Highly Diastereoselective Radical Cyclisation of Chiral Sulfinimines

Elise M. Rochette, William Lewis, Al G. Dossetter and Robert A. Stockman

School of Chemistry, University of Nottingham, Nottingham, NG7 2RD

e-mail: Robert.stockman@nottingham.ac.uk

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General experimental procedures
All anhydrous reactions were performed in flame-dried glassware under an inert atmosphere of nitrogen or argon. Evaporation of solvents was carried out using a rotary evaporator and a high vacuum pump. All yields refer to isolated material, homogeneous by TLC or NMR unless otherwise stated. Compound names are assigned according to standard IUPAC nomenclature. AIBN was recrystallised from acetone at -17 °C. All other reagents were purchased from commercial sources and used without additional purification unless otherwise stated. Tetrahydrofuran (THF) was freshly distilled under argon from the sodium anion of benzophenone. All other anhydrous solvents were purchased or obtained from in-house solvent purification towers. Toluene was degassed by repeat "freeze-thaw" cycles under an inert argon atmosphere unless stated otherwise. Brine refers to a saturated aqueous solution of sodium chloride. Column chromatography was performed on Fluka™ silica gel 60 or Merck aluminium oxide 90. Thin layer chromatography was conducted on Merck silica gel 60 F254 or Fluka aluminium plates and visualisation was obtained using ultraviolet lamps (254 nm), aqueous alkaline potassium permanganate solution or iodine stain.
All microwave experiments were carried out in a Biotage Initiator 2.0 Microwave Reactor. Melting points are uncorrected and were recorded using Stuart Scientific SMP3. High resolution mass spectra data were recorded using the open access Bruker MicroTOF mass spectrometre. NMR spectra were recorded using Bruker AV-400, AV(III)400, DPX300 or DPX400 spectrometers, and are quoted in ppm downfield of a tetramethylsilane internal standard. Nucleus and operating frequency are indicated for each set of data and coupling constant values $J$ are given in hertz. Infrared spectra data were recorded using a Perkin-Elmer 1600 FT-IR spectrophotometer.

**General procedure A: Horner-Wadsworth-Emmons reaction**

![Chemical structure](image1)

Sodium hydride (60% in mineral oil, 1.2 equiv.) was suspended in dry THF at 0 °C and triethyl phosphonoacetate (1.2 equiv.) was added dropwise. The solution was stirred at 0 °C for 30 min and a solution of aldehyde (1 equiv.) in dry THF was added. The reaction mixture was warmed to room temperature and stirred overnight. A saturated aqueous solution of ammonium chloride was added and the resulting aqueous phase was separated and extracted 3 times with dichloromethane. The combined organic phases were washed with water, dried over magnesium sulfate and the solvent was removed *in vacuo*. The resulting residue was purified using column chromatography on silica gel (9:1, petroleum ether/ethyl acetate) to give the desired $\alpha,\beta$-unsaturated ester.

**General procedure B: Reduction of $\alpha,\beta$-unsaturated esters using Super Hydride®**

![Chemical structure](image2)

To a solution of $\alpha,\beta$-unsaturated ester (1 equiv.) in dry THF (0.8 M) at -78 °C under argon was added Super Hydride® (1.0 M in THF, 4 equiv.) dropwise over 1 hour. The solution was stirred for 1 hour at -78 °C and was then warmed to room temperature and stirred overnight. Water (8 mL) was added slowly and the reaction mixture was heated to reflux for 2 hours. The reaction mixture was then cooled to room temperature and a 3 M aqueous solution of sodium hydroxide (20 mL) was added. The reaction mixture was cooled to 0 °C and a 27% aqueous solution of H$_2$O$_2$ (20 mL) was added dropwise. After complete addition, the reaction mixture was warmed to room temperature and stirred for 1 hour. The reaction mixture was
then diluted with water (10 mL) and the product was extracted with diethyl ether (3 x 30 mL). The combined organic phases were washed with water (3 x 40 mL) and dried over sodium sulfate. The solvent was removed in vacuo to give the desired alcohol. The alcohol was used in the subseq. uent step without further purification.

**General procedure C: Oxidation of alcohols using PCC**

\[
\text{R-CH}_2\text{OH} \xrightarrow{\text{PCC, CH}_2\text{Cl}_2} \text{R-C=O}
\]

The alcohol (1 equiv.) was dissolved in dichloromethane (0.2 M), pyridinium chlorochromate (1.1 equiv.) and silica gel (8 equiv.) was added. The reaction mixture was stirred overnight and silica gel was then added and the mixture was stirred for 5 min. The reaction mixture was then filtered through a pad of silica gel and washed with diethyl ether. The solvent was removed in vacuo to give the desired aldehyde. The aldehyde was used in the subsequent step without further purification unless otherwise stated.

**General procedure D: Sulfinimine synthesis using titanium(IV) ethoxide**

\[
\text{R-C=O} + \text{H}_2\text{N-S}^\text{O}_{\text{R}_1} \xrightarrow{\text{Ti(OR)}_4, \text{THF}} \text{R-C=S}^\text{O}_{\text{R}_1}
\]

The aldehyde (1 equiv.) was dissolved in dry THF (0.1 M) and titanium ethoxide (3 equiv.) was added. The reaction mixture was stirred for 10 min and the sulfinamide (1.1 equiv.) was added. The solution was stirred overnight at room temperature. Water was added and the mixture was filtered through a pad of celite and the resulting cake was washed with ethyl acetate. The aqueous layer was separated and extracted 3 times with ethyl acetate. The combined organic phases were dried over sodium sulfate. The solvent was removed in vacuo and purified by column chromatography on silica gel (4:1, petroleum ether/ethyl acetate) to give the desired sulfinimine.

