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 (\(^1\text{H NMR}\)) and carbon nuclear magnetic resonance (\(^{13}\text{C NMR}\)) spectra were recorded in CDCl\(_3\) 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 (\(^1\text{H NMR}: 7.26\) ppm for CDCl\(_3\); \(^{13}\text{C NMR}: 77.0\) ppm for CDCl\(_3\)). 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 \(\mu\)m) silica gel unless otherwise stated. Standard solvents were distilled under nitrogen prior to use; \(\text{Et}_2\text{O}\) and THF from sodium-benzophenone ketyl, \(\text{CH}_2\text{Cl}_2\) 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 from 1,4-diols

To a solution of the diol (1.0 equiv.) in CH₂Cl₂ was added CSA (1 mol%) and trimethylorthoformate (2.0 equiv.). The reaction mixture was stirred at rt for 1 h before addition of NEt₃. 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 H₂O, dried (MgSO₄) 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 CH₂Cl₂ at 0 °C was added NEt₃ (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. NaHCO₃ (×2). The organic phase was dried (MgSO₄) 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. NH₄Cl, H₂O and sat. aq. NH₄Cl.
The organic phase was dried (MgSO₄), 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 CH₂Cl₂ and H₂O. The aqueous phase was washed with CH₂Cl₂ (×5). The combined organic washings were dried (MgSO₄), 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 Et₂O and H₂O and the aqueous layer acidified to pH 1 with 2 M aq. HCl. The aqueous layer was then extracted with Et₂O (×3) and the organic layers combined, dried (MgSO₄) 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 CH₂Cl₂ at 0 °C was added EDCI (1.1 equiv.) portionwise. The reaction mixture was allowed to warm to rt and stirred for 16 h. The reaction mixture was partitioned between H₂O and CH₂Cl₂, the organic layer was washed with sat. aq. NH₄Cl and H₂O, dried (MgSO₄) 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 H₂O, dried (MgSO₄) and concentrated under reduced pressure to give the desired cyclopropane.
General Procedure I: preparation of 1,4-diols from furan-2(5H)-ones

To a solution of furan-2(5H)-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 H₂O, dried (Na₂SO₄) and concentrated under reduced pressure. Purification by chromatography gave the desired 1,4-diol.
3. Synthesis and reactions of α-tosyllactone 13

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

According to general procedure C, a solution of alcohol 8\(^1\) (1.72 g, 13.0 mmol, 1.0 equiv.) in CH\(_2\)Cl\(_2\) (65 mL) was treated 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); \(\delta_H\) (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, CHCH\(_2\)OS), 4.62 (2H, s, OCH\(_2\)O), 4.17 (2H, d, \(J\) 6.5 Hz, CHCH\(_2\)OMOM), 3.37 (3H, s, OCH\(_3\)), 3.01 (3H, s, SCH\(_3\)) \(\delta_C\) (67.5 MHz, CDCl\(_3\)) 132.6 (CHCH\(_2\)OMOM), 124.9 (CHCH\(_2\)OMs), 95.8 (OCH\(_2\)O), 65.3 (CH\(_2\)OS), 62.7 (=CH-CH\(_2\)) OCH\(_3\)), 38.1 (SCH\(_3\)).

*(Z)-tert-Butyl 6-(methoxymethoxy)-2-tosylhex-4-enoate 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); \(\nu_{\text{max}}\) (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\(^{-1}\); \(\delta_H\) (500 MHz, CDCl\(_3\)) 7.74 (2H, d, \(J\) 8.5 Hz, o-SO\(_2\)Ar), 7.33 (2H, d, \(J\) 8.5 Hz, m-SO\(_2\)Ar), [5.68–5.63, 5.44–5.39] (2H, m, -CH=CH-), 4.58 (2H, s, -OCH\(_2\)O-), [4.10, 4.01] (2× 1H, dd, \(J\) 12.5, 6.5 Hz, =CH-CH\(_2\)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-CH\(_2\)-CH=), 2.43
(3H, s, Ts-CH₃), 1.31 (9H, s, -C(CH₃)₃); δc (75 MHz, CDCl₃) 164.4 (C=O), 145.3 (4°), 134.4 (4°), 130.2 (3°), 129.6 (3°), 129.4 (3°), 126.2 (3°), 95.8 (-OCH₂O-), 83.3 (-C(CH₃)₃), 70.6 (Ts-CH-COO-), 62.8 (-OCH₂=CH-), 55.3 (-OCH₃), 27.6 (-C(CH₃)₃), 25.3 (Ts-CH-CH₂-CH=), 21.7 (Ts-CH₃); m/z (CI) 402 [M+NH₄]+, 358 [M+NH₄-CH₂OCH₃]+, 346, 323, 314, 302, 288, 284, 232, 197, 192, 174, 139 (Found: [M+NH₄]+, 402.1948. C₁₉H₂₈O₆S requires [M+NH₄]+, 402.1950) (Found: C, 59.21; H, 7.37. C₁₉H₂₈O₆S requires C, 59.35; H, 7.34%).

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

According to general procedure E, a solution of ester 11 (882 mg, 2.29 mmol, 1.0 equiv.) in MeCN (25 mL) and 2 M aq. HCl (5 mL) was heated under reflux. Purification by recrystallisation from CHCl₃–petrol gave (Z)-6-hydroxy-2-tosylhex-4-enoic acid 12 (577 mg, 81%) as a colourless crystalline solid; mp 124–126 °C; νmax (film) 3480, 3029, 1732, 1597, 1444, 1401, 1383, 1319, 1303, 1292, 1246, 1146, 1084, 1016, 815, 711, 663 cm⁻¹; δH (300 MHz, DMSO-d₆) 7.75 (2H, d, J 7.0 Hz, o-SO₂Ar), 7.47 (2H, d, J 7.0 Hz, m-SO₂Ar), [5.60-5.53, 5.30-5.22] (2H, m, -CH=CH-), 4.20 (1H, dd, J 7.5, 3.5 Hz, Ts-CH<), 3.99-3.83 (2H, m, HO-CH₂-), 2.56-2.50 (2H, m, Ts-CH-CH₂-CH=), 2.42 (3H, s, Ts-CH₃); δc (75 MHz, DMSO-d₆) 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+NH₄-H₂O]+, 258, 240, 223, 174, 156, 139, 130 (Found: [M+NH₄-H₂O]+, 284.0968. C₁₃H₁₄O₅S requires [M+NH₄-H₂O]+, 284.0957) (Found: C, 54.76; H, 5.49. C₁₃H₁₄O₅S requires C, 54.92; H, 5.67%).

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

According to general procedure G, a solution of (Z)-6-hydroxy-2-tosylhex-4-enoic acid 12 (2.50 g, 8.80 mmol, 1.0 equiv.) in CH₂Cl₂ (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(3H)-one 13 (1.83 g, 78%) as a colourless powder; mp 144–146 °C; Rf 0.56 (50% EtOAc–petrol); νmax (film) 3041, 1745, 1597, 1471, 1435, 1400, 1377, 1352, 1321, 1257, 1176, 1146, 1084, 1049, 1016, 943, 912, 879, 816, 800, 766, 729, 706, 660 cm−1; δH (500 MHz, CDCl3) 7.98 (2H, d, J 8.0 Hz, o-SO2Ar), 7.38 (2H, d, J 8.0 Hz, m-SO2Ar), [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, -OCH2-), 4.70 (1H, dd, J 13.0, 4.0 Hz, Ts-CH<), [3.16-3.10, 2.69-2.61], (2H, m, Ts-CH-CH2-CH=), 2.45 (3H, s, Ts-CH3); δC (67.5 MHz, CDCl3) 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 (-OCH2-), 27.1 (Ts-CH-CH2-CH=), 21.8 (Ts-CH3); m/z (Cl) 284 [M+NH4]+, 189, 174, 130, 77 (Found: [M+NH4]+, 284.0957. C13H14O4S requires [M+NH4]+, 284.0957) (Found: C, 58.51; H, 5.47. C13H14O4S requires C, 58.63; H, 5.30%).

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

![Diagram of 13 and 14](https://via.placeholder.com/150)

A solution of lactone 13 (150 mg, 560 μmol, 1.0 equiv.) in CH2Cl2 (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 CH2Cl2, washed with 2 M aq. HCl and H2O, dried (MgSO4) and concentrated under reduced pressure to give (1R*,2S*)-1-tosyl-2-vinylcyclopropanecarboxylic acid 14 (150 mg, 100%) as a colourless solid; mp 118–120 °C; νmax (nujol) 3339, 2717, 2590, 1694, 1596, 1318, 1289, 1145, 1084, 929, 817, 726, 665 cm−1; δH (270 MHz, DMSO-d6) 7.78 (2H, d, J 8.0 Hz, o-SO2Ar), 7.33 (2H, d, J 8.0 Hz, m-SO2Ar), 5.58 (1H, ddd, J 17.0, 10.0, 8.5 Hz, CH=CH2), 5.39 (1H, dd, J 17.0, 1.5 Hz, CH=CH2 cis), 5.22 (1H, dd, J 10.0, 1.5 Hz, CH=CH2 trans), 3.02 (1H, m, SCCH), 2.44 (3H, s, ArCH3), 2.16 (1H, dd, J 10.0, 5.5 Hz, SCCH2), 1.96 (1H, dd, J 8.5, 5.5 Hz, SCCH2); δC (100 MHz, DMSO-d6) 168.0 (C=O), 145.2, 136.0 (4°), 130.6, 129.8, 128.8 (3°), 121.2 (CH=CH2), 50.5 (SC), 33.0 (SCCH), 21.7 (ArCH3), 20.3 (SCCH2); m/z (Cl) 284 [M+NH4]+, 242, 240, 174, 162, 145, 102, 85 (Found: [M+NH4]+, 284.0964. C13H14O4S requires [M+NH4]+, 284.0957).
**p-Tolyl (1R*,2S*)-2-vinylcyclopropyl sulfone 15**

![Chemical Structure](image)

According to general procedure H, a solution of 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 (1R*,2S*)-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_2 Ar), 7.44 (2H, d, J 8.0 Hz, m-SO_2 Ar), 5.38 (1H, ddd, J 17.0, 10.0, 8.5 Hz, CH=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, SCHCH), [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=CH_2), 38.7 (SCH), 22.3 (SCHCH), 21.0 (ArCH_3), 12.3 (SCHCH_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(5H)-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(5H)-one as a colourless solid; \(R_f\) 0.57 (1% AcOH–EtOAc); \(\nu\)\(_{\text{max}}\) (film) 3111, 2929, 1793, 1734, 1621, 1450, 1331, 1167, 1048, 894, 862, 771, 684 cm\(^{-1}\); \(\delta_H\) (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\(_2\)); \(\delta_C\) (100 MHz) 173.9 (C=O), 163.9, 131.8 (4°), 129.7, 129.3, 126.4 (3°), 113.1 (CH), 71.0 (CH\(_2\)); \(m/z\) (Cl) 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(5H)-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); \(\nu_{\text{max}}\) (film) 3298, 2885, 1685, 1598, 1493, 1445, 1000, 758, 697 cm\(^{-1}\); \(\delta_H\) (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, CCH\(_2\)OH), 4.42 (2H, d, \(J\) 7.0 Hz, CHCH\(_2\)), 2.04 (2H, s, OH); \(\delta_C\) (75 MHz) 142.9, 140.4 (4°), 129.8, 128.6, 127.8, 126.4 (3°), 60.4 (CCH\(_2\)OH), 59.0 (CHCH\(_2\)OH); \(m/z\) (Cl) 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 CH₂Cl₂ (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; Rₐ 0.59 (50% EtOAc–petrol); νₚₕ (film) 2940, 2869, 2842, 1599, 1494, 1446, 1344, 1279, 1209, 1133, 1102, 1088, 1034, 753, 701 cm⁻¹; δₗ (300 MHz) 7.29 (5H, m, Ph), 5.88 (1H, tt, J 4.0, 1.0 Hz, CH₂), 5.47 (1H, s, OCH), 4.88 (1H, dd, J 15.5, 2.0 Hz, CCH₂), 4.61 (1H, ddd, J 16.0, 4.0, 2.0, 2.0 Hz, CHCH₂), 4.50 (1H, ddd, J 16.0, 3.5, 1.5 Hz, CCH₂), 4.28 (1H, ddd, J 16.0, 4.0, 2.0, 2.0 Hz, CHCH₂), 3.45 (3H, s, CH₃); δc (75 MHz) 141.1, 139.5 (4°), 128.5, 127.5, 126.3, 126.1 (3°), 113.8 (CHO), 64.0 (CCH₂O), 61.3 (CH₂O), 53.6 (CH₃); m/z (ESI) 229 [M+Na]⁺, 206, 147, 129, 115, 91, 78 (Found [M+Na]⁺, 229.0835. C₁₂H₁₄O₃ requires [M+Na]⁺, 229.0835) (Found: C, 69.79; H, 6.90. C₁₂H₁₄O₃ 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: Rₐ 0.28 (50% EtOAc–heptane); νₚₕ (film) 3411, 2934, 2884, 1493, 1445, 1377, 1149, 1089, 1033, 1013, 945, 917, 766, 697 cm⁻¹; δₗ (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, OCH2O), 4.55 (2H, d, J 6.5 Hz, CH2OH), 4.35 (2H, d, J 7.0 Hz, CHCH2), 3.42 (3H, s, CH3), 2.37 (1H, t, J 6.5 Hz, OH); δC (75 MHz) 144.1, 140.5 (4°), 128.5, 127.8, 126.5, 126.4 (3°), 95.3 (OCH2O), 63.2 (CH2OH), 60.2 (CHCH2), 55.4 (OCH3); m/z (CI) 226 [M+NH4]+, 129 (Found [M+NH4]+, 226.1438. C12H16O3 requires [M+NH4]+, 226.1438) (Found: C, 69.29; H, 7.72. C12H16O3 requires C, 69.21; H, 7.74); (Z)-4-methoxymethoxy-3-phenylbut-2-en-1-ol: Rf 0.22 (50% EtOAc–heptane); νmax (film) 3388, 2932, 2883, 1494, 1446, 1384, 1210, 1147, 1097, 1034, 945, 920, 757, 699 cm−1; δH (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, OCH2O), 4.56 (2H, s, CCH2), 4.38 (2H, d, J 6.5 Hz, CH2OH), 3.38 (3H, s, CH3); δC (100 MHz) 140.5, 138.4 (4°), 131.8, 128.5, 127.7, 126.3 (3°), 95.1 (OCH2O), 63.7 (CH2OH), 58.9 (CHCH2), 55.5 (OCH3); m/z (CI) 226 [M+NH4]+, 191, 161, 159, 131, 129 (Found [M+NH4]+, 226.1438. C12H16O3 requires [M+NH4]+, 226.1438) (Found: C, 69.27; H, 7.80. C12H16O3 requires C, 69.21; H, 7.74).

