, 7.0 Hz, CH_2OH), 4.17 (2H, 2 × sept, *J* 6.5 Hz, *o*-ArCH), 3.96 (1H, d, *J* 11.5 Hz, SCH), [3.44, 3.22, 2.85] (2H, 3 × m, SCHCH_2), 2.91 (1H, 2 × sept, *J* 7.0 Hz, *p*-ArCH), 1.18–1.10 (18H, m, CH(CH_3)$_2$); δ_C (100 MHz; CD_3OD) 169.0, 168.7 (C=O), 162.9, 160.5 (CF), 153.7, 153.5, 150.5,

150.4, 138.7, 138.1, 135.8, 129.4 (4°), 137.9, 137.4, 136.9, 135.4, 135.3, 130.8, 130.6, 130.4, 130.2, 130.1, 126.8, 126.6 (3°), 124.4 (CFCH*C*H), 119.2, 119.0, 118.8 (*C*CF), 112.8, 112.7, 112.7, 112.5, 112.5 (CF*C*HCH), 74.6 (SCH), 59.2, 59.1 (CH_2OH), 35.4 (*p*-ArCH), 30.3 (*o*-ArCH), 25.1, 25.0, 24.9 (*o*-ArCH(CH_3)$_2$), 24.1 (*p*-ArCH(CH_3)$_2$); *m/z* (CI) 621 $[M\text{-}CO_2+NH_4]^+$, 370, 301 (Found $[M\text{-}CO_2+NH_4]^+$, 621.2609. $C_{33}H_{39}F_2NO_6S_2$ requires $[M+NH_4]^+$, 621.2632) (Found: C, 61.18; H, 6.14; N, 2.16. $C_{33}H_{39}F_2NO_6S_2$ requires C, 61.19; H, 6.07; N, 2.16).

*(±)-5-(2,6-Difluorophenyl)-3-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)-4,7-dihydrooxepin-2(3*H*)-one* **23c**