**General procedure E: Oxidative cleavage of alkenes with osmium tetroxide**

\[
\text{R-CH=CH}_2 \xrightarrow{\text{OsO}_4, \text{dioxane/water}} \text{R-C=O}
\]

The alkene (1equiv.) was dissolved in dioxane and water (3:1, 0.1 M) and osmium tetroxide (4% in water, 0.025 equiv.). The reaction mixture was stirred at room temperature for 30 minuted and sodium periodate (1.7 equiv.). The reaction mixture was stirred for 2 hours and
water was added followed by ethyl acetate. The phases were separated and the aqueous phase was extracted with ethyl acetate 3 times. The combined organic phases were dried over sodium sulphate. The solvent was removed \textit{in vacuo} to give the desired aldehyde.

**General procedure F: Radical cyclisation AIBN/Bu$_3$SnH**

![Chemical structure]

Sulfinimine (1 equiv.) was dissolved in degassed benzene (0.1 M) and tributyltin hydride (1.2 equiv.) was added followed by AIBN (1 equiv.). The reaction was heated to 75 °C for 2 hours under argon. The solvent was removed \textit{in vacuo} and the product was purified by flash column chromatography on 10% w/w potassium carbonate-silica gel (from 1:0 to 4:1 petroleum ether/ethyl acetate) to give the product.

**General procedure G: Radical cyclisation Et$_3$B/O$_2$/Bu$_3$SnH**

![Chemical structure]

Sulfinimine (1 equiv.) was dissolved in degassed benzene (0.1 M) and tributyltin hydride (1.2 equiv.) was added followed by triethylborane (1 M in hexane, 1.5 equiv.). The septum was pierced and the reaction was heated for 2 hours at 40 °C. The solvent was removed \textit{in vacuo} and the product was purified by flash column chromatography on 10% w/w potassium carbonate-silica gel (from 1:0 to 4:1 petroleum ether/ethyl acetate) to give the product.

**General procedure H: Radical cyclisation AIBN/NHC-borane**

![Chemical structure]

Sulfinimine (1 equiv.) was dissolved in degassed benzene (0.1 M) and NHC-borane (1 equiv.) was added followed by AIBN (1 equiv.). The reaction was heated to 75 °C for 2 hours under argon. The solvent was removed \textit{in vacuo} and the product was purified by flash column chromatography on silica gel (from 1:0 to 4:1 petroleum ether/ethyl acetate) to give the product.

**General procedure I: Radical cyclisation Et$_3$B/O$_2$/NHC-borane**
Sulfinimine (1 equiv.) was dissolved in degassed benzene (0.1 M) and NHC-borane (1 equiv.) was added followed by triethylborane (1 M in hexane, 1 equiv.). The septum was pierced and the reaction was heated to 40 °C overnight. The solvent was removed in vacuo and the product was purified by flash column chromatography on silica gel (from 1:0 to 4:1 petroleum ether/ethyl acetate) to give the product.

**General reaction scheme for the synthesis of aldehyde (1)**

\[
\begin{align*}
R' & \rightarrow O^+ \xrightarrow{\text{EtOH}} \text{EtO}^- \xrightarrow{\text{NaH}} \text{THF} \xrightarrow{\text{R}} \text{O} \xrightarrow{\text{LiBEtH}} \text{THF} \xrightarrow{\text{A}} \text{O} \xrightarrow{\text{PCC}} \text{CH}_2\text{Cl}_2 \xrightarrow{\text{R}} \text{O} \\
\end{align*}
\]

**Ethyl-3-(2-bromophenyl)prop-2-enoate (A1)**

General procedure A was followed to give A1 as a pale yellow oil (12.5 g, 49.1 mmol, 91%).

δ\text{H} (400 MHz, CDCl\textsubscript{3}), 8.06 (1H, d, J 16.1), 7.63 (1H, dd, J 3.2 and 1.5), 7.61 (1H, dd, J 3.7 and 1.7), 7.31 - 7.36 (1H, m), 7.23 (1H, td, J 8.2 and 1.7), 6.40 (1H, d, J 16.1), 4.29 (2H, q, J 7.0), 1.36 (3H, t, J 7.0). δ\text{C} (100 MHz, CDCl\textsubscript{3}), 166.4, 143.0, 134.6, 133.5, 131.2, 127.8, 127.7, 125.3, 121.2, 60.7, 14.3. \text{υ}_{\text{max}} (\text{CHCl}_3)/\text{cm}^{-1}, 2986, 2862, 1711, 1683. m/z (ESI+) 277 (96%, [M+Na]\textsuperscript{+}), 279 (100%); HRMS calculated for C\textsubscript{11}H\textsubscript{11}BrO\textsubscript{2}: 255.0015 [M+H]\textsuperscript{+}, found 255.0004. Data consistent with literature\textsuperscript{1}.

**Ethyl 3-(2-iodophenyl)acrylate (A2)**

General procedure A was followed to give A2 as a pale yellow oil (10.0 g, 33.1 mmol, 85%).