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

![Methanesulfonic acid (Z)-4-methoxymethoxy-2-phenylbut-2-enyl ester](image)

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 CH2Cl2 (2 mL) was treated with NEt3 (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; Rf 0.34 (50% EtOAc–heptane); νmax (film) 3025, 2937, 2888, 1447, 1354, 1174, 1150, 1103, 1037, 929, 845, 772, 699 cm−1; δH (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, CCH2), 4.70 (2H, s, OCH2O), 4.39 (2H, d, J 6.5 Hz, CHCH2), 3.41 (3H, s, OCH3), 2.90 (3H, s, SCH3); δC (100 MHz) 138.6, 135.6 (4°), 132.0, 128.6, 128.3, 126.3 (3°), 96.0 (OCH2O), 65.8 (CH2OS), 63.3 (CHCH2), 55.5 (OCH3), 38.2 (SO2CH3); m/z (CI) 304 [M+NH4]+ (Found [M+NH4]+, 304.1226. C13H18O5S requires [M+NH4]+, 304.1219).
4-(2,4-Difluorophenyl)furan-2(5H)-one

To 4-bromofuran-2(5H)-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$_2$SO$_4$) and concentrated under reduced pressure. Purification by chromatography (20–40% EtOAc–petrol) gave 4-(2,4-difluorophenyl)furan-2(5H)-one (2.39 g, 99%) as a colourless solid; R$_f$ 0.40 (50% EtOAc–petrol); $\nu$$_{max}$ (film) 3118, 3059, 1799, 1735, 1618, 1609, 1585, 1508, 1490, 1456, 1425, 1333, 1266, 1163, 1148, 1106, 1049, 996, 961, 897, 888, 872, 809, 734 cm$^{-1}$; $\delta$$_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$_2$); $\delta$$_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 (CFCHCH), 114.7, 114.6, 114.5 (CCF), 112.9, 112.8, 112.6, 112.6 (CFCHCH), 105.8, 105.4, 105.1 (CFCHCF) 71.7 (CH$_2$); m/z (EI) 214 [M+NH$_4^+$], 197 (Found [M+H]$^+$), 197.0409. C$_{10}$H$_6$F$_2$O$_2$ requires [M+H]$^+$, 197.0409 (Found: C, 61.29; H, 3.06. C$_{10}$H$_6$F$_2$O$_2$ 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(5H)-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); $\nu$$_{max}$ (film) 3305, 2884, 1613, 1592,
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 CH₂Cl₂ (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; R₁ 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; δH (300 MHz) 7.18 (1H, m, o-ArF), 6.80 (2H, m, m-ArF), 5.80 (1H, t, J 4.0 Hz, CHCH₂), 5.45 (1H, s, OCH), 4.74 (1H, ddd, J 15.5, 2.0, 2.0 Hz, CCH₂), 4.59 (1H, dddd J 16.5, 4.0, 2.0, 2.0 Hz, CHCH₂), 4.39 (1H, ddd, J 15.5, 3.5, 2.0, 2.0 Hz, CCH₂), 4.26 (1H, dddd, J 16.5, 4.0, 2.0, 2.0 Hz, CHCH₂), 3.43 (CH₃); δC (75 MHz) 164.1, 164.0, 161.5, 161.3, 160.8, 160.7, 158.2, 158.0 (CF), 136.5, 130.5, 130.3 (CFCHCH), 129.5, 124.0, 123.9, 123.8, 123.7 (CCF), 113.8 (CHO), 111.6, 111.5, 111.3, 111.2 (CFCHCH), 104.5, 104.1, 103.8 (CFCHCF), 63.9, 63.8 (CCH₂O), 61.1 (CHCH₂O), 53.7 (CH₃); m/z (ESI) 265 [M+Na]⁺, 183, 165, 151, 127 (Found [M+Na]⁺, 265.0646. C₁₂H₁₂F₂O₃ requires [M+Na]⁺, 265.0647) (Found: C, 59.59; H, 4.89. C₁₂H₁₂F₂O₃ requires C, 59.50; H, 4.99).
According to general procedure B, 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 as colourless oils; (Z)-2-(2,4-difluorophenyl)-4-(methoxymethoxy)but-2-en-1-ol: R\text{f} 0.25 (50% EtOAc–petrol); ν\text{max} (film) 3394, 2939, 2886, 1616, 1592, 1501, 1422, 1266, 1139, 1097, 967, 850, 815 cm\textsuperscript{-1}; δ\text{H} (300 MHz) 7.30 (1H, m, o-\text{ArF}), 6.83 (2H, m, m-\text{ArF}), 5.90 (1H, t, J 7.0 Hz, CH), 4.71 (2H, s, OCH\textsubscript{2}O), 4.47 (2H, s, \text{CHCCH}), 4.34 (2H, t, J 7.0 Hz, \text{CHCCH}_2), 3.41 (3H, s, CH\textsubscript{3}), 2.22 (1H, t, J 6.0 Hz, OH); δ\text{C} (100 MHz) 163.7, 163.5, 161.2, 161.1, 158.5, 158.6 (CF), 138.9 (4°), 131.1, 131.0 (CFCHCH), 130.2 (3°), 125.1, 124.9 (CCF), 111.5, 111.4, 111.3, 111.2 (CFCHCH), 104.3, 104.1, 103.8 (CFCHCF), 95.6 (OCH\textsubscript{2}O), 63.0 (CH\textsubscript{2}OH), 60.7, 60.6 (CHCH\textsubscript{2}O), 55.4 (CH\textsubscript{3}); m/z (Cl) 262 [M+NH\textsubscript{4}]\textsuperscript{+}, 227, 183 (Found [M+NH\textsubscript{4}]\textsuperscript{+}, 262.1249). C\textsubscript{12}H\textsubscript{14}F\textsubscript{2}O\textsubscript{3} requires [M+NH\textsubscript{4}]\textsuperscript{+}, 262.2412) (Found: C, 58.92; H, 6.94. C\textsubscript{12}H\textsubscript{14}F\textsubscript{2}O\textsubscript{3} requires C, 59.01; H, 5.78); (Z)-3-(2,4-difluorophenyl)-4-(methoxymethoxy)but-2-en-1-ol: R\text{f} 0.19 (50% EtOAc–petrol); ν\text{max} (film) 3404, 2945, 2887, 1616, 1593, 1501, 1422, 1266, 1140, 1097, 1039, 1007, 966, 919, 850, 815 cm\textsuperscript{-1}; δ\text{H} (300 MHz) 7.29 (1H, m, o-\text{ArF}), 6.83 (2H, m, m-\text{ArF}), 6.07 (1H, t, J 7.0 Hz, CH), 4.62 (2H, s, OCH\textsubscript{2}O), 4.47 (2H, s, CHCH\textsubscript{2}), 4.37 (2H, t, J 6.0 Hz, CH\textsubscript{2}OH), 3.34 (3H, s, CH\textsubscript{3}) 2.14 (1H, t, J 6.0 Hz, OH); δ\text{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, 130.8, 125.2, 125.1, 125.0, 124.9 (CCF), 111.4, 111.4, 111.2, 111.1 (CFCHCH), 104.4, 104.0, 103.7 (CFCHCF), 95.4 (OCH\textsubscript{2}O), 64.4 (CH\textsubscript{2}OH), 58.7 (CH\textsubscript{2}) 55.5 (CH\textsubscript{3}); m/z (El) 262 [M+NH\textsubscript{4}]\textsuperscript{+}, 227, 197, 167 (Found [M+NH\textsubscript{4}]\textsuperscript{+},

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

According to general procedure C, a solution of (Z)-2-(2,4-difluorophenyl)-4-(methoxymethoxy)but-2-en-1-ol (68 mg, 0.28 mmol, 1.0 equiv.) in CH₂Cl₂ (1 mL) was treated with NEt₃ (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, 1367, 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, CCH₂), 4.69 (2H, s, OCH₂O), 4.36 (2H, d, J 6.5 Hz, CHCH₂), 3.41 (3H, s, OCH₃), 2.92 (3H, s, SCH₃); 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 (CFCHCH), 123.1, 123.1, 123.0, 123.0 (CCF), 111.8, 111.8, 111.6, 111.5 (CFCHCH), 104.5, 104.2, 104.0 (CFCHCF), 96.0 (OCH₂O), 66.3, 66.3 (CHCH₂), 63.0 (CCH₂), 55.5 (OCH₃), 37.7 (SCH₃); m/z (CI) 340 [M+NH₄]⁺, 165 (Found [M+NH₄]⁺, 340.1025. C₁₁H₁₄F₂O₅S requires [M+NH₄]⁺, 340.1025).

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

To 4-bromofuran-2(5H)-one (4.25 g, 26.1 mmol, 1.0 equiv.) and PdCl₂(PPh₃)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 (MgSO₄) and concentrated under reduced pressure.
Purification by chromatography (30–50% EtOAc–petrol) gave 4-(2,6-difluorophenyl)furan-2(5H)-one (4.40 g, 86%) as a colourless solid; Rf 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; δH (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, CH2); δC (100 MHz) 173.3 (C=O), 162.5, 162.4, 160.0, 159.9 (CF), 153.3 (CCH), 133.0, 132.9, 132.8 (CFCHCH), 119.4, 119.3, 119.2 (CCH), 112.7, 112.4 (CHCF), 108.5, 108.4, 108.2 (CCF), 73.1, 73.0 (CH2); m/z (CI) 197 [M+H]+, 410, 214 (Found [M+H]+, 197.0421. C10H6F2O2 requires [M+H]+, 197.0414) (Found: C, 61.18; H, 2.99. C10H6F2O2 requires C, 61.23; H, 3.08).