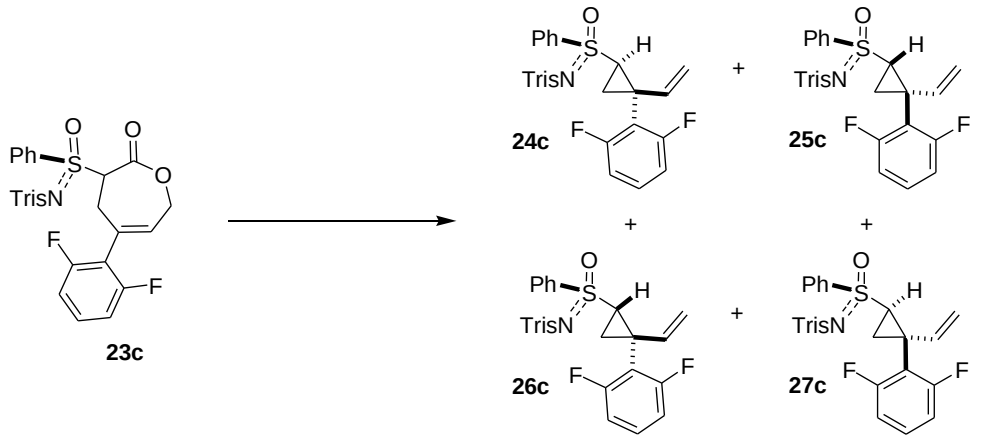


23c

According to general procedure **G**, (±)-(*E*)-4-(2,6-difluorophenyl)-6-hydroxy-2-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoic (360 mg, 0.56 mmol, 1.0 equiv.) in CH_2Cl_2 (2.8 mL) at 0 °C was treated with EDCI (118 mg, 0.62 mmol, 1.1 equiv.). Purification by chromatography (30% EtOAc–petrol) (±)-5-(2,6-difluorophenyl)-3-(*N*-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)-4,7-dihydrooxepin-2(3*H*)-one **23c** (289 mg, 82%) as a colourless solid; mp 86–87 °C; R_f 0.69 (50% EtOAc–petrol); ν_{max} (film) 2959, 1756, 1623, 1599, 1464, 1401, 1267, 1234, 1148, 1092, 1064, 1023, 998, 738 cm^{-1}; δ_H (400 MHz) 8.12 (2H, 2 × d, *J* 8.5 Hz, *o*-Ph), 7.69 (1H, 2 × t, *J* 8.5 Hz, *p*-Ph), 7.56 (2H, 2 × t, *J* 8.0 Hz, *m*-Ph), 7.27 (1H, m, *o*-ArF), [7.12, 7.10] (2H, 2 × s, *m*-SO_2Ar), 6.91 (2H, m, *m*-ArF), 5.98 (1H, m, C*H*CH_2O), [5.96, 5.90] (1H, 2 × dd, *J* 13.0, 3.5 Hz, SCH), [5.27, 5.21] (1H, 2 × ddd, 16.0, 13.0, 3.5 Hz, OCH_2), 4.68 (1H, ddd, *J* 16.0, 7.5, 4.5 Hz, OCH_2), 4.3 (2H, sept, *J* 6.5 Hz, *o*-ArCH), [3.54, 3.36] (1H, 2 × d, *J* 17.5 Hz, SCHCH_2), 2.88 (1H, sept, *J* 6.5 Hz, *p*-ArCH), 2.78 (1H, m, SCHCH_2) 1.27–1.12 (18H, m, CH(CH_3)$_2$); δ_C (100 MHz) 166.0, 165.9 (C=O), 161.0, 161.0, 160.9, 158.6, 158.5, 158.4 (CF), 152.3, 152.2, 149.3, 149.0, 137.1, 136.6, 134.9, 133.7, 133.6, (4°), 131.0, 130.9, 130.1, 130.0, 129.9 (CFCH*C*H), 128.9, 128.8, 127.9, 127.7, 123.5 (3°), 117.7, 117.6, 117.5, 117.4, 117.3, 117.2 (*C*CF), 112.0, 111.9, 111.7, 111.7 (CF*C*HCH), 66.0, 65.4 (SCH), 63.8, 63.7

(OCH_2), 34.1 (*p*-ArCH), 31.7, 30.5 ($SCHCH_2$), 29.3 (*o*-ArCH), 24.7, 24.5 (*o*-ArCH(CH_3)$_2$), 23.6 (*p*-ArCH(CH_3)$_2$); *m/z* (CI) 647 $[M+NH_4]^+$, 603, 586, 425, 370, 352, 335, 301, 240 (Found $[M+NH_4]^+$, 647.2405. $C_{33}H_{37}F_2NO_5S_2$ requires $[M+NH_4]^+$, 647.2425) (Found: C, 62.83; H, 5.85; N, 2.15. $C_{33}H_{37}F_2NO_5S_2$ requires C, 62.94; H, 5.92; N, 2.22).

(S*$_S$,*1*R,*2*R)-S-*(2-(2,6-Difluorophenyl)-2-vinylcyclopropyl)*-S-*phenyl*-N-*(2,4,6-triisopropylphenylsulfonyl)sulfoximine* **24c**, (S*$_S$,*1*S,*2*S)-S-*(2-(2,6-difluorophenyl)-2-vinylcyclopropyl)*-S-*phenyl*-N-*(2,4,6-triisopropylphenylsulfonyl)sulfoximine* **25c**, (S*$_S$,*1*S,*2*R)-S-*(2-(2,6-difluorophenyl)-2-vinylcyclopropyl)*-S-*phenyl*-N-*(2,4,6-triisopropylphenylsulfonyl)sulfoximine* **26c**, *and* (S*$_S$,*1*R,*2*S)-S-*(2-(2,6-difluorophenyl)-2-vinylcyclopropyl)*-S-*phenyl*-N-*(2,4,6-triisopropylphenylsulfonyl)-sulfoximine* **27c**