δ\text{H} (300 MHz, CDCl\textsubscript{3}), 7.86 - 7.95 (2H, m), 7.57 (1H, dd, J 7.9), 7.32 - 7.40 (1H, m), 7.06 (1H, td, J 7.7, 1.6 Hz), 6.32 (1H, d, J 15.8 Hz), 4.29 (2H, q, J 7.1 Hz), 1.36 (3H, t, J 7.1 Hz). δ\text{C} (75 MHz, CDCl\textsubscript{3}), 166.3, 147.7, 140.0, 137.9, 131.2, 128.6, 127.4, 121.3, 101.1, 60.7, 14.3. \text{υ}_{\text{max}} (\text{CHCl}_3)/\text{cm}^{-1}, 2987, 1711, 1582, 1462, 1314, 1182. m/z (ESI+) 303 (100%, [M+H]\textsuperscript{+}), 320 (1.2%, [M+NH\textsubscript{4}]\textsuperscript{+}), 325 (72.9%, [M+Na]\textsuperscript{+}); HRMS calculated for C\textsubscript{11}H\textsubscript{11}I\textsuperscript{127}O\textsubscript{2}: 302.9876 [M+H]\textsuperscript{+}, found 302.9878. Data consistent with literature\textsuperscript{2}.
Ethyl 3-(6-bromo-1,3-benzodioxol-5-yl)prop-2-enoate (A3)

General procedure A was followed to give A3 as a white solid (2.0 g, 6.7 mmol, 77%). m.p. = 78-80 °C. δH (300 MHz, CDCl3), 7.86 (1H, d, J 15.9), 7.13 (1H, s), 6.94 (1H, s), 6.11 (1H, d, J 15.9), 5.89 (2H, s), 4.14 (2H, q, J 7.1), 1.21 (3H, t, J 7.1). δC (75 MHz, CDCl3), 166.6, 150.0, 147.9, 142.7, 127.7, 119.1, 117.8, 113.1, 106.4, 102.2, 60.6, 14.3. υ max (CHCl3)/ cm⁻¹, 2985, 2904, 1705, 1632, 1505, 1474, 1119. m/z (ESI+) 230 (8.9%, [M+H]+), 321 (100%, [M+Na]+), 323 (99.2%); HRMS calculated for C12H1179BrO4: 298.9913 [M+H]+, found: 298.9902.

3-(2-Bromophenyl)propan-1-ol (B1)

General procedure B was followed to give B1 as a yellow oil (2.0 g, 9.4 mmol, 98%). δH (400 MHz, CDCl3), 7.56 (1H, dd, J 7.9 and 0.7), 7.24 - 7.29 (1H, m), 7.04 - 7.13 (2H, m), 3.73 (2H, t, J 6.4), 2.80 - 2.91 (2H, m), 1.86 - 1.98 (3H, m). δC (75 MHz, CDCl3), 141.1, 132.8, 130.4, 127.7, 127.5, 124.5, 32.8, 32.4. υ max (CHCl3)/ cm⁻¹, 3626, 2970, 2940, 1469. m/z (ESI+) 251 (8.2%, [M+H]+), 236 (30.3%, [M+Na]+), 222 (100%); HRMS calculated for C9H1179BrO: 236.9885 [M+Na]+, found 236.9881. Data consistent with literature1.

3-(2-Iodophenyl)propan-1-ol (B2)

General procedure B was followed to give B2 as a yellow oil (7.53 g, 28.73 mmol, 93%). δH (300 MHz, CDCl3), 7.81 - 7.88 (1H, m), 7.23 - 7.36 (2H, m), 6.87 - 6.96 (1H, m), 3.74 (2H, t, J 6.4 Hz), 2.80 - 2.89 (2H, m), 1.84 - 1.96 (2H, m). δC (75 MHz, CDCl3), 144.4, 139.5, 129.5, 128.4, 127.8, 100.6, 62.1, 37.0, 33.1. υ max (thin film)/ cm⁻¹, 3345, 3058, 2943, 1720, 1562, 1466, 1435, 1057, 1010, 749, 647. m/z (ESI+) 285 (100%, [M+Na]+), 415 (57%); HRMS calculated for C9H11127IO: 284.9747 [M+Na]+, found 284.9747. Data consistent with literature3.

3-(6-Bromo-1,3-benzodioxol-5-yl)propan-1-ol (B3)
General procedure B was followed to give B3 as a white solid (0.78 g, 3.0 mmol, 90%). m.p. = 73-75 °C. \( \delta_H \) (300 MHz, CDCl\(_3\)), 6.99 (1H, s), 6.73 (1H, s), 5.95 (2H, s), 3.61 - 3.82 (2H, m), 2.66 - 2.81 (2H, m), 1.76 - 1.93 (2H, m). \( \delta_C \) (75 MHz, CDCl\(_3\)), 147.3, 146.6, 134.1, 114.3, 112.7, 110.0, 101.6, 62.0, 32.9, 32.3. \( \nu_{\text{max}} \) (CHCl\(_3\))/ cm\(^{-1}\), 3624, 3011, 2961, 1712, 1505, 1476, 1410, 1241, 1041. m/z (ESI+) 279 (10.8%, \[M+NH_4^+\]), 283 (14%, \[M+Na^+\]), 325 (100%).

3-(2-Bromophenyl)propanal (C1)

General procedure C was followed to give C1 as a colourless oil (0.6 g, 3.0 mmol, 71%). \( \delta_H \) (400 MHz, CDCl\(_3\)), 9.84 (1H, t, J 1), 7.51 - 7.58 (1H, m), 7.21 - 7.27 (1H, m), 7.04 - 7.13 (2H, m), 3.03 - 3.13 (2H, m), 2.78 - 2.84 (2H, m). \( \delta_C \) (75 MHz, CDCl\(_3\)), 201.1, 133.0, 130.5, 128.1, 127.7, 124.3, 43.7, 28.7. \( \nu_{\text{max}} \) (CHCl\(_3\))/ cm\(^{-1}\), 3011, 2848, 1725, 1589, 1568, 1469, 1135, 1025. m/z (ESI+) 275 (7.8%, \[M+NH_4^+\]), 281 (11.1%, \[M+Na^+\]), 447 (100%).