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

According to general procedure I, a solution of 4-(2,6-difluorophenyl)furan-2(5H)-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; Rf 0.15 (50% EtOAc–petrol); ν max (film) 3338, 2886, 1622, 1586, 1462, 1269, 1231, 1000, 788 cm−1; δH (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, CCH2), 4.45 (2H, d, J 7.0 Hz, CHCH2), 2.14 (2H, br s, OH); δC (100 MHz) 161.6, 161.5, 159.1, 159.1 (CF) 136.0 (CHCH2OH), 131.3 (CCH2), 128.9, 128.8 (CFCHCH), 118.1 (CCF), 111.6, 111.5, 111.4, 111.3 (CFCH), 61.3 (CCH2), 58.9 (CHCH2); m/z (CI) 218 [M+NH4]+, 200 (Found [M+NH4]+, 218.0999. C10H10F2O2 requires [M+NH4]+, 218.0993) (Found: C, 59.97; H, 5.01. C10H10F2O2 requires C, 60.00; H, 5.04).
According to general procedure A, a solution of (Z)-2-(2,6-difluorophenyl)but-2-ene-1,4-diol (1.60 g, 7.99 mmol, 1.0 equiv.) in CH₂Cl₂ (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; Rᵣ 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, CHCH₂), 5.49 (1H, s, OCH), 4.69 (2H, m, CCH₂), 4.38 (2H, m, CHCH₂), 3.47 (3H, s, CH₃); δ_C (100 MHz) 161.4, 161.3, 158.9, 158.8 (CF) 132.3 (CCH₂), 129.7 (CHCH₂), 128.9, 128.8, 128.7 (CFCHCH), 116.7 (CCF), 113.7 (CHO), 111.7, 111.6, 111.5, 111.4 (CFCH), 63.9 (CCH₂), 61.3 (CHCH₂), 53.7 (CH₃); m/z (CI) 143 [M+H]^+, 502, 260, 228, 211, 200, 182 (Found [M+H]^+, 243.0841. C₁₂H₁₂F₂O₃ requires [M+H]^+, 243.0833) (Found: C, 59.58; H, 5.05. C₁₂H₁₂F₂O₃ 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, a solution of 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% Et₂O–CH₂Cl₂) 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: Rf 0.39 (20% Et2O–CH2Cl2); v_max (film) 3433, 2939, 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, OCH2O), 4.42 (2H, s, CCH2OH), 4.39 (2H, d, J 7.0 Hz, CH2OH), 3.42 (3H, s, CH3), 2.16 (1H, br s, OH); δ_C (100 MHz) 161.7, 161.6, 159.2, 159.1 (CF), 132.9 (CCH2), 129.0, 128.9, 128.8 (CFCH2), 118.3, 118.1, 117.9 (CCF), 111.5, 111.5, 111.4, 111.3 (CFCH), 95.3 (OCH2O), 62.5 (CH2OH), 60.8 (CHCH2), 55.5 (CH3); m/z (CI) 262 [M+NH4]⁺, 506, 230 (Found [M+NH4]⁺, 262.1263. C12H14F2O3 requires [M+NH4]⁺, 262.1255) (Found: C, 59.01; H, 5.78. C12H14F2O3 requires C, 59.06; H, 5.78); (Z)-3-(2,6-difluorophenyl)-4-(methoxymethoxy)but-2-en-1-ol: Rf 0.31 (20% Et2O–CH2Cl2); v_max (film) 3412, 2932, 1586, 1464, 1360, 1271, 1254, 1196, 1151, 1047, 999, 789, 735 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, OCH2O), 4.46 (2H, s, CCH2), 4.39 (2H, d, J 7.0 Hz, CH2OH), 3.35 (3H, s, CH3), 2.11 (1H, br s, OH); δ_C (100 MHz) 161.7, 161.6, 159.2, 159.2 (CF) 137.2 (CCH2), 128.9, 128.8, 128.7 (CFCHCH2), 127.8 (CCH2), 118.2, 118.0, 117.8 (CCF), 111.5, 111.4, 111.3 (CFCH), 95.0 (OCH2O), 64.1 (CH2OH), 58.7 (CCH2) 55.4 (CH3); m/z (CI) 262 [M+NH4]⁺, 506, 230 (Found [M+NH4]⁺, 262.1263. C12H14F2O3 requires [M+NH4]⁺, 262.1255) (Found: C, 59.12; H, 5.69. C12H14F2O3 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, a solution of (Z)-2-(2,6-difluorophenyl)-4-(methoxymethoxy)but-2-en-1-ol (349 mg, 1.43 mmol, 1.0 equiv.) in CH2Cl2 (7.2 mL) was treated with NEt3 (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, which was used without further purification; Rf 0.64 (50% EtOAc–petrol); v_max (film) 3436, 3004, 2934, 2887, 1622, 1586, 1464, 1360, 1271, 1254, 1196, 1151, 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, CCH2), 4.69 (2H, s, OCH2O), 4.38 (2H, d, J 6.5 Hz, CHCH2), 3.40 (3H, s, OCH3), 2.93 (3H, s, SCH3); δC (100 MHz) 161.6, 161.5, 159.1, 159.1 (CF), 137.3 (CCH2), 129.8, 129.7, 129.6 (CFCHCH), 125.1 (CHCH2), 116.2, 116.1, 115.9 (CCF), 111.7, 111.7, 111.5, 111.5 (CFCHCH), 95.9 (OCH2O), 66.6 (CHCH2), 62.8 (CCH2), 55.5 (OCH3), 37.9 (SCH3); m/z (Cl) 340 [M+NH4]⁺, 102 (Found [M+NH4]⁺, 340.1020. C11H16F2O5S requires [M+NH4]⁺, 340.1030).
5. Synthesis and reactions of γ-aryl-α-tosyllactones 16a–c

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

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 \( \text{10}^2 \) (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); \( \nu_{\text{max}} \) (film) 2980, 2933, 1732, 1597, 1493, 1446, 1370, 1327, 1151, 1084, 1047, 919, 836, 816, 766, 714, 699, 566 cm\(^{-1}\); \( \delta_{\text{H}} \) (400 MHz) 7.77 (2H, d, \( J \) 8.0 Hz, o-SO\(_2\)Ar), 7.37 (2H, d, \( J \) 8.0 Hz, m-SO\(_2\)Ar), 7.29 (5H, m, Ph), 5.91 (1H, t, \( J \) 6.5 Hz, CHCH\(_2\)OH), 4.66 (2H, s, OCH\(_2\)O), 4.32 (1H, dd, \( J \) 13.0, 7.0 Hz, CHCH\(_2\)O), 4.18 (1H, dd, \( J \) 13.0, 6.0 Hz, CHCH\(_2\)O), 3.82 (1H, dd, \( J \) 4.5, 1.0 Hz, SCH), 3.39 (3H, s, OCH\(_3\)), 3.25 (2H, m, CHCH\(_2\)O), 2.48 (3H, s, ArCH\(_3\)), 1.23 (9H, s, C(CH\(_3\))\(_3\)); \( \delta_{\text{C}} \) (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\(_2\)O), 83.1 (C(CH\(_3\))\(_3\)), 69.4 (SCH), 64.0 (OCH\(_2\)CH), 55.3 (OCH\(_3\)), 27.5 (C(CH\(_3\))\(_3\)), 27.2 (SCHCH\(_2\)), 21.7 (ArCH\(_3\)); \( m/z \) (Cl) 478 [M+NH\(_4\)]\(^+\) (Found [M+NH\(_4\)]\(^+\), 478.2260. C\(_{25}\)H\(_{32}\)O\(_6\)S requires [M+NH\(_4\)]\(^+\), 478.2263) (Found: C, 65.19; H, 7.00. C\(_{25}\)H\(_{32}\)O\(_6\)S 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(3H)-one 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 CH₂Cl₂ (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(3H)-one 16a (69 mg, 35% over three steps) as a colourless solid; Rᶠ 0.40 (50% EtOAc–petrol); νₘₐₓ (film) 2925, 1739, 1596, 1324, 1269, 1158, 1143, 1087, 1056, 1019, 746, 692, 662 cm⁻¹; δₕ (300 MHz) 7.99 (2H, d, J 8.5 Hz, o-SO₂Ar), 7.39–7.29 (7H, m, m-SO₂Ar and Ph), 6.07 (1H, m, CHCH₂O), [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, OCH₂), [4.68, 4.62] (1H, 2 × d, J 7.5 Hz, OCH₂), [3.57, 3.51] (1H, 2 × m, SCHCH₂), 3.03 (1H, m, SCHCH₂), 2.45 (3H, s, CH₃); δₐ (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 (CHCH₂O), 64.3 (SCH), 64.0 (OCH₂), 29.7, 29.5 (SCHCH₂), 21.8 (ArCH₃); m/z (CI) 360 [M+NH₄]⁺, 187 (Found [M+NH₄]⁺, 360.1263. C₁₉H₁₈O₄S requires [M+NH₄]⁺, 360.1264) (Found: C, 66.63; H, 5.30. C₁₉H₁₈O₄S requires C, 66.65; H, 5.30).

((1R*,2R*)-2-Phenyl-2-vinylcyclopropyl) p-tolyl sulfone 17a and ((1R*,2S*)-2-phenyl-2-vinylcyclopropyl) p-tolyl sulfone 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 (19.1 μL, 0.08 mmol, 1.0 equiv.) to give a diastereomeric mixture (3:2) of ((1R*,2R*)-2-phenyl-2-vinylcyclopropyl) p-tolyl sulfone 17a and ((1R*,2S*)-2-phenyl-2-vinylcyclopropyl) p-tolyl sulfone 18a (20 mg, 87%), which were separable by chromatography (20% EtOAc–petrol) as colourless oils; 17a: Rᶠ 0.57 (50% EtOAc–petrol); νₘₐₓ (film) 2924, 1633, 1598, 1446, 1403, 1318, 1266, 1148, 1088,
738, 701 cm\(^{-1}\); \(\delta_H\) (400 Hz) 7.86 (2H, d, \(J = 8.0\) Hz, \(o\)-SO\(_2\)Ar), 7.37 (2H, d, \(J = 8.0\) Hz, \(m\)-SO\(_2\)Ar), 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, \(CH=CH_2\)), 5.18 (1H, dd, \(J = 10.5, 1.0\) Hz, \(CH=CH_2\) \textit{trans}), 4.57 (1H, dd, \(J = 17.0, 10.5\) Hz, \(CH=CH_2\) \textit{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\(_2\)); \(\delta_C\) (100 Hz) 144.4, 140.0, 138.2, 138.2 (4\(^\circ\)), 129.7, 129.5, 128.5, 127.6, 127.6 (3\(^\circ\)), 118.3 (CH=CH\(_2\)), 46.9 (SCH), 38.6 (SCHC), 21.7 (ArCH\(_3\)), 19.4 (SCHCH\(_2\)); m/z (CI) 316 [M+NH\(_4\)]\(^+\), 143 (Found [M+NH\(_4\)]\(^+\), 316.1382. C\(_{18}\)H\(_{18}\)O\(_2\)S requires [M+NH\(_4\)]\(^+\), 316.1371); 18a: \(R_f\) 0.50 (50% EtOAc–petrol); \(\nu_{\text{max}}\) (film) 3059, 2925, 1633, 1598, 1495, 1446, 1323, 1298, 1266, 1149, 1087, 914, 737, 702 cm\(^{-1}\); \(\delta_H\) (400 Hz) 7.56 (2H, d, \(J = 8.0\) Hz, \(o\)-SO\(_2\)Ar), 7.33–7.26 (7H, m, \(m\)-SO\(_2\)Ar and Ph), 5.64 (1H, dd, \(J = 17.0, 10.5\) Hz, \(CH=CH_2\)), 5.02 (1H, dd, \(J = 10.5, 0.5\) Hz, \(CH=CH_2\) \textit{trans}), 4.75 (1H, dd, \(J = 17.0, 0.5\) Hz, \(CH=CH_2\) \textit{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\(_2\)); \(\delta_C\) (100 Hz) 144.1, 141.7, 138.2, 134.8 (4\(^\circ\)), 130.6, 129.6, 128.1, 127.7, 127.6 (3\(^\circ\)), 115.3 (CH=CH\(_2\)), 45.8 (SCH), 38.3 (SCHC), 21.6 (ArCH\(_3\)), 18.0 (SCHCH\(_2\)); m/z (CI) 316 [M+NH\(_4\)]\(^+\) (Found [M+NH\(_4\)]\(^+\), 316.1382. C\(_{18}\)H\(_{18}\)O\(_2\)S requires [M+NH\(_4\)]\(^+\), 316.1371).