According to general procedure **H**, lactone **23c** (74 mg, 0.12 mmol, 1.0 equiv.) in DMF (0.6 mL) was treated with KOAc (1.2 mg, 0.012 mmol, 0.1 equiv.) and BSA (29 μL, 0.12 mmol, 1.0 equiv.). Purification by chromatography (10–20% Et_2O–petrol) gave the sulfoximines **24c**–**27c** as a colourless gum (56 mg, 78%) as an inseparable mixture of diastereoisomers (ratio **24c**:**25c**:**26c**:**27c** = 49:11:36:4); R_f 0.75 (50% EtOAc–petrol); ν_{max} (film) 2960, 2869, 1625, 1599, 1585, 1467, 1448, 1312, 1296, 1236, 1148, 1100, 1052, 1006, 910, 788, 772, 735, 684 cm^{-1}; δ_H (500 MHz) [8.09, 8.02] (2H, 2 × d, *J* 7.5 Hz, *o*-Ph), 7.71–7.47 (m, Ph), 7.24 (m, Ph), [7.14, 7.08] (2H, 2 × s, SO_2Ar), 6.84 (2H, t, *J* 8.0 Hz, *m*-ArF), 6.56 (1H, t, *J* 8.0 Hz, *p*-ArF), 6.42 (1H, dd, *J* 17.0, 10.5 Hz, C*H*=CH_2 **24c**), 6.11 (1H, dd, *J* 17.0, 10.5 Hz, C*H*=CH_2 **25c**), 5.62 (1H, dd, *J* 17.0, 10.5 Hz, C*H*=CH_2 **27c**), 5.59 (1H, dd, *J* 17.0, 10.5 Hz, C*H*=CH_2 **26c**), 5.18 (1H, d, *J* 10.5 Hz, CH=CH_2 *cis* **24c**), 5.10 (1H, d, *J* 10.5 Hz, CH=CH_2 *cis* **27c**),

5.09 (1H, d, *J* 10.5 Hz, CH=CH_2 *cis* **25c**), 5.06 (1H, d, *J* 10.5 Hz, CH=CH_2 *cis* **26c**), 4.87 (1H, d, *J* 17.0 Hz, CH=CH_2 *trans* **27c**), 4.80 (1H, d, *J* 17.0 Hz, CH=CH_2 *trans* **26c**), 4.70 (1H, d, *J* 17.0 Hz, CH=CH_2 *trans* **24c**), 4.55 (1H, d, *J* 17.0 Hz, CH=CH_2 *trans* **25c**), [4.44, 4.39, 4.30] (2H, 3 × sept, *J* 6.5 Hz, *o*-ArCH), [3.40, 2.94, 2.82] (1H, 3 × m, SCH), 2.91 (1H, sept, *J* 6.5 Hz, *p*-ArCH), [2.51, 2.38] (1H, 4 × dd, *J* 6.5, 6.5 Hz, SCHCH_2), [2.11, 1.82] (1H, 2 × dd, *J* 9.0, 7.0 Hz, SCHCH_2), 1.30–1.19 (18H, m, CH(CH_3)$_2$); δ_C (125 MHz) 162.4, 162.4, 160.4, 160.4 (CF), 151.8, 149.3, 149.0, 139.8, 137.8, 137.7, 137.6, 137.1 (4°), 133.8, 133.3 (*C*H=CH_2), 129.2, 128.9, 128.4, 127.7, 123.3, 123.2, 123.2 (3°), 130.2, 130.1, 130.0, 129.9, 129.8, 129.7 (CFC*C*H), 118.3, 115.5 (CH=*C*H_2), 112.2, 112.0, 111.8, 111.6, 111.2, 111.0 (CF*C*HCH), 49.2, 46.0 (SCH), 34.1 (*p*-ArCH), 29.8, 29.7, 29.5 29.3, 29.2, 29.1 (*o*-ArCH), 24.9, 24.7, 24.7, 24.6, 24.6 23.8, 23.8, 23.7, 23.6 (CH(*C*H_3)$_2$), 20.2, 18.5, 18.4 (SCH*C*H_2); *m/z* (CI) 603 $[M+NH_4]^+$, 586, 425 (Found $[M+H]^+$, 586.2255. requires $[M+H]^+$, 586.2261).

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