3-(2-Iodophenyl)propanal (C2)

General procedure C was followed to give C2 as a colourless oil (4.92 g, 23.09 mmol, 82%). \( \delta_H \) (300 MHz, CDCl\(_3\)), 9.85 (1H, t, J 1.2 Hz), 7.83 (1H, dd, J 7.8, 1.0 Hz), 7.20 - 7.34 (2H, m), 6.85 - 6.96 (1H, m), 3.01 - 3.12 (2H, m), 2.73 - 2.85 (2H, m). \( \delta_C \) (75 MHz, CDCl\(_3\)), 200.9, 142.9, 139.7, 129.6, 128.6, 128.4, 100.2, 44.0, 33.2. \( \nu_{\text{max}} \) (CHCl\(_3\))/ cm\(^{-1}\), 3059, 2987, 2685, 2306, 1749, 1713, 1422, 1226.

3-(6-Bromo-1,3-benzodioxol-5-yl)propanal (C3)

General procedure C was followed to give C3 as a yellow oil (0.59 g, 2.3 mmol, 85%). \( \delta_H \) (300 MHz, CDCl\(_3\)) 9.82 (1H, t, J 1.3), 6.99 (1H, s), 6.74 (1H, s), 5.95 (2H, s), 2.93 - 3.01 (2H, m), 2.72 - 2.79 (2H, m). \( \delta_C \) (75 MHz, CDCl\(_3\)), 201.1, 147.5, 147.0, 132.6, 114.2, 112.8, 110.2, 101.7, 43.9, 28.6. \( \nu_{\text{max}} \) (CHCl\(_3\))/ cm\(^{-1}\), 2980, 2822, 1726, 1470, 1240, 1041.
General reaction scheme for the synthesis of aldehyde (2)

\[
\begin{align*}
\text{General reaction scheme for the synthesis of aldehyde (2)}
\end{align*}
\]

1-(Allyloxy)-2-iodobenzene (D1)

Iodophenol (10 g, 45.45 mmol) was dissolved in dry DMF (85 mL) under nitrogen and potassium carbonate (12.56 g, 90.91 mmol) was added. The reaction mixture was heated to 70 °C and allylbromide (5.90 ml, 68.18 mmol) was added. The reaction mixture was stirred for 3 hours at 70 °C and overnight at room temperature. Water (20 mL) was added followed by diethyl ether (30 mL) and the phases were separated. The organic phase was washed with water (3 x 20 mL) and dried with magnesium sulfate. The solvent was removed \textit{in vacuo} to give D1 as an orange oil (10.96 g, 93%). \(\delta^H\) (400 MHz, CDCl\(_3\)), 7.71 (1H, dd, \(J\ 7.8\) and 1.6), 7.20 (1H, ddd, \(J\ 8.2, 7.4\) and 1.3), 6.74 (1H, dd, \(J\ 8.2\) and 1.2), 6.64 (1H, td, \(J\ 7.6\) and 1.3), 6.04 – 5.94 (1H, m), 5.45 (1H, dq, \(J\ 17.3\) and 1.7), 5.24 (1H, dq, \(J\ 10.6\) and 1.5), 4.53 (2H, dt, \(J\ 7.6\)), \(\delta^C\) (100 MHz, CDCl\(_3\)), 157.2, 139.5, 132.6, 129.4, 122.8, 117.6, 112.6, 86.7, 69.7. \(\nu_{\text{max}}\) (thin film)/ cm\(^{-1}\), 3074, 3009, 2934, 1163, 1123, 932, 830. m/z (ESI+) 282 (14%, [M+Na\(^+\)], 385 (100%); HRMS calculated for C\(_9\)H\(_9\)I\(_2\): 282.9590 [M+Na\(^+\)], found 282.9581. Data consistent with literature\(^4\)

1-(But-3-en-1-yloxy)-2-iodobenzene (D2)

Iodophenol (1.45 g, 6.57 mmol) was dissolved in dry DMF (13 mL) under nitrogen and potassium carbonate (1.82 g, 13.2 mmol) was added. The reaction was heated to 70 °C and 4-bromobutene (1 mL, 9.85 mmol) was added. The reaction mixture was stirred for 3 hours at 70 °C and overnight at room temperature. Water (20 mL) was added followed by diethyl ether (10 mL) and the phases were separated. The organic phase was washed with water (3 x 20 mL) and dried with magnesium sulfate. The solvent was removed \textit{in vacuo} and purified by column chromatography on silica gel (4:1, petroleum ether/ethyl acetate) to give D2 as a colourless oil (0.4 g, 1.46 mmol, 22%). \(\delta^H\) (300 MHz, CDCl\(_3\)), 7.78 (1 H, dd, \(J\ 7.7, 1.6\) Hz) 7.29 (1 H, dd, \(J\ 1.6, 0.8\) Hz) 6.81 (1 H, dd, \(J\ 8.2, 1.3\) Hz) 6.71 (1 H, td, \(J\ 7.6, 1.4\) Hz) 5.99 (1 H, ddt, \(J\ 17.1, 10.3, 6.8, 6.8\) Hz) 5.18 - 5.26 (1 H, m) 5.14 (1 H, ddt, \(J\ 10.2, 1.9, 1.1, 1.1\) Hz)
4.07 (2 H, t, J 6.6 Hz) 2.62 (2 H, qt, J 6.7, 1.3 Hz). δC (75 MHz, CDCl₃), 191.0, 157.4, 139.5, 134.3, 129.4, 122.5, 117.3, 112.2, 68.6, 33.6. vmax (thin film)/ cm⁻¹, 3075, 2929, 1642, 1581, 1277, 1248, 1121, 917, 748. m/z (ESI⁺) 297 (100%, [M+Na⁺]), 227 (78%); HRMS calculated for C₁₀H₁₁I₂O: 296.9745 [M+Na⁺], found 296.9745. Data consistent with literature⁵