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

![Diagram](E) 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 \textit{tert}-butyl 2-tosylacetate \textbf{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 \textit{tert}-butyl (\textit{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-3H-oxepin-2-one 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 CH₂Cl₂ (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(3H)-one 16b (73 mg, 74% over three steps) as a colourless solid; Rf 0.36 (50% EtOAc–petrol); νmax (film) 1745, 1594, 1501, 1321, 1305, 1291, 1265, 1139, 1084, 972, 850, 813, 670 cm⁻¹; δH (400 MHz) 7.95 (2H, d, J 8.5 Hz, o-SO₂Ar), 7.36 (2H, d, J 8.0 Hz, m-SO₂Ar), 7.17 (1H, td, J 8.5, 6.5 Hz, o-ArF), 6.90–6.79 (2H, m, m-ArF), 5.95 (1H, m, CH₂O), [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, OCH₂), [4.67, 4.62] (1H, 2 × d, J 7.5 Hz, OCH₂), [3.43, 3.37] (1H, 2 × m, SCHCH₂), 3.01 (1H, m, SCHCH₂), 2.45 (3H, s, CH₃); δC (75 MHz) 166.3 (C=O), 164.6, 164.4, 161.3, 161.2, 161.2, 158.1, 157.9 (CF), 145.8, 136.8, 133.6 (4°), 130.4, 130.3, 130.3, 129.9 (CFCHCH), 130.5, 129.7, 125.1, (3°), 124.8, 124.7, 124.6, 124.5 (CCF), 111.9, 111.8, 111.6, 111.6 (CFCHCH), 104.9, 104.5, 104.2 (CFCHCF), 64.4, 63.6 (OCH₂), 63.7 (SCH), 30.0, 29.9 (SCHCH₂), 21.7 (CH₃); m/z (CI) 396 [M+NH₄]⁺ (Found [M+NH₄]⁺, 396.1075. C₁₉H₁₆F₂O₄S requires [M+NH₄]⁺, 396.1076).
According to general procedure H, a solution of 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 ((1R*,2R*)-2-(2,4-difluorophenyl)-2-vinylcyclopropyl) p-tolyl sulfone 17b and ((1R*,2S*)-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: Rf 0.55 νmax (film) 3056, 2926, 1618, 1508, 1426, 1266, 1148, 1090, 738 cm−1; δH (500 MHz) 7.84 (2H, d, J 8.0 Hz, o-SO2Ar), 7.36 (2H, d, J 8.0 Hz, m-SO2Ar), 7.01 (1H, ddd, J 8.5, 8.5, 6.5 Hz, CFCH2), 6.80 (1H, dddd, J 8.0, 8.0, 2.5, 1.0 Hz, CFCCH), 6.72 (1H, ddd, J 10.0, 9.0, 2.5 Hz, CFCHCF), 6.39 (1H, dd, J 17.0, 10.5 Hz, CH=CH2), 5.18 (1H, d, J 10.5 Hz, CH=CH2 trans), 4.56 (1H, d, J 17.0 Hz, CH=CH2 cis), 2.84 (1H, dd, J 9.0, 6.5 Hz, SCH), 2.47 (3H, s, ArCH3), 2.19 (1H, dd, J 6.0, 6.0 Hz, SCHCH2), 1.79 (1H, dd, J 9.0, 6.0 Hz, SCHCH2); δC (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 (CCF), 118.7 (CFCHCH), 115.4 (CH=CH2), 111.2, 111.1, 111.0 (CFCHCH), 104.3, 104.1, 103.9 (CFCHCF), 45.4 (SCH), 29.7 (SCHC), 21.6 (ArCH3), 18.7 (SCHCH2); δF (376 MHz) –109.3 (1F, ddd, J 16.5, 8.0, 6.5 Hz, p-CF); m/z (CI) 352 [M+NH4]+, 316 (Found [M+NH4]+, 352.1198. C18H16F2O2S requires [M+NH4]+, 352.1183); 18b: Rf 0.59 (50% EtOAc–petrol); νmax (film) 3923, 1598, 1505, 1425, 1321, 1290, 1148, 1088, 967, 851, 741, 659 cm−1; δH (400 MHz) 7.66 (2H, d, J 8.0 Hz, o-SO2Ar), 7.45 (1H, dd, J 15.0, 8.5 Hz, CFCHCH), 7.32 (2H, d, J 8.0 Hz, m-SO2Ar), 6.90 (1H, ddd, J 9.0, 9.0, 2.5, 1.0 Hz, CFCHCH), 6.80 (1H, ddd, J 10.5, 9.0, 2.5 Hz, CFCHCF), 5.55 (1H, dd, J 17.0, 10.5 Hz, CH=CH2), 5.04 (1H, d, J 10.5 Hz, CH=CH2 trans), 4.74 (1H, d, J 17.0 Hz, CH=CH2 cis), 2.82 (1H, dd, J 8.5, 6.5 Hz, SCH), 2.45 (3H, s, ArCH3), 2.17 (1H, dd, J 6.0, 6.0 Hz, SCHCH2), 1.64 (1H, dd, J 8.5, 6.0 Hz, SCHCH2); δC (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 (CCF), 135.5, 129.7, 127.6 (3°), 123.1, 123.0 (CFCHCH), 117.6 (CH=CH₂), 111.6, 111.6, 111.4, 111.4 (CFCHCH), 104.5, 104.2, 104.0 (CFCHCF), 46.7 (SCH), 29.7 (SCHCH), 21.7 (ArCH₃), 19.4 (SCHCH₂); δF (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 (Cl) 352 [M+NH₄⁺], 316, 298 (Found [M+NH₄⁺], 352.1198. C₁₈H₁₆F₂O₂S requires [M+NH₄⁺], 352.1183);

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

\[ 
\begin{align*}
\text{Ts} & - \text{OCMe} + \text{OMOMO} \rightarrow \text{OMOMO} \text{-F} \text{-Ts} \text{-OCMe}
\end{align*}
\]

According to general procedure D, a suspension of sodium hydride (40.2 mg, 1.00 mmol, 1.2 equiv.) in DMF (1.5 mL) was treated with methyl 2-tosylacetate (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; Rf 0.64 (50% EtOAc–petrol).

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

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; Rf 0.33 (50% EtOAc–petrol); νmax (film) 3055, 2986, 1741, 1620, 1463, 1423, 1265, 1149, 1085, 895, 738 cm⁻¹; δH (400 MHz) 7.70 (2H, d, J 8.0 Hz, o-SO₂Ar), 7.35 (2H, d, J 8.0 Hz, m-SO₂Ar), 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, CHCH₂OH), 4.36 (1H, dd, J 13.5, 7.5 Hz, CH₂OH), 4.18 (1H, dd, J 13.5,
According to general procedure F, a solution of (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\text{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-SO₂Ar), 7.33 (2H, d, J 8.5, 0.5 Hz, m-SO₂Ar), 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, CH₂OH), 4.42 (1H, dd, J 13.0, 8.5 Hz, CH₂OH), 4.12 (1H, dd, J 13.0, 6.0 Hz, CH₂OH), 3.81 (1H, dd, J 12.0, 3.0 Hz, SCH), 3.30 (1H, dd, J 14.0, 12.0 Hz, SCH₂H), 2.96 (1H, dd, J 14.0, 2.0 Hz, SCH₂H), 2.44 (3H, s, ArCH₃); 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 (CFCH₂), 125.9 (CH₂OH), 117.3, 117.1, 116.9 (CCF), 111.8, 111.7, 111.6, 111.5 (CFCH), 86.7 (SCH), 58.4 (CH₂OH), 28.2 (SCH₂H), 21.8 (ArCH₃); m/z (CI) 370 [M−CO₂+NH₄]⁺, 412, 396, 352, 335, 174 (Found [M+NH₄]⁺, 414.1185. C₁₉H₁₈F₂O₅S requires [M+NH₄]⁺, 414.1187) (Found: C, 57.62; H, 4.49. C₁₉H₁₈F₂O₅S requires C, 57.57; H, 4.58).
According to general procedure G, a solution of (E)-4-(2,6-difluorophenyl)-6-hydroxy-2-tosylhex-4-enoic acid (98 mg, 0.25 mmol, 1.0 equiv.) in CH₂Cl₂ (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(3H)-one 16c (73 mg, 74% over three steps) as a colourless solid; Rf 0.60 (50% EtOAc–petrol); νmax (film) 3139, 1748, 1622, 1463, 1398, 1321, 1267, 1231, 1144, 1084, 1002, 781, 735, 666 cm⁻¹; δH (400 MHz) 7.95 (2H, d, J 8.5 Hz, o-SO₂Ar), 7.36 (2H, d J 8.0 Hz, m-SO₂Ar), 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, CHCH₂O), [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, OCH₂), [4.68, 4.64] (1H, 2 × d, J 7.5 Hz, OCH₂), 3.29 (1H, d, J 17.5 Hz, SCHCH₂), 3.02 (1H, m, SCHCH₂), 2.45 (3H, s, CH₃); δC (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 (CFCHCH), 127.5 (CHCH₂OH), 117.6 (CCF), 111.9, 111.8, 111.7, 111.6 (CFCHCH), 64.4 (OCH₂), 63.6 (SCH), 29.8 (SCHCH₂), 21.7 (CH₃); m/z (Cl) 396 [M+NH₄]+, 254, 242, 174 (Found [M+NH₄]+, 396.1081) (Found: C, 60.38; H, 4.19. C₁₉H₁₆F₂O₄S requires [M+NH₄]+, 396.1081). C₁₉H₁₆F₂O₄S requires C, 60.31; H, 4.26).

According to general procedure H, a solution of 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 ((1R*,2R*)-2-(2,6-difluorophenyl)-2-vinylcyclopropyl) p-tolyl sulfone 17c and ((1R*,2S*)-2-(2,6-difluorophenyl)-2-vinylcyclopropyl) p-tolyl sulfone 18c
(1R*,2S*)-2-(2,6-difluorophenyl)-2-vinylcyclopropyl) p-tolyl sulfone 18c (47 mg, 82%) as a colourless oil, separable by chromatography (10% Et2O–petrol); 17c: Rf 0.34 (50% Et2O–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-SO2Ar), 7.21 (1H, tt,  𝐽 = 10.5 Hz, CH=CH2), 5.17 (1H, d,  𝐽 = 10.5 Hz, CH=CH2 trans), 4.62 (1H, d,  𝐽 = 17.0 Hz, CH=CH2 cis), 2.91 (1H, dd,  𝐽 = 9.0 Hz, SCHCH2), 2.46 (3H, s, ArCH3), 2.30 (1H, dd,  𝐽 = 6.5 Hz, SCHCH2), 1.8 (1H, dd,  𝐽 = 9.0 Hz, m-SO2Ar);  𝛿_{C} (100 MHz) 162.9, 162.8, 160.4, 160.3 (CF), 144.4, 137.5 (4°), 134.5 (CH=CH2), 129.9, 129.8, 129.7 (CFCHCH), 129.5, 128.1 (3°), 117.2 (CH=CH2), 111.8, 111.5 (CFCH), 46.6 (SCH), 27.9 (SCHCH2), 21.7 (ArCH3), 19.8 (CH2); m/z (CI) 352 [M+NH4]+ (Found [M+NH4]+, 352.1183. C18H16F2O2S requires [M+NH4]+, 352.1183) (Found: C, 64.69; H, 4.75. C18H16F2O2S requires C, 64.65; H, 4.82); 18c: Rf 0.27 (50% Et2O–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-SO2Ar), 7.32 (2H, d,  𝐽 = 8.0 Hz, m-SO2Ar), 7.30 (1H, tt,  𝐽 = 8.5 Hz, CH=CH2), 5.56 (1H, dd,  𝐽 = 10.5 Hz, CH=CH2 trans), 4.82 (1H, d,  𝐽 = 17.0 Hz, CH=CH2 cis), 2.85 (1H, ddd,  𝐽 = 6.5 Hz, 2.0 Hz, SCHCH2), 2.44 (3H, s, ArCH3), 2.23 (1H, ddd,  𝐽 = 6.5 Hz, SCHCH2), 1.71 (1H, dd,  𝐽 = 9.0 Hz, SCHCH2);  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 (CH=CH2), 129.5, 129.6, 129.7 (CFCHCH), 129.7, 127.7 (3°), 115.2 (CH=CH2), 112.4, 112.2, 112.2, 112.1 (CFCHCF), 111.8, 111.8, 111.7, 111.6, 111.4, 111.4, 111.3, 111.2 (CFCH), 44.9 (SCH), 29.1 (SCHCH2), 21.6 (ArCH3), 18.9 (CH2); m/z (CI) 352 [M+NH4]+ (Found [M+NH4]+, 352.1197. C18H16F2O2S requires [M+NH4]+, 352.1183) (Found: C, 64.77; H, 4.73. C18H16F2O2S requires C, 64.65; H, 4.82).
6. Synthesis and reactions of γ-aryl-α-sulfoximinyllactones 19 and 20

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

![Chemical Structure](image)

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 CH₂Cl₂ (100 mL). Solid chloramine-T trihydrate (dried under vacuum over P₂O₅; 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 H₂O (×2), the organic layer dried (MgSO₄) 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; Rf 0.07 (20% EtOAc–petrol); νmax (nujol) 1593, 1295, 1142, 1086, 1021, 989, 932, 826, 766, 746, 689, 652 cm⁻¹; δH (270 MHz) 7.68 (4H, m, o-Ph, o-SO₂Ar), 7.49 (3H, m, m-/p-Ph), 7.14 (2H, d, J 8.0 Hz, m-SO₂Ar), 2.82 (3H, s, SCH₃), 2.33 (3H, s, ArCH₃); δC (100 MHz) 141.7, 141.2, 136.1 (4°), 132.4, 129.9, 129.2, 126.2, 125.8 (3°), 39.1 (SCH₃), 21.3 (ArCH₃); m/z (CI) 294 [M+H]⁺, 206, 189; data were in accordance with those previously reported.⁷

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

![Chemical Structure](image)

To a solution of the (±)-S-methyl-S-phenyl-N-tosylsulfilimine (13.5 g, 46.0 mmol, 1.0 equiv.) in CCl₄ (100 mL) and MeCN (100 mL) was added RuO₂·xH₂O (12.2 mg, 0.92 mmol, 2.0 mol%). A solution of NaIO₄ (19.7 g, 92.0 mmol, 2.0 equiv.) in H₂O (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 CH₂Cl₂. The organic layers were combined and iPrOH (4.5 mL) added and the reaction mixture stirred for a further 1 h, then filtered over celite, dried (MgSO₄), 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; νmax (nujol) 1597, 1580, 1327, 1314, 1230, 1146, 1090, 1067, 982, 811, 754, 740, 689, 653 cm⁻¹; δH (270
MHz) 8.00 (2H, d, J 7.5 Hz, o-Ph), 7.84 (2H, d, J 8.5 Hz, o-SO2Ar), 7.72–7.56 (3H, m, m-/p-Ph), 7.24 (2H, d, J 8.5 Hz, m-SO2Ar), 3.41 (3H, s, S−C3), 2.38 (3H, s, ArCH3); δ (67.5 MHz) 142.9, 140.7, 138.6 (4°), 134.5, 129.8, 129.4, 127.6, 126.7 (3°), 46.7 (S−C3), 21.6 (ArCH3); m/z (CI) 327 [M+NH4]+, 294, 189, 52; data were in accordance with those previously reported.8

(±)-S-Methyl-S-phenylsulfoximine

O
Ph
S
Me
NTs

A solution of (±)-S-methyl-S-phenyl-N-tosylsulfoximine (11.8 g, 38.1 mmol, 1.0 equiv.) was heated in conc. H2SO4 (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 CH2Cl2 (×2), and the organic layer dried (MgSO4) and concentrated under reduced pressure to give (±)-S-methyl-S-phenylsulfoximine (5.83 g, 99%) as a colourless oil; νmax (film) 3268, 3191, 3091, 3062, 3018, 1446, 1409, 1320, 1222, 1097, 1070, 1029, 1010, 950, 769, 742, 690 cm−1; δH (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, S−C3); δC (67.5 MHz) 143.4 (4°), 133.2, 129.4, 127.8 (3°), 46.2 (S−C3); m/z (CI) 156 [M+H]+; data were in accordance with those previously reported.9

(−)-(R5)-S-Methyl-S-phenylsulfoximine-(−)-camphorsulfonic acid

O
Ph
S
Me
O

A solution of (−)-(R)-camphorsulfonic acid (4.28 g, 18.4 mmol, 0.5 equiv.) in dry acetone (distilled over P2O5; 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 (−)-(R5)-S-methyl-S-phenylsulfoximine-(−)-camphorsulfonic acid (5.40 g, 40% from a possible 50%) as a colourless powder; mp 172–174 °C; νmax (nujol) 1728, 1580, 1415, 1253, 1231, 1190, 1140, 1038, 669, 748 cm−1; δH (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, S−C3), [3.11 and 2.62] (2H, 2 × d, J 15.0 Hz, SCH2), [2.42, 2.24] (2H, 2 × m, SCH2CCH2), 1.96 (1H, dd, J 4.0, 4.0 Hz).
Hz, \(\text{CHCH}_2\text{CO}\), 1.89 (1H, dd, \(J 8.0, 4.0\) Hz, \(\text{CHCH}_2\text{CO}\)), 1.80 (1H, d, \(J 18.5\) Hz, \(\text{CHCH}_2\text{CO}\)), 1.48 (1H, ddd, \(J 13.0, 9.5, 4.0\) Hz, \(\text{CHCH}_2\text{CH}_2\)), 1.28 (1H, ddd, \(J 13.0, 9.5, 4.0\) Hz, \(\text{CHCH}_2\text{CH}_2\)); \(\delta_c\) (125 MHz, DMSO-d\(_6\)) 215.9 (C=O), 137.9 (4°), 130.2, 128.2, 125.5 (3°), 58.0 (SO\(_2\text{CH}_2\text{C}\)), 47.1 (CCH\(_3\)), 46.9 (SO\(_2\text{CH}_2\)), 43.5 (SCH\(_3\)), 42.2 (CH\(_2\text{CO}\)), 42.1 (CHCO), 26.3 (SO\(_2\text{CH}_2\text{CCH}_2\)), 24.1 (CH\(_2\text{CCO}\)), 19.9, 19.5 (C(CH\(_3\))\(_2\)); \(m/z\) (Cl) 156; data were in accordance with those previously reported.\(\text{10}\)

\((-\text{R}_S\text{-S-Methyl-S-phenyl-N-tosylsulfoximine}\)

\((-\text{R}_S\text{-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\(_2\text{O}\) and extracted with CH\(_2\text{Cl}_2\). The organic layers were combined, washed with 2 M aq. HCl (×2) and H\(_2\text{O}\), dried (MgSO\(_4\)) and concentrated under reduced pressure to give \((-\text{R}_S\text{-S-methyl-S-phenyl-N-tosylsulfoximine (6.07 g, 88%)}\) as a colourless crystalline solid; mp 106–107 °C; \([\alpha]_D^{22} -40.0\) (c 5.0, CH\(_2\text{Cl}_2\)); \(\nu_{\text{max}}\) (nujol) 2361, 1735, 1312, 1239, 1061, 965, 805, 685, 651 cm\(^{-1}\); \(\delta_H\) (270 MHz) 7.99 (2H, d, \(J 8.0\) Hz, o-Ph), 7.82 (2H, d, \(J 8.0\) Hz, o-SO\(_2\text{Ar}\)), 7.72–7.55 (3H, m, m-/p-Ph), 7.23 (2H, d, \(J 8.0\) Hz, m-SO\(_2\text{Ar}\)), 3.41 (3H, s, SCH\(_3\)), 2.38 (3H, s, ArCH\(_3\)); \(\delta_c\) (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.\(\text{11}\)

\(\text{Methyl (R}_S\text{-2-(N-toslyphenylsulfonimidoyl)acetate}\)

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 \((-\text{R}_S\text{-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 H2O and the product extracted with Et2O (×5). The combined organic layers were washed with sat. aq. NaHCO3 and H2O, dried (MgSO4) and concentrated under reduced pressure. The yellow oil was then treated with EtOH to give methyl (R)-2-(N-tosylphenylsulfonimidoyl)acetate (1.39 g, 78%) as a colourless solid; mp 76–77 °C; [α]D22 −32.2 (c 5.0, CH2Cl2); Rf 0.43 (50% EtOAc–petrol); vmax (film) 1742, 1643, 1496, 1447, 1318, 1153, 814, 666 cm−1; δH (270 MHz) 7.99 (2H, d, J 7.5 Hz, o-Ph), 7.86 (2H, d, J 8.5 Hz, o-SO2Ar), 7.70 (1H, m, p-Ph), 7.58 (2H, m, m-Ph), 7.25 (2H, d, J 8.5 Hz, m-SO2Ar), 4.79, 4.58 (2H, AB doublet, J 14.5 Hz), 3.64 (3H, s, OCH3), 2.38 (3H, s, ArCH3); δC (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 (CH2), 53.4 (OCH3), 21.6 (ArCH3); m/z (Cl) 385 [M+NH4]+, 279, 208, 189; data were in accordance with those previously reported.12

Methyl (R,S,Z)-6-(methoxymethoxy)-2-(N-tosylphenylsulfonimidoyl)hex-4-enoate

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)-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; Rf 0.42 (50% EtOAc–petrol); vmax (film) 2952, 1746, 1598, 1447, 1321, 1245, 1152, 1087, 1061, 1018, 997, 815, 765, 685, 666 cm−1; δH (500 MHz) 7.96 (2H, m, o-Ph), 7.88 (2H, m, o-SO2Ar), 7.76 (1H, m, p-Ph), 7.63 (2H, m, m-Ph), 7.28 (2H, m, m-SO2Ar), 5.71 (1H, dt, J 11.0, 6.5 Hz, OCH2CH), 5.40 (1H, m, SCHCH2CH), [4.89, 4.64] (1H, dd, J 11.0, 3.5 Hz, SCH), [4.59, 4.57] (2H, 2 × s, OCH2O), 4.08–3.98 (2H, m, CHCH2O), [3.74, 3.69] (3H, 2 × s, CO2CH3), [3.35, 3.33] (3H, 2 × s, CH2OCH3), [2.91–2.84, 2.72–2.54] (2H, 2 × m, SCHCH2), 2.42 (3H, s, ArCH3); δC (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 (OCH2O), 71.1, 70.4 (SCH), 62.6 (OCH2CH), 55.3 (CH2OCH3), 53.4, 53.3 (CO2CH3), 26.4, 25.1 (SCH2CH2), 21.6 (ArCH3); m/z (CI) 499 [M+NH4]+, 455, 450, 420, 385, 313, 189 (Found [M+NH4]+, 499.1591. C22H27NO7S2 requires [M+NH4]+, 499.1573) (Found: C, 54.89; H, 5.63; N, 2.92. C22H27NO7S2 requires C, 54.87; H, 5.65; N, 2.91).

**Methyl (R,S,Z)-6-hydroxy-2-(N-toslyphenylsulfonylimidoyl)hex-4-enoate**

According to general procedure E, a solution of methyl (R,S,Z)-6-(methoxymethoxy)-2-(N-toslyphenylsulfonylimidoyl)hex-4-enoate (1.40 g, 2.90 mmol, 1.0 equiv.) in MeCN (30 mL) and 2 M aq. HCl (6 mL) was heated under reflux to give methyl (R,S,Z)-6-hydroxy-2-(N-toslyphenylsulfonylimidoyl)hex-4-enoate (1.13 g, 89%) as a viscous, colourless oil; Rf 0.13 (50% EtOAc–petrol); νmax (film) 3525, 2954, 1744, 1598, 1447, 1318, 1242, 1153, 1088, 1062, 998, 815, 754, 685. 665 cm⁻¹; δH (400 MHz) 7.94 (2H, d, J 8.5 Hz, o-Ph), 7.87 (2H, m, o-SO2Ar), 7.76 (1H, m, p-Ph), 7.62 (2H, m, m-Ph), 7.28 (2H, m, m-SO2Ar), 5.77 (1H, m, CHCH2OH), 5.35 (1H, m, SCHCH2CH), [4.99, 4.67] (1H, dd, J 11.5, 3.5 Hz, SCH), 4.16–4.05 (2H, m, CH2OH), [3.76, 3.61] (3H, 2 × s, OCH3), 2.96–2.84 (1H, m, SCHCH2), [2.77, 2.69] (1H, m, SCHCH2), 2.41 (3H, s, ArCH3); δC (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 (CH2OH), 53.5, 53.4 (OCH3), 26.4, 25.0 (SCHCH2), 21.6 (ArCH3); m/z (CI) 455 [M+NH4]+, 300, 189, 160 (Found [M+NH4]+, 455.1295. C20H23NO6S2 requires [M+NH4]+, 455.1311) (Found: C, 55.02; H, 5.27; N, 3.09. C20H23NO6S2 requires C, 54.90; H, 5.30; N, 3.20).
(R<sub>s</sub>,Z)-6-Hydroxy-2-(N-tosylphenylsulfonimidoyl)hex-4-enoic acid

According to procedure F, a solution of methyl (R<sub>s</sub>,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<sub>s</sub>,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<sub>H</sub> (400 MHz, DMSO-d<sub>6</sub>); 7.91–7.88 (2H, m, o-Ph), 7.85–7.79 (1H, m, p-Ph), 7.72–7.63 (4H, m, o-SO<sub>2</sub>Ar and m-Ph), 7.35–7.31 (2H, m, m-SO<sub>2</sub>Ar), 5.82–5.75 (1H, m, CH<sub>2</sub>OH), 5.48–5.41 (1H, m, SCH<sub>2</sub>CH<sub>2</sub>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<sub>2</sub>OH), [2.82–2.80, 2.69–2.61] (2H, 2 × m, SCH<sub>2</sub>H), 2.41 (3H, s, ArCH<sub>3</sub>); δ<sub>C</sub> (100 MHz, DMSO-d<sub>6</sub>) 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, 128.5, 126.4, 125.0, 122.9, 122.4 (3°) 70.3, 70.1 (SCH), 57.1, 57.1 (CH<sub>2</sub>OH), 25.4, 24.7 (SCH<sub>2</sub>H), 21.4 (ArCH<sub>3</sub>); m/z (FAB<sup>+</sup>) 424 [M+H]<sup>+</sup>, 406, 392, 296, 167, 125, 89, 77 (Found [M+H]<sup>+</sup>), 424.0887. C<sub>19</sub>H<sub>21</sub>NO<sub>6</sub>S<sub>2</sub> requires [M+H]<sup>+</sup>, 424.0889) (Found: C, 53.91; H, 4.94; N, 3.24. C<sub>19</sub>H<sub>21</sub>NO<sub>6</sub>S<sub>2</sub> requires C, 53.88; H, 5.00; N, 3.31).

(R<sub>s</sub>)-3-(N-Tosylphenylsulfonimidoyl)-4,7-dihydrooxepin-2(3H)-one 19

According to general procedure G, a solution of (R<sub>s</sub>,Z)-6-hydroxy-2-(N-tosylphenylsulfonimidoyl)hex-4-enoic acid (0.84 g, 1.99 mmol, 1.0 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> (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<sub>s</sub>)-3-(N-tosylphenylsulfonimidoyl)-4,7-dihydrooxepin-2(3H)-one 19 (0.68 g, 84%) as a colourless crystalline solid; mp 74–76 °C; R<sub>f</sub> 0.26 (50% EtOAc–petrol); ν<sub>max</sub> (film)
3441 (br), 3056, 1748, 1448, 1386, 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-SO2Ar), 7.70 (1H, m, p-Ph), 7.58 (2H, dt, J 7.5, 7.5 Hz, m-Ph), 7.28 (2H, m, m-SO2Ar), [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, OCH₂), [3.31, 3.15] (1H, dd, J 17.5, 3.5 Hz, SCH₂), 2.45–2.36 (1H, m, SCH₂), 2.40 (3H, s, ArCH₃);

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, 128.9, 128.6, 126.7, 126.7, 124.9, 124.5, (3°), 65.4, 65.3 (SCH), 64.2, 64.1 (OCH₂), 28.9, 27.5 (SCH₂), 21.5 (ArCH₃);

m/z (CI) 423 [M+NH₄⁺], 379, 189, 128 (Found [M+NH₄⁺], 423.1055. C₁₉H₁₉NO₅S₂ requires [M+NH₄⁺], 423.1048) (Found: C, 56.21; H, 4.80; N, 3.52. C₁₉H₁₉NO₅S₂ requires C, 56.28; H, 4.72; N, 3.45).