2-(2-Iodophenoxy)acetaldehyde (E1)

General procedure E was followed to give E₁ as an orange oil (1.97 g, 7.53 mmol, 98%). δH (300 MHz, CDCl₃), 9.92 (1 H, t, J 1.2 Hz) 7.83 (1 H, dd, J 7.8, 1.6 Hz) 7.74 - 7.81 (1 H, m) 7.28 - 7.35 (2 H, m) 4.61 (2 H, d, J 1.2 Hz) δC (75 MHz, CDCl₃), 199.0, 156.7, 140.0, 129.7, 123.9, 112.5, 73.7, 67.1. m/z (ESI⁺) 285 (5%, [M+Na⁺]), 317 (100%); HRMS calculated for C₈H₇I₂O: 262.9563 [M+H⁺], found 262.9561. vmax (CHCl₃)/ cm⁻¹, 3009, 2883, 1741, 1583, 1475, 1440, 1278, 1248, 1019.

3-(2-Iodophenoxy)propanal (E₂)

General procedure E was followed to give E₂ as on orange oil (0.4 g, 1.4 mmol, 98%). δH (300 MHz, CDCl₃), 9.95 (1 H, t, J 1.5 Hz) 7.78 (1 H, dd, J 7.8, 1.6 Hz) 7.31 (1 H, ddd, J 8.2, 7.4, 1.6 Hz) 6.87 (1 H, dd, J 8.2, 1.3 Hz) 6.75 (1 H, td, J 7.6, 1.3 Hz) 4.37 (2 H, t, J 6.1 Hz) 2.99 (2 H, td, J 6.2, 1.5 Hz). δC (75 MHz, CDCl₃), 200.1, 174.5, 157.1, 139.6, 129.5, 123.2, 112.4, 63.2, 43.1. vmax (thin film)/ cm⁻¹, 3075, 2929, 1642, 1581, 1465, 1438, 1277, 1248, 1018, 917, 748.

General reaction scheme for the synthesis of aldehyde (3)

N-(2,2-Dimethoxyethyl)-N-(3-iodopropyl)-4-methylbenzenesulfonamide (F)

Electronic Supplementary Material (ESI) for Chemical Communications
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N-(2,2-Dimethoxyethyl)-4-methylbenzenesulfonamide (1 g, 3.85 mmol) was dissolved in dry THF (15 mL) under nitrogen and the solution was cooled to 0 °C. Sodium hydride (60% in oil, 0.23 g, 5.78 mmol) was added and the reaction mixture was stirred for 10 minutes at 0 °C. The mixture was warmed to room temperature and diiodopropane (0.89 mL, 7.71 mmol) was added. The reaction was refluxed for 19 hours and cooled to room temperature. Water (20 mL) was added followed by DCM (10 mL) and the phases were separated. The aqueous phase was extracted with DCM (3 x 20 mL) and the combined organic phases were dried over magnesium sulfate. The solvent was removed in vacuo and purified by column chromatography on silica gel (4:1, petroleum ether/ethyl acetate) to give F as a orange oil (1.1 g, 2.61 mmol, 68%). δH (300 MHz, CDCl3), 7.69 - 7.75 (2 H, m) 7.28 - 7.35 (2 H, m) 3.93 (2 H, d, J 6.4 Hz, 4-H2) 3.42 (2 H, s) 3.39 (5 H, s) 3.22 (2 H, d, J 5.4 Hz) 2.42 - 2.45 (3 H, m). Data consistent with literature6

N-(3-Iodopropyl)-4-methyl-N-(2-oxoethyl)benzenesulfonamide (G)

Acetal F (1.1 g, 2.57 mmol) was dissolved in acetone (12 mL) and water (6 mL) and concentrated hydrochloric acid (5 mL) was added. The mixture was stirred for 48 hours at room temperature and water (10 mL) was added followed by dichloromethane (10 mL). The phases were separated and the aqueous phase was extracted with dichloromethane (3 x 10 mL). The combined organic phases were washed with a saturated solution of sodium hydrogen carbonate (10 mL) and dried over magnesium sulfate. The solvent was removed in vacuo to give G as a orange oil (0.86 g, 2.25 mmol, 87%). δH (300 MHz, CDCl3), 9.60 (1 H, t, J 1.4 Hz) 7.71 (2 H, d, J 8.3 Hz) 7.34 (2 H, dd, J 8.5, 0.6 Hz) 5.62 - 5.77 (1 H, m) 5.13 - 5.26 (2 H, m) 3.90 (1 H, d, J 1.2 Hz) 3.83 (2 H, d, J 6.6 Hz) 3.80 (2 H, d, J 1.4 Hz) 2.45 (3 H, s). δC (75 MHz, CDCl3), 198.2, 131.9, 129.9, 127.4, 120.8, 86.1, 55.9, 52.3, 21.6. Data consistent with literature6

General reaction scheme for the synthesis of aldehyde (4)
Ethyl 1-(but-3-en-1-yl)cyclohexanecarboxylate (H)

LDA (1 M in THF, 17.6 mL, 17.6 mmol) was added to ethyl cyclohexane carbonate (2.7 mL, 16 mmol) under nitrogen at -78 °C. The reaction mixture was stirred for 1.5h and a solution of 4-bromobutene (1.8 mL, 17.6 mmol) in DMSO (3 mL) was added. The reaction mixture was stirred for 30 minutes at -78 °C and overnight at room temperature. 2 M hydrochloric acid solution (20 mL) was added and the product was extracted with diethyl ether (3 x 20 mL). The combined organic phases were dried over sodium sulfate and concentrated in vacuo to give H as a colourless oil (3.29 g, 15.7 mmol, 98%). δH (300 MHz, CDCl₃), 5.77 (1H, ddt, J 17.0 Hz, 10.3 Hz, 6.5 Hz), 4.88 - 5.04 (2H, m), 4.12 - 4.20 (2H, m), 2.61 - 2.72 (1H, m), 2.09 (2H, d, J 12.6 Hz), 1.91 - 2.01 (3H, m), 1.52 - 1.62 (5H, m), 1.24 - 1.30 (3H, m). υmax (thin film)/ cm⁻¹, 2933, 2855, 2361, 2340, 1726, 1453, 1134, 910. Data consistent with literature⁷

(1-(But-3-en-1-yl)cyclohexyl)methanol (I)

Ester H (2 g, 9.5 mmol) was dissolved in dry dichloromethane (95 mL) and DIBAL (25% w/w in toluene, 4 mL, 24.7 mmol) was added at -78 °C under nitrogen. The reaction mixture was stirred for 1 h and 2 N hydrochloric acid solution was added slowly. The phases were separated and the aqueous phase was extracted with dichloromethane (3 x 20 mL). The combined organic phases were dried over magnesium sulfate. The solvent was removed in vacuo and purified by column chromatography on silica gel (4:1, petroleum ether/ethyl acetate) to give I as a colourless oil (1 g, 6.02 mmol, 63%). δH (300 MHz, CDCl₃), 5.85 (1H, ddt, J 17.0 Hz, 10.3 Hz, 6.5 Hz), 4.91 - 5.09 (2H, m), 3.44 (2H, s), 1.95 - 2.06 (2H, m), 1.40 -
1.50 (8H, m), 1.28 - 1.36 (5H, m). \( \delta_C \) (75 MHz, CDCl\(_3\)), 139.7, 114.0, 68.3, 37.0, 34.0, 32.4, 27.5, 26.4, 21.4. Data consistent with literature\(^7\)

**1-(But-3-en-1-yl)-1-(iodomethyl)cyclohexane (J)**

![Chemical structure of 1-(But-3-en-1-yl)-1-(iodomethyl)cyclohexane (J)](image)

Alcohol I (1g, 5.94 mmol) was dissolved in dry THF (60 mL) at 0 °C under nitrogen. Imidazole (1.5 g, 22.6 mmol) and triphenyl phosphine (4.2 g, 16.04 mmol) was added. The resulting mixture was stirred for 10 minutes at 0 °C and iodine (3.5 g, 13.7 mmol) was added. The reaction mixture was warmed to room temperature and stirred overnight. A saturated solution of sodium thiosulfate (50 mL) was added followed by diethyl ether (20 mL). The phases were separated and the organic phase was washed with brine (20 mL) and dried over sodium sulfate. The solvent was removed *in vacuo* and purified by column chromatography on silica gel (9:1, petroleum ether/ethyl acetate) to give J as a yellow oil (0.8 g, 2.88 mmol, 48%). \( \delta_H \) (300 MHz, CDCl\(_3\)), 5.84 (1H, ddt, \( J = 17.0 \) Hz, 10.2 Hz, 6.6 Hz), 4.90 - 5.10 (2H, m), 3.25 (2H, s), 1.94 (2H, dtt, \( J = 10.5 \) Hz, 6.5 Hz, 1.3 Hz), 1.33 - 1.52 (13H, m). \( \delta_C \) (75 MHz, CDCl\(_3\)), 139.0, 114.4, 37.2, 35.0, 27.1, 26.1, 21.8. Data consistent with literature\(^7\)

**2-Allyl-3-bromothiophene (K)**

![Chemical structure of 2-Allyl-3-bromothiophene (K)](image)

3-Bromothiophene (2 g, 12.26 mmol) was dissolved in dry THF (55 mL) under nitrogen and the reaction mixture was cooled to -78 °C. LDA (1.5 M in THF, 9.8 mL, 14.72 mmol) was added and the reaction was stirred for 30 minutes. Allyl bromide (1.8 g, 14.72 mmol) was added and the reaction mixture stirred 1 hour at -78 °C and 1 hour at room temperature. A 1 M aqueous hydrochloric solution (40 mL) was added and the phases were separated. The aqueous phase was extracted with ethyl acetate (3 x 50 mL). The combined organic phases were dried over magnesium sulfate and the solvent was removed *in vacuo* to give K as an orange oil. \( \delta_H \) (300 MHz, CDCl\(_3\)), 7.16 (1H, d, \( J = 5 \) Hz), 6.94 (1H, d, \( J = 5 \) Hz), 5.95 (1H, ddt, \( J = 17, 10 \) and 6 Hz), 5.12 - 5.21 (2H, m), 3.54 (2H, dt, \( J = 6 \) and 1 Hz), \( \delta_C \) (75 MHz, CDCl\(_3\)), 133.1, 128.3, 122.0, 115.3, 107.2, 86.1, 31.7.