(R₈,IR,2S)-S-Phenyl-S-(2-vinylcyclopropyl)-N-tosylsulfoximine and (R₈,1S,2R)-S-Phenyl-S-(2-vinylcyclopropyl)-N-tosylsulfoximine 21

According to general procedure H, a solution of 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 (R₈,1R,2S)-S-phenyl-S-(2-vinylcyclopropyl)-N-tosylsulfoximine and (R₈,1S,2R)-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-SO2Ar), 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-SO2Ar), 5.55 (1H, ddd, J 17.5, 10.0, 7.5 Hz, CH=CH₂ minor), 5.35 (1H, ddd, J 17.5, 10.0, 7.5 Hz, CH=CH₂ major), 5.28 (1H, d, J 17.5 Hz, CH=CH₂ cis minor), 5.15 (1H, d, J 10.0 Hz, CH=CH₂ trans minor), 5.07 (1H, d, J 17.0 Hz, CH=CH₂ cis major), 5.01 (1H, d, J 10.0 Hz, CH=CH₂ trans major), 2.70 (1H, m, SCH major and minor), 2.63 (1H, m, SCHCH minor), 2.42 (3H, s, ArCH₃), 2.23 (1H, m, SCHCH major), 1.95 (1H, dt, J 10.0, 5.5 Hz, SCHCH₂ major), 1.42 (1H, dt, J 8.0, 6.5 Hz, SCHCH₂ major), 1.53 (1H, dt, J 10.0, 5.5 Hz, SCHCH₂ minor), 1.16 (1H, dt, J 8.0, 6.5 Hz, SCHCH₂ 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=CH₂), 41.7, 41.6 (SCH), 24.1, 23.3 (SCHCH), 21.5 (ArCH₃), 14.4, 12.7 (SCHCH₂); m/z (CI) 362 [M+H]⁺, 379, 189, 52 (Found [M+H]⁺, 362.0888. C₁₈H₁₉NO₃S₂ requires [M+H]⁺, 362.0885) (Found: C, 59.81; H, 5.26; N, 3.89. C₁₈H₁₉NO₃S₂ requires C, 59.81; H, 5.30; N, 3.87).

\(+\)-(S₅)-S-Methyl-S-phenyl-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximine

To a solution of \(+\)-(S₅)-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 H₂O and 2 M aq. HCl added. The organic layer was extracted with CH₂Cl₂, and then washed with 2 M aq. HCl and H₂O, until pH 8 was achieved. The organic layer was dried (MgSO₄) and concentrated under reduced pressure. The orange oil was treated with EtOH to give \(+\)-(S₅)-S-methyl-S-phenyl-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (14.15 g, 59%) as a colourless solid; Rf 0.60 (50% EtOAc–petrol); mp 139–141 °C; [α]D₂₀ +20.0 (c 5.0, CH₂Cl₂); νmax (film) 3055, 2963, 2870, 1599, 1463, 1448, 1423, 1312, 1294, 1265, 1238, 1148, 1100, 1069, 741, 704 cm⁻¹; δH (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-SO₂Ar), 4.40 (2H, sept, J 6.5 Hz, o-ArCH), 3.44 (3H, s, CH₃), 2.90 (1H, sept, J 7.0 Hz, p-ArCH), 1.29–1.24 (18H, m, CH(CH₃)₂); δC (100 MHz) 152.0, 149.0, 138.8, 137.2 (4°), 134.3, 129.6, 127.5, 123.4 (3°), 47.0 (SCH₂), 34.1 (p-ArCH), 29.3 (o-ArCH), 24.7, 24.6 (o-ArCH(CH₃)₂), 23.7 (p-ArCH(CH₃)₂); m/z (CI) 439 [M+NH₄]⁺, 422, 299, 208, 156, 141, 80; data were in accordance with those previously reported.\(^{13}\)

\(+\)-Methyl (S₅)-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$_2$O and the product extracted with Et$_2$O (∗5). The combined organic layers were washed with sat. aq. NaHCO$_3$ and H$_2$O, 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)phenylsulfinimidoyl)acetate (0.29 g, 75%) as a colourless solid; mp 111–112 °C; R$_f$ 0.40 (100% CH$_2$Cl$_2$); [α]$_D$$^{20}$ +11.0 (c 5.0, CH$_2$Cl$_2$); $\nu$$_{max}$ (film) 3055, 2960, 1749, 1599, 1265, 1149, 1095, 1065, 738, 704 cm$^{-1}$; $\delta$$_{H}$ (400 MHz) 8.04 (2H, d, J 7.5 Hz, o-Ph), 7.74 (1H, t, J 7.5 Hz, p-Ph) 7.62 (2H, t, J 8.0 Hz, m-Ph), 7.14 (2H, s, m-SO$_2$Ar), [4.76, 4.62] (2H, AB doublet, J 14.5 Hz, CH$_2$), 4.40 (2H, sept, J 6.5 Hz, o-ArCH), 3.68 (3H, s, OCH$_3$), 2.90 (1H, sept, J 7.0 Hz, p-ArCH), 1.29–1.21 (18H, m, CH(C$_3$H$_3$)$_2$); $\delta$$_{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 (Cl) 497 [M+NH$_4$]$^+$, 301, 208 (Found [M+NH$_4$]$^+$, 497.2141. C$_{26}$H$_{33}$NO$_5$S$_2$ requires [M+NH$_4$]$^+$, 497.2144).

**Methyl (S$_S$,Z)-6-(methoxymethoxy)-2-(N-(2,4,6-triisopropylphenylsulfonyl)phenylsulfinimidoyl)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)phenylsulfinimidoyl)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$_2$O (∗5). The combined organic
layers were washed with sat. aq. NaHCO₃ and H₂O, dried (MgSO₄) and concentrated under reduced pressure. The yellow oil was purified by chromatography (100% CH₂Cl₂) to give recovered (+)-methyl (S₅)-2-(N-(2,4,6-triisoproplyphenylsulfonyl)phenylsulfonimidoyl)acetate (2.06 g, 36%) as a colourless solid, and methyl (S₅,Z)-6-(methoxymethoxy)-2-(N-(2,4,6-triisoproplyphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoate (3.01 g, 47%) as a yellow oil; R₇ 0.17 (100% CH₂Cl₂); νₘₐₓ (film) 2958, 1747, 1600, 1448, 1362, 1317, 1244, 1196, 1150, 1094, 1048, 998, 940, 922, 844, 768, 749, 685, 665 cm⁻¹; δₜ (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 11.0, 3.0 Hz, m-Ph), 7.13 (2H, s, m-SO₂Ar), 5.70 (1H, dt, J 11.0, 6.5 Hz, OCH₂CH₃), 5.39 (1H, dd, J 11.0, 7.0 Hz, SCHCH₂CH₃), [4.57, 4.56] (2H, 2 × s, CH₂OCH₃), 4.06–3.95, (2H, m, o-ArCH), [3.72, 3.62] (3H, 2 × s, CO₂CH₃), [3.32, 3.31] (3H, 2 × s, CH₂OCH₃), 2.88 (1H, sept, J 7.0 Hz, p-ArCH), 1.28–1.19 (18H, m, CH(CH₃)₂); δc (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 (OCH₂O), 71.4, 70.7 (SCH), 62.6, 62.6 (OCH₂OCH₃), 55.4, 55.3 (CH₂OCH₃), 53.3, 53.2 (CO₂CH₃), 34.1, (p-ArCH), 29.3, 29.3 (o-ArCH), 26.5, 25.2 (SCHCH₂), 24.7, 24.6 (o-ArCH(CH₃)₂), 23.6, (p-ArCH(CH₃)₂); m/z (CI) 611 [M+NH₄]⁺, 567, 532, 497, 425, 301 (Found [M+NH₄]⁺, 611.2388. C₃₀H₄₃NO₇S₂ requires [M+NH₄]⁺, 611.2825) (Found: C, 60.59; H, 7.18; N, 2.26. C₃₀H₄₃NO₇S₂ requires C, 60.68; H, 7.30; N, 2.36).

**Methyl (S₅,Z)-6-hydroxy-2-(N-(2,4,6-triisoproplyphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoate**

According to general procedure E, a solution of methyl (S₅,Z)-6-(methoxymethoxy)-2-(N-(2,4,6-triisoproplyphenylsulfonyl)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 (S₅,Z)-6-hydroxy-2-(N-(2,4,6-triisoproplyphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoate (2.14 g, 93%) as a yellow oil; R₇ 0.24 (50% EtOAc–petrol); νₘₐₓ (film) 3425, 2960, 1743, 1643, 1600, 1448, 1314, 1245, 1149, 1093, 1054 cm⁻¹; δₜ (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
(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; δH (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-SO2Ar), 5.76 (1H, dd, J 17.5, 7.0 Hz, CHCH2OH), 5.58 (1H, br s, CO2H), 5.42 (1H, dd, J 16.0, 10.0 Hz, SCHCH2CH), [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, CH2OH), 2.95–2.56 (3H, m, p-ArCH and SCHCH2), 1.29–1.20 (18H, m, CH(CH3)2); δC (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 (CH2OH), 34.2 (p-ArCH), 29.3 (o-ArCH), 26.2, 25.1 (SCHCH2), 24.7, 24.7, 24.6, 24.6 (o-ArCH(CH3)2), 23.6 (p-ArCH(CH3)2); m/z (FAB) 536 [M+NH4]+, 538, 518, 446, 282, 267, 203, 125, 93 (Found [M+NH4]+, 536.2122.
C$_{27}$H$_{37}$NO$_6$S$_2$ requires [M+NH$_4$]$^+$, 536.2141) (Found: C, 60.55; H, 6.91; N, 2.63.
C$_{27}$H$_{37}$NO$_6$S$_2$ requires C, 60.53; H, 6.96; N, 2.61).

(S)$_3$-3-(N-(2,4,6-Triisopropylphenylsulfonyl)phenylsulfonimidoyl)-4,7-dihydrooxepin-2(3H)-one 20

According to general procedure G, a solution of (S$_3$,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$_2$Cl$_2$ (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$_3$)-3-(N-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)-4,7-dihydrooxepin-2(3H)-one 20 (0.87 g, 90%) as a colourless crystalline solid; mp 77–79 °C; R$_f$ 0.63 (50% EtOAc–petrol); $\nu$$_{\max}$ (film) 3442 (br), 3055, 1752, 1638, 1422, 1265, 1148, 1093, 1054, 895, 735 cm$^{-1}$; $\delta$$_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$_2$Ar), [6.00, 5.73] (1H, dd, $J$ 13.0, 3.5 Hz, 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$_3$)$_3$)$_2$; $\delta$_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(CH$_3$)$_2$), 23.6 (p-ArCH(CH$_3$)$_2$); $m/\zeta$ (Cl) 535 [M+NH$_4$]$^+$, 491, 425, 301 (Found [M+NH$_4$]$^+$, 535.2300. C$_{27}$H$_{38}$NO$_5$S$_2$ requires [M+NH$_4$]$^+$, 535.2300) (Found: C, 62.54; H, 6.71; N, 2.87. C$_{27}$H$_{38}$NO$_5$S$_2$ requires C, 62.64; H, 6.81; N, 2.71).
(S\textsubscript{5},1R,2S)-S-Phenyl-S-(2-vinylcyclopropyl)-N-tosylsulfoximine and (S\textsubscript{5},1S,2R)-S-Phenyl-S-(2-vinylcyclopropyl)-N-tosylsulfoximine 22

According to general procedure I, a solution of lactone 20 (50.0 mg, 97.0 \textmu mol, 1.0 equiv.) was treated with BSA (23.9 \textmu l, 97.0 \textmu mol, 1.0 equiv.) and KOAc (1.0 mg, 9.70 \textmu mol, 0.1 equiv.) in DMF (1 mL) to give a diastereomeric mixture (3:2, unassigned) of (S\textsubscript{5},1R,2S)-S-phenyl-S-(2-vinylcyclopropyl)-N-tosylsulfoximine and (S\textsubscript{5},1S,2R)-S-phenyl-S-(2-vinylcyclopropyl)-N-tosylsulfoximine 22 (32 mg, 69\%) as a brown oil; R\textsubscript{f} 0.80 (50\% EtOAc–petrol); \nu\textsubscript{max} (film) 3449 (br), 3057, 1639, 1421, 1264, 1148, 1100, 737 cm\textsuperscript{-1}; \delta\textsubscript{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\textsubscript{2}Ar major), 7.10 (1H, s, m-SO\textsubscript{2}Ar minor), 5.50 (1H, ddd, J = 17.0, 10.0, 7.5 Hz, CH=CH\textsubscript{2} minor), 5.32 (1H, ddd, J = 17.0, 10.0, 7.5 Hz, CH=CH\textsubscript{2} major), 5.23 (1H, d, J = 17.0 Hz, CH=CH\textsubscript{2} cis minor), 5.11 (1H, d, J = 10.0 Hz, CH=CH\textsubscript{2} trans minor), 5.04 (1H, d, J = 17.0 Hz, CH=CH\textsubscript{2} cis major), 4.98 (1H, d, J = 10.0 Hz, CH=CH\textsubscript{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, SCHCH minor), 2.23 (1H, m, SCHCH\textsubscript{2} minor), [1.92, 1.37] (2H, 2 × m, SCHCH\textsubscript{2} major), [1.50, 1.10] (2H, 2 × m, SCHCH\textsubscript{2} minor), 1.28–1.20 (18H, m, CH(CH\textsubscript{3})\textsubscript{2}); \delta\textsubscript{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 (CH=CH\textsubscript{2}), 117.5, 117.2 (CH=CH\textsubscript{2}), 42.0 (SCH), 34.1 (p-ArCH), 29.2, 29.2 (o-ArCH), 24.7, 24.7, 24.6, 24.6 (o-ArCH(CH\textsubscript{3})\textsubscript{2}), 23.7, 23.2 (SCHCH), 23.6 (p-ArCH(CH\textsubscript{3})\textsubscript{2}), 14.2, 12.4 (SCHCH\textsubscript{2}); m/z (CI) 491 [M+NH\textsubscript{4}]\textsuperscript{+}, 474 [M+H]\textsuperscript{+}, 301, 52 (Found [M+H]\textsuperscript{+}, 474.2157. C\textsubscript{28}H\textsubscript{35}NO\textsubscript{3}S\textsubscript{2} requires [M+H]\textsuperscript{+}, 474.2137) (Found: C, 66.00; H, 7.44; N, 2.80. C\textsubscript{28}H\textsubscript{35}NO\textsubscript{3}S\textsubscript{2} requires C, 65.92; H, 7.45; N, 2.96).
7. Synthesis and reactions of γ-aryl-α-sulfoximynlactones 23a–c

(±)-Methyl (E)-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 (E)-6-methoxymethoxy-4-phenyl-2-(N-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoate, which was used without further purification; Rf 0.40 (50% EtOAc–petrol).