**3-(3-Bromothiophen-2-yl)propan-1-ol (L) and 3-(3-bromothiophen-2-yl)propanal (M)**
Alkene **K** (2 g, 9.85 mmol) was dissolved in dry THF (30 mL) and borane dimethyl sulphide (0.37 mL, 3.94 mmol) was added. The reaction mixture was stirred for 1 hour at room temperature and dry DCM (30 mL) was added followed by PCC (6.37 g, 29.54 mmol) and cruched 3 Å molecular sieves. The mixture was stirred for 3 hours and silica gel was added. The reaction mixture was filtered through a pad of celite and the residue was washed with diethyl ether. The solvent was removed *in vacuo* and purified by column chromatography on silica gel (4:1, petroleum ether/ethyl acetate) to give alcohol **L** as an orange oil (0.33 g, 1.48 mmol, 15%) and the aldehyde **M** as yellow oil (0.53 g, 2.42 mmol, 25%).

Alcohol **L** δH (300 MHz, CDCl3), 7.14 (1H, d, J 5 Hz), 6.92 (1H, d, J 5 Hz), 3.71 (2H, t, J 6 Hz), 2.87 - 2.95 (2H, m), 1.88 - 1.99 (2H, m), 1.62 (1H, br. s). δC (75 MHz, CDCl3), 138.7, 129.9, 123.2, 108.9, 61.7, 33.4, 25.4. v_max (thin film)/ cm⁻¹, 3346, 2940, 1521, 1442, 1345, 1057, 873, 700.

Aldehyde **M** δH (300 MHz, CDCl3), 9.84 (1H, t, J 1 Hz), 7.15 (1H, d, J 5 Hz), 6.92 (1H, d, J 5 Hz), 3.09 - 3.18 (2H, m), 2.80 – 2.88 (2H, m). δC (75 MHz, CDCl3), 200.4, 130.1, 123.7, 109.3, 86.1, 58.5, 44.1, 21.7. v_max (thin film)/ cm⁻¹, 3109, 2930, 17.24, 1521, 1440, 1124, 859, 703.

**S**-**N**-(3-(2-Bromophenyl)propylidene)-2-methylpropane-2-sulfinamide (**1a**)

General procedure D was followed to give **1a** as a pale yellow oil (0.48 g, 1.5 mmol, 60%). δH (300 MHz, CDCl3), 8.16 (1H, t, J 4.2), 7.56 (1H, d, J 7.8), 7.22 - 7.30 (2H, m), 7.09 (1H, m), 3.04 - 3.16 (2H, m), 2.82 - 2.93 (2H, m), 1.19 (9H, s). δC (75 MHz, CDCl3), 168.1, 139.7, 133.0, 130.4, 128.1, 127.6, 124.4, 56.6, 36.0, 31.9, 22.3. m/z (ESI+) 338 (97.2%, [M+Na]⁺), 340 (100%); HRMS calculated for C_{13}H_{18}^{79}BrNOS: 316.0365 [M+Na]⁺, found 316.0360. v_max (CHCl3)/ cm⁻¹, 3010, 2980, 2843, 1625, 1466, 1065. Data consistent with literature.

**S**-**N**-(3-(2-Iodophenyl)propylidene)-2-methylpropane-2-sulfinamide (**1b**)
General procedure D was followed to give 1b as a pale yellow oil (0.36 g, 1.0 mmol, 52%).
\( \delta_H \) (300 MHz, CDCl\(_3\)), 8.16 (1H, t, \( J \) 4.1 Hz), 7.83 (1H, dd, \( J \) 7.9, 1.1 Hz), 7.21 - 7.33 (2H, m), 6.91 (1H, ddd, \( J \) 7.9, 6.9, 2.2 Hz), 3.03 - 3.14 (2H, m), 2.79 - 2.90 (2H, m), 1.19 (9H, s).
\( \delta_C \) (75 MHz, CDCl\(_3\)), 168.0, 143.0, 139.7, 129.4, 128.6, 128.2, 100.4, 56.7, 36.5, 36.3, 22.4.
m/z (ESI+)364 (14.0%, [M+H]\(^+\)), 386 (100%, [M+Na]\(^+\)); HRMS calculated for C\(_{13}\)H\(_{18}\)INOS: 386.0046 [M+Na]\(^+\), found 832.0041.

(S)-N-[3-(2-Iodophenyl)propyldiene]-2,4,6-trimethylbenzenesulfinamide (1c)

General procedure D was followed to give 1c as a yellow solid (0.56 g, 1.32 mmol, 69%).
m.p. = 75-77 °C. \( \delta_H \) (300 MHz, CDCl\(_3\)), 8.38 (1H, t, \( J \) 4.4 Hz), 7.82 (1H, dd, \( J \) 7.9, 0.9 Hz), 7.16 - 7.29 (2H, m), 6.90 (1H, ddd, \( J \) 7.9, 6.7, 2.4 Hz), 6.83 - 6.87 (2H, m), 3.02 - 3.11 (2H, m), 2.45 (6H, s), 2.29 (3H, s). \( \delta_C \) (75 MHz, CDCl\(_3\)), 166.5, 158.4, 142.9, 141.7, 139.7, 138.3, 130.9, 129.6, 128.5, 128.3, 100.3, 36.5, 36.1, 21.1, 18.8. m/z (ESI+)426 (100%, [M+H]\(^+\)), 386 (448%, [M+Na]\(^+\)); HRMS calculated for C\(_{18}\)H\(_{20}\)\(_{127}\)INOS: 426.0383 [M+H]\(^+\), found 426.0383.

υ\(_{\text{max}}\) (CHCl\(_3\))/ cm\(^{-1}\), 3047, 2929, 2361, 1620, 1466.