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

According to general procedure E, a solution of (±)-methyl (E)-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 (E)-6-hydroxy-4-phenyl-2-(N-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoate as a colourless oil; Rf 0.16 (50% EtOAc–petrol); \( \nu_{\text{max}} \) (film) 2957, 2869, 1743, 1599, 1447, 1313, 1296, 1243, 1195, 1147, 1091, 1048, 1021, 997, 764, 683 cm\(^{-1}\); \( \delta_H \) (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-SO2Ar), 5.97 (1H, 2 × t, \( J \) 6.5 Hz, CHCH2OH), [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, CH2OH), [3.48, 3.41] (3H, 2 × s, OCH3), 3.17 (2H, m, SCHCH2), 2.87 (1H, 2 × sept, \( J \) 7.0 Hz, p-ArCH), [2.04, 1.84] (1H, 2 × dd, \( J \) 7.0, 5.0 Hz).
Hz, SCHCH$_2$), 1.27–1.18 (18H, m, CH(CH$_3$)$_2$); $\delta$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$_2$Ar), 70.6, 70.4 (SCH), 58.9, 58.8 (CH$_2$OH), 53.1, 53.1 (OCH$_3$), 34.1 (p-ArCH), 29.3 (o-ArCH), 27.8, 26.7, (SCHCH$_2$), 24.7, 24.6 (o-ArCH(CH$_3$)$_2$), 23.6 (p-ArCH(CH$_3$)$_2$); m/z (Cl) 643 [M+NH$_4$]$^+$ (Found [M+NH$_4$]$^+$, 643.2873. C$_{34}$H$_{43}$NO$_6$S$_2$ requires [M+NH$_4$]$^+$, 643.2870) (Found: C, 65.29; H, 6.93; N, 2.24.

C$_{34}$H$_{43}$NO$_6$S$_2$ requires C, 65.25; H, 6.93; N, 2.24.).

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

According to general procedure F, a solution of (±)-methyl (E)-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 (±)-(E)-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; $\nu$$_{max}$ (film) 3420, 2959, 1738, 1599, 1447, 1311, 1295, 1244, 1147, 1092, 1049, 1021, 997, 764, 753, 743, 684 cm$^{-1}$; $\delta$H (300 MHz; CD$_3$OD) 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$_2$Ar), 7.25–7.09 (5H, m, Ph), [5.93, 5.87] (1H, 2 × t, J 6.5 Hz, CH$_2$OH), 4.20 (2H, 2 × sept, J 6.5 Hz, o-ArCH), 4.29–4.04 (3H, m, SCH and CH$_2$OH), 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$_3$)$_2$); $\delta$C (75 MHz; CD$_3$OD) 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$_2$OH), 35.4 (p-ArCH), 30.5, 30.5 (p-ArCH), 28.6, 28.0 (SCHCH$_2$), 25.1, 25.1 (p-ArCH(CH$_3$)$_2$), 24.1 (p-ArCH(CH$_3$)$_2$); m/z (Cl) 629 [M+NH$_4$]$^+$, 594, 550 (Found [M+NH$_4$]$^+$, 629.2717. C$_{33}$H$_{41}$NO$_6$S$_2$ requires [M+NH$_4$]$^+$, 629.2714).
(±)-5-Phenyl-3-(N-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonimidoyl)-4,7-dihydrooxepin-2(3H)-one 23a

According to general procedure G, a solution of (±)-(E)-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$_2$Cl$_2$ (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-dihydrooxepin-2(3H)-one 23a (103 mg, 36% over four steps) as a colourless solid; R$_f$ 0.45 (50% EtOAc–petrol); $\nu_{\max}$ (film) 2958, 1753, 1599, 1446, 1311, 1246, 1148, 1093, 1057 cm$^{-1}$; $\delta$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$_2$Ar), [6.15, 5.91] (1H, dd, J 13.0, 3.5 Hz, SCH), 6.05 (1H, dddd, J 9.5, 5.5, 3.5, 2.0 Hz, OCH$_2$CH), 5.26 (1H, dddd, 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$_3$)$_2$); $\delta$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$_5$S$_2$ requires [M+NH$_4$]$^+$, 611.2613) (Found: C, 66.66; H, 6.53; N, 2.27. C$_{33}$H$_{39}$NO$_5$S$_2$ requires C, 66.75; H, 6.62; N, 2.36.).
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\text{max} (film) 2960, 1600, 1463, 1447, 1423, 1311, 1265, 1149, 1097, 1051, 739, 703 cm\(^{-1}\); δ\text{H} (400 Hz) 8.04 (2H, d, J 7.5 Hz, o-Ph), 7.68 (1H, t, J 7.5 Hz, p-Ph), 7.60 (2H, t, J 7.5 Hz, m-Ph), 7.20 (3H, m, Ph), 7.11 (2H, s, m-SO\text{2}Ar), 6.82 (2H, m, Ph), 6.12 (1H, dd, J 17.0, 10.5 Hz, CH=CH\(_2\)), 5.04 (1H, dd, J 10.5, 1.0 Hz, CH=CH\(_2\) \text{trans}), 4.42 (1H, d, J 17.0 Hz, CH=CH\(_2\) cis), 4.39 (2H, sept, J 7.0 Hz, o-ArCH), 3.32 (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\text{C} (100 MHz) 151.9, 149.1, 139.2, 139.1, 137.3 (4°), 138.8 (CH=CH\(_2\)), 134.0, 129.2, 128.6, 127.8, 127.7, 123.3 (3°), 119.0 (CH=CH\(_2\)), 48.4 (SCH), 39.4 (SCHC), 34.1 (p-ArCH), 29.2 (o-ArCH), 24.7, 24.6, 23.7, 23.6 (CH(CH\(_3\))\(_2\)), 20.0 (SCHCH\(_2\)) m/z (CI) 550 [M+H]\(^{+}\), 567, 425, 301 (Found [M+H]\(^{+}\), 550.2457. C\(_{32}\)H\(_{39}\)NO\(_3\)S\(_2\) requires [M+H]\(^{+}\), 550.2450); 24a (isolated as a single diastereoisomer): R\_f 0.41 (50% EtOAc–petrol); ν\text{max} (film) 2961, 2929, 1600, 1463, 1447, 1423, 1311, 1265, 1149, 1097, 1051, 739, 703 cm\(^{-1}\); δ\text{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-
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)phenylsulfinimidoyl)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.
triisopropylphenylsulfonyl)phenylsulfonimidoyl)hex-4-enoate as a colourless gum, which was used without further purification; Rf 0.44 (50% EtOAc–petrol); ν\text{max} (film) 2955, 2925, 1744, 1599, 1501, 1315, 1243, 1148, 1091, 1039, 1022, 997, 961, 845, 684 cm\(^{-1}\); δ\(\text{H}\) (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-SO2Ar), 7.13–7.03 (1H, m, ArF), 6.85–6.70 (2H, m, ArF), 5.76 (1H, t, J 6.5 Hz, CHCH2O), 4.58 (2H, s, OCH2O), 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, OCH2CH3), 3.54 (3H, s, CO2CH3), 3.34 (3H, s, CH2OC2H5), [3.21, 3.17] (1H, 2 × m, SCH2), 3.00 (1H, 2 × d, J 12.0 Hz, SCHCH2), 2.86 (1H, sept, J 7.0 Hz, p-ArCH), 1.25–1.16 (18H, m, CH(CH3)2); δ\(\text{C}\) (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 (CFCH2CH2), 124.0, 123.9, 123.8, 123.7 (CCF), 111.5, 111.5 111.3, 111.2 (CFCHCH2), 104.6, 104.2, 103.9 (CFCHCF), 95.9 (OCH2O), 70.1 (SCH), 63.3 (CH2CH2O), 55.4 (CH2OCH2), 53.1 (CO2CH3), 34.1 (p-ArCH), 29.7, 29.0 (SCHCH2), 29.3 (o-ArCH), 24.7 (o-ArCH(CH3)2), 23.6 (p-ArCH(CH3)2); m/z (El) 723 [M+NH4]+ (Found [M+NH4]+, 723.2943. C36H45F2NO7S2 requires [M+NH4]+, 723.2944) (Found: C, 61.23; H, 6.42; N, 1.95. C36H45F2NO7S2 requires C, 61.26; H, 6.43; N, 1.98.).

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

According to general procedure E, \((\pm)\)-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 \((\pm)\)-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; Rf 0.21 (50% EtOAc–petrol); ν\text{max} (film) 2958, 1743, 1599, 1501, 1447, 1423, 1312, 1295, 1242, 1147, 1091, 1048, 1021, 997, 966, 846, 769, 740, 684 cm\(^{-1}\); δ\(\text{H}\) (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-SO2Ar), 6.79 (2H, m, m-ArF), 5.84 (1H, 2 × t, $J$ 6.5 Hz, $CHCH_2OH$), [4.69, 4.38] (1H, 2 × dd, $J$ 11.5, 3.5 Hz, $CHCH_2OH$), 4.30 (2H, m, $CH_2OH$), 4.24 (2H, m, o-ArCH), [3.53, 3.46] (3H, 2 × s, OCH3), [3.33, 3.25] (1H, 2 × dd, $J$ 6.5 Hz, $CHCH_2OH$), [4.69, 4.38] (1H, t, $J$ 6.0 Hz, OH), 1.21 (18H, m, CH(CH3)2); δC (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 (CCF), 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, 131.1, 131.1, 131.0, 131.0 (CFCHCH), 111.7, 111.5, 111.3 (CFCHCH), 104.6, 104.4, 104.2, 104.0 (CFCHCF), 70.7, 70.3 (SCH), 58.7, 58.5 (CH2OH), 53.2, 53.2 (OCH3), 34.1 (p-ArCH), 29.3, 29.3 (o-ArCH), 28.9, 27.8 (SCHCH2), 24.7, 24.6 (o-ArCH(CH3)2), 23.6 (p-ArCH(CH3)2); δF (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 (El) 679 [M+NH4]+, 644, 408 (Found [M+NH4]+, 679.2680. C34H41F2NO6S2 requires [M+NH4]+, 679.2682) (Found: C, 61.80; H, 6.32; N, 2.18. C34H41F2NO6S2 requires C, 61.70; H, 6.24; N, 2.12).

(±)-(E)-4-(2,4-Difluorophenyl)-6-hydroxy-2-(N-(2,4,6-trisopropylphenylsulfonyl)phenylsulfonylimidoyl)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-trisopropylphenylsulfonyl)phenylsulfonylimidoyl)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-trisopropylphenylsulfonyl)phenylsulfonylimidoyl)hex-4-enoic acid (290 mg, 91%) as a colourless foam, which was used without further purification; νmax (film) 2958, 2556, 1731, 1599, 1501, 1448, 1423, 1293, 1244, 1141, 1091, 1049, 1021, 997, 966, 848, 765, 741, 684 cm⁻¹; δH (300 MHz; CD3OD) 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-SO2Ar), 6.96–6.81 (2H, m, m-ArF), 5.77 (1H, 2 × t, $J$ 6.5 Hz, $CHCH_2OH$), 4.29–4.03 (3H, m, SCH and $CH_2OH$), 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$_3$)$_2$); $\delta$C (75 MHz; CD$_2$OD) 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 (CCF), 133.2, 133.1, 133.0, 133.0, 131.5, 124.5 (3°), 130.9, 130.8, 130.6, 130.4 (CFCHCH), 112.7, 112.4, 112.3 (CFCHCH), 105.4, 105.0, 104.7 (CFCHCF) 72.0, 71.4 (SCH), 59.3, 59.2 (CH$_2$OH), 35.4 (p-ArCH), 30.5 (o-ArCH), 29.7, 29.0 (SCHCH$_2$) 25.1, 25.1, 25.0 (o-ArCH(CH$_3$)$_2$), 24.1 (p-ArCH(CH$_3$)$_2$); m/z (EI) 665 [M+NH$_4^+$], 630 (Found [M+NH$_4^+$], 665.2524. C$_{33}$H$_{39}$F$_2$NO$_6$S$_2$ requires [M+NH$_4^+$], 665.2525) (Found: C, 61.06; H, 5.99; N, 2.09. C$_{33}$H$_{39}$F$_2$NO$_6$S$_2$ 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(3H)-one 23b

According to general procedure G, a solution of (±)-(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$_2$Cl$_2$ (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(3H)-one 23b (89 mg, 35%) as a colourless solid; mp 86–87 °C; R$_f$ 0.48 (50% EtOAc–petrol); $\nu_{\text{max}}$ (film) 2959, 1754, 1502, 1231, 1141, 1048, 998, 972, 847, 733, 682 cm$^{-1}$; $\delta$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$_2$Ar), 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, CHCH$_2$O), 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$_3$)$_2$); $\delta$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, 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, 123.4 (3°), 124.7, 124.7, 124.6, 124.5 (CCF), 111.9, 111.8, 111.8, 111.7, 111.7, 111.6, 111.6, 111.6 (CCFCH), 104.7, 104.5, 104.3 (CFCHCF), 65.8, 65.4 (SCH), 64.0, 63.8 (OCH2), 34.1, 34.1 (p-ArCH), 32.0, 30.6 (SCH2), 29.3, 29.3 (o-ArCH), 24.7, 24.6, 24.4 (o-ArCH(CH3)2), 23.6 (p-ArCH(CH3)2); m/z (EI) 647 [M+NH4]+, 630 [M+H]+ (Found [M+H]+, 630.2156. C33H37F2NO5S2 requires [M+H]+, 630.2154) (Found: C, 63.07; H, 5.97; N, 2.18. C33H37F2NO5S2 requires C, 62.94; H, 5.92; N, 2.22).

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

According to general procedure H, a solution of 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): Rf 0.60 (50% EtOAc–petrol); νmax (film) 2985, 1740, 1447, 1374, 1240, 1047, 938, 847, 737, 634, 608 cm⁻¹; δH (500 MHz) 8.00 (2H, dd, J 8.5, 8.5 Hz).
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-SO₂Ar), 6.89 (1H, dt, J 8.5, 6.5 Hz, CFCHCH) 6.78 (1H, t, J 8.0, Hz, CFCHCH) 6.67 (1H, ddd, J 10.0, 9.0, 2.5 Hz, CFCHCF) 6.11 (1H, dd, J 17.0, 10.5 Hz, CH=CH₂), 5.06 (1H, dd, J 10.5, 1.0 Hz, CH=CH₂ trans) 4.44 (1H, d, J 17.0 Hz, CH=CH₂ cis) 4.40 (2H, sept, J 7.0 Hz, o-ArCH) 3.29 (1H, dd, J 9.0, 6.0 Hz, SCH)

δC (125 MHz) 163.6, 163.5, 162.3, 162.2, 160.1 (CF), 152.0, 149.1, 138.2, 137.1 (4°), 134.2 (CH=CH₂), 134.1 (p-Ph), 132.0, 131.9, 131.9 (CFCH), 129.0 (m-Ph), 128.1 (o-ArCH), 123.3 (m-SO₂Ar), 122.3, 122.2 (CCF), 118.4 (CH=CH₂), 111.7, 111.6 (CFCHCH), 104.5, 104.3, 104.1 (CFCHCF), 48.0 (SCH), 34.1 (SCHC), 34.1 (p-ArCH), 29.2 (o-ArCH), 24.7, 24.6, 23.7, 23.6 (CH(CH₃)₂), 20.3 (SCHCH₂); m/z (CI) 603 [M+NH₄]+=, 586, 301 (Found [M+H]+=, 586.2257. requires [M+H]+=, 586.2261);

24b and 26b (isolated as a mixture of the two diastereoisomers): R₇ 0.67 (50% EtOAc–petrol); νmax (film) 2985, 1740, 1447, 1374, 1240, 1094, 1047, 938, 847, 737, 634, 608 cm⁻¹; δH (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-SO₂Ar 24b), 7.06 (2H, s, m-SO₂Ar 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, CH=CH₂ 24b), 5.60 (1H, dd, J 17.0, 10.5 Hz, CH=CH₂ 26b), 5.11 (1H, dd, J 10.5, 1.0 Hz, CH=CH₂ trans 24b), 5.02 (1H, d, J 10.5Hz, CH=CH₂ trans 26b), 4.74 (1H, dd, J 17.0, 1.5 Hz, CH=CH₂ 24b), 4.64 (1H, d, J 17.0Hz, CH=CH₂ cis 26b), 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, SCHCH₂ 26b), 2.13 (1H, dd, J 6.5 Hz, SCHCH₂ 24b), 1.96 (1H, dd, J 9.0, 6.5 Hz, SCHCH₂ 26b), 1.71 (1H, dd, J 9.0, 6.0 Hz, SCHCH₂ 24b), 1.30–1.17 (18H, m, CH(CH₃)₂); δC (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 (CH=CH₂), 134.0, 133.9, 129.4, 129.0, 128.0, 127.6 (3°), 132.9, 132.9, 132.8, 132.8 (CFCHCH), 123.3, 122.8, 122.7, 122.6 (CCF), 118.3, 115.6 (CH=CH₂), 117.0, 117.0, 111.7, 111.5, 111.5, 111.2, 111.0 (CFCHCH), 104.4, 104.2, 104.1, 104.0, 103.9, 103.7 (CFCHCF), 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(CH₃)₂), 19.7, 17.7
(SCHCH₂); m/z (CI) 603 [M+NH₄]+, 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

![Chemical structure]

According to general procedure D, a suspension of 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; Rf 0.71 (50% EtOAc–heptane).

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

![Chemical structure]

According to general procedure E, a solution of (±)-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; Rf 0.36 (50% EtOAc–heptane); νmax (film) 2958, 1744, 1621, 1462, 1316, 1237, 1150, 1095, 1057 cm⁻¹; δH (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-SO₂Ar), 6.86 (2H, 2 × t, J 8.0 Hz, m-ArF), 5.84 (1H, 2 × t, J 6.5 Hz, CHCH₂OH),...
4.64 (1H, dd, J 12.0, 3.0 Hz, SCH), 4.37 (1H, dd, J 11.0, 4.5 Hz, SCH), 4.29 (2H, m, CH$_2$OH), 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 (CH$_3$CH$_2$OH), 134.9, 134.8, 129.6, 129.5, 129.3, 129.2, 123.4 (3°), 124.1, 124.0 (CFCHCH$_2$), 117.1 (CCF), 111.7, 111.6, 111.5, 111.3 (CFCHCH$_2$), 70.4, 70.1 (SCH), 58.6, 58.5 (CH$_2$OH), 53.2, 53.1 (OCH$_3$), 34.1 (p-ArCH), 29.3 (o-ArCH), 29.0, 27.8 (SCHCH$_2$), 24.6, 24.6 (o-ArCH(CH$_3$)$_2$), 23.6 (p-ArCH(CH$_3$)$_2$); m/z (CI) 679 [M+NH$_4$]$^+$, 586, 425, 301, 272 (Found [M+H]$^+$, 662.2416. C$_{34}$H$_{41}$F$_2$NO$_6$S$_2$ requires [M+H]$^+$, 662.2422) (Found: C, 61.77; H, 6.18; N, 2.11. C$_{34}$H$_{41}$F$_2$NO$_6$S$_2$ requires C, 61.70; H, 6.24; N, 2.12).

(±)-(E)-4-(2,6-Difluorophenyl)-6-hydroxy-2-(N-(2,4,6-trisopropylphenylsulfonyl)phenylsulfinimidoyl)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-trisopropylphenylsulfonyl)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-trisopropylphenylsulfonyl)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$_3$OD) 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$_2$Ar), 6.92 (2H, 2 × t, J 8.0 Hz, m-ArF), [5.80, 5.74] (1H, 2 × t, J 6.5 Hz, CHCH$_2$OH), [4.39, 4.29] (2H, 2 × dd, J 13.5, 7.0 Hz, CH$_2$OH), 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$_3$OD) 169.0, 168.7 (C=O), 162.9, 160.5 (CF), 153.7, 153.5, 150.5,
(±)-5-(2,6-Difluorophenyl)-3-(N-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonylimidoyl)-4,7-dihydrooxepin-2(3H)-one 23c

According to general procedure G, a solution of (±)-(E)-4-(2,6-difluorophenyl)-6-hydroxy-2-(N-(2,4,6-triisopropylphenylsulfonyl)phenylsulfonylimidoyl)hex-4-enoic (360 mg, 0.56 mmol, 1.0 equiv.) in CH₂Cl₂ (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)phenylsulfonylimidoyl)-4,7-dihydrooxepin-2(3H)-one 23c (289 mg, 82%) as a colourless solid; mp 86–87 °C; Rf 0.69 (50% EtOAc–petrol); νmax (film) 2959, 1756, 1623, 1599, 1464, 1401, 1267, 1234, 1148, 1092, 1064, 1023, 998, 738 cm⁻¹; δH (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-SO₂Ar), 6.91 (2H, m, m-ArF), 5.98 (1H, m, CH₂O), [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, OCH₂), 4.68 (1H, ddd, J 16.0, 7.5, 4.5 Hz, OCH₂), 4.3 (2H, sept, J 6.5 Hz, o-ArCH), [3.54, 3.36] (1H, 2 × d, J 17.5 Hz, SCHCH₂), 2.88 (1H, sept, J 6.5 Hz, p-ArCH), 2.78 (1H, m, SCHCH₂) 1.27–1.12 (18H, m, CH(CH₃)₂); δC (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 (CFCH₂), 128.9, 128.8, 127.9, 127.7, 123.5 (3°), 117.7, 117.6, 117.5, 117.4, 117.3, 117.2 (CCF), 112.0, 111.9, 111.7, 111.7 (CFCH₂), 66.0, 65.4 (SCH),
63.8, 63.7 (OCH₂), 34.1 (p-ArCH), 29.3 (o-ArCH), 24.7, 24.5 (o-ArCH(CH₃)₂), 23.6 (p-ArCH(CH₃)₂); m/z (CI) 647 [M+NH₄]⁺, 603, 586, 425, 370, 352, 335, 301, 240 (Found [M+NH₄]⁺, 647.2405. C₃₃H₃₇F₂NO₅S₂ requires [M+NH₄]⁺, 647.2425) (Found: C, 62.83; H, 5.85; N, 2.15. C₃₃H₃₇F₂NO₅S₂ requires C, 62.94; H, 5.92; N, 2.22).

(S*₂,R₂,R₂)-S-(2-(2,6-Difluorophenyl)-2-vinylcyclopropyl)-S-phenyl-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximine 24c, (S*₂,S₂,2S₂)-S-(2-(2,6-difluorophenyl)-2-vinylcyclopropyl)-S-phenyl-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximine 25c, (S*₂,S₂,2S₂)-S-(2-(2,6-difluorophenyl)-2-vinylcyclopropyl)-S-phenyl-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximine 26c, and (S*₂,R₂,2S₂)-S-(2-(2,6-difluorophenyl)-2-vinylcyclopropyl)-S-phenyl-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximine 27c

![Chemical Structure](image)

According to general procedure H, a solution of 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% Et₂O–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); Rₓ 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; δH (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, SO₂Ar), 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, CH=CH₂ 24c), 6.11 (1H, dd, J 17.0, 10.5 Hz, CH=CH₂ 25c), 5.62 (1H, dd, J 17.0, 10.5 Hz, CH=CH₂ 26c), 5.59 (1H, dd, J 17.0, 10.5 Hz, CH=CH₂ 27c), 5.18 (1H, d, J 10.5 Hz, CH=CH₂ cis 24c), 5.10 (1H, d, J 10.5 Hz, CH=CH₂ 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$_3$)$_2$); δc (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 (CH=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 (CFCHCH), 118.3, 115.5 (CH=CH$_2$), 112.2, 112.0, 111.8, 111.6, 111.2, 111.0 (CFCHCH), 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(CH$_3$)$_2$), 20.2, 18.5, 18.4 (SCHCH$_2$); m/z (CI) 603 [M+NH$_4$]$^+$, 586, 425 (Found [M+H]$^+$, 586.2255. requires [M+H]$^+$, 586.2261).
8. X-Ray crystallographic data

The X-ray crystal structure of 25b

The ortho fluorine on the C(9)-based phenyl ring was found to be disordered between the C(10) and C(14) positions. This disorder was modelled by refining a partial occupancy fluorine atom in each site (along with an appropriate partial occupancy hydrogen atom), restraining the isotropic thermal parameters of the two fluorine atoms to be approximately the same, and allowing the occupancies to refine. This resulted in a ca. 83% occupancy fluorine atom bound to C(10), and a ca. 17% occupancy fluorine atom bound to C(14); the major occupancy fluorine atom was refined anisotropically whilst the minor occupancy fluorine atom was refined isotropically. Note that this disorder is equivalent to a 180° rotation about the C(3)–C(9) single bond.

Fig. S1 The molecular structure of 25b (50% probability ellipsoids).

Fig. S2 The molecular structure of 25b showing the F(10)/F(14) disorder. The F(10) site is ca. 83% occupancy, whilst the F(14) site is ca. 17% occupancy.
Fig. S2

crude 17c, 18c 1H nmr spectrum
crude 24-27a 1H nmr spectrum
crude 24-27b 1H nmr spectrum
crude 24-27c 1H nmr spectrum