(S)-N-(2-(2-Iodophenoxy)ethylidene)-2,4,6-trimethylbenzenesulfinamide (4a)

General procedure D was followed to give 4a as a pale yellow oil (0.4 g, 0.96 mmol, 36%).
m.p. = 129-131 °C. \([\alpha]_D = +6.93 \text{ (c 4.635, MeOH, 20°C)}\), \( \delta_H \) (400 MHz, CDCl\(_3\)), 8.50 (1 H, t, \( J \) 3.9 Hz) 7.81 (1 H, dd, \( J \) 8.0, 1.6 Hz) 7.27 (1 H, dd, \( J \) 15.6, 1.6 Hz) 6.87 (2 H, d, \( J \) 0.4 Hz) 6.74 - 6.80 (2 H, m) 4.89 - 5.01 (2 H, m) 2.48 (6 H, s) 2.30 (3 H, s). \( \delta_C \) (100 MHz, CDCl\(_3\)), 163.1, 156.6, 142.0, 139.9, 138.4, 134.2, 131.0, 129.5, 123.7, 112.7, 86.6, 70.2, 21.1, 18.8. m/z (ESI+)450 (100%, [M+Na]\(^+\)); HRMS calculated for C\(_{17}\)H\(_{18}\)\(_{127}\)INO\(_2\)S: 428.0176 [M+H]\(^+\), found 428.0176. υ\(_{\text{max}}\) (CHCl\(_3\))/ cm\(^{-1}\), 2979, 1602, 1582, 1469, 1380, 1278.
(S)-N-(3-(2-Iodophenoxy)propylidene)-2,4,6-trimethylbenzenesulfinamide (4b)

General procedure D was followed to give 4b as a pale yellow oil (0.2 g, 0.46 mmol, 35%). 

\[ \alpha_D = +86.60 \text{ (c 5.01, CH}_2\text{Cl}_2, 22 ^\circ\text{C}) \]

\[ \delta_{\text{H}} (400 \text{ MHz, CDCl}_3), 8.50 (1 \text{ H, t, } J 4.5 \text{ Hz}) 7.77 (1 \text{ H, dd, } J 7.7, 1.6 \text{ Hz}) 7.28 - 7.31 (1 \text{ H, m}) 6.85 (2 \text{ H, s}) 6.82 (1 \text{ H, dd, } J 8.2, 1.2 \text{ Hz}) 6.70 - 6.76 (1 \text{ H, m}) 4.27 - 4.40 (2 \text{ H, m}) 3.09 (2 \text{ H, td, } J 6.3, 4.4 \text{ Hz}) 2.47 (6 \text{ H, s}) 2.28 (3 \text{ H, s}). \]

\[ \delta_{\text{C}} (100 \text{ MHz, CDCl}_3), 164.9, 141.8, 139.6, 138.3, 130.9, 130.2, 129.4, 123.1, 122.4, 115.2, 112.6, 86.9, 65.6, 35.6, 21.1, 19.3. \]

\[ \nu_{\text{max}} (\text{CHCl}_3)/ \text{cm}^{-1}, 3010, 2361, 2336, 1582, 1468, 1247, 1079, 1052. \]

(S)-N-(3-Iodopropyl)-N-(2-((mesitylsulfinyl)imino)ethyl)-4-methylbenzenesulfonamide (7a)

General procedure D was followed and the product was purified by flash column chromatography on silica gel (1:1, petroleum ether/ethyl acetate) to give 7a (1 g, 1.87 mmol, 83%). 

\[ \alpha_D = -51.51 \text{ (c 0.465, CH}_2\text{Cl}_2, 22 ^\circ\text{C}) \]

\[ \delta_{\text{H}} (400 \text{ MHz, CDCl}_3), 8.12 (1 \text{ H, t, } J 3.6 \text{ Hz}) 7.67 (2 \text{ H, m, } J 8.4 \text{ Hz}) 7.23 (2 \text{ H, m, } J 8.0 \text{ Hz}) 6.85 (2 \text{ H, s}) 5.61 - 5.74 (1 \text{ H, m}) 5.07 - 5.25 (3 \text{ H, m}) 4.16 - 4.32 (2 \text{ H, m}) 3.76 - 3.85 (4 \text{ H, m}) 2.41 (6 \text{ H, s}) 2.29 (3 \text{ H, s}). \]

\[ \delta_{\text{C}} (100 \text{ MHz, CDCl}_3), 163.4, 143.7, 138.3, 132.2, 130.9, 129.8, 129.7, 127.4, 51.4, 50.2, 21.1, 18.7, 14.2. \]

\[ \nu_{\text{max}} (\text{CHCl}_3)/ \text{cm}^{-1}, 3009, 2928, 1599, 1452, 1405, 1329, 1162, 1091. \]

(S)-N-(3-(1-(Iodomethyl)cyclohexyl)propylidene)-2,4,6-trimethylbenzenesulfinamide (7b)

General procedure D was followed to give 7b as a colourless oil (0.17 g, 0.39 mmol, 30%). 

\[ \alpha_D = -20.64 \text{ (c 0.435, CH}_2\text{Cl}_2, 22 ^\circ\text{C}) \]

\[ \delta_{\text{H}} (400 \text{ MHz, CDCl}_3), 8.32 (1 \text{ H, t, } J 4.9 \text{ Hz}) 6.85 - 6.88 (2 \text{ H, m}) 3.24 (2 \text{ H, s}) 2.47 (6 \text{ H, s}) 2.43 (2 \text{ H, ddd, } J 9.6, 7.2, 5.3 \text{ Hz}) 2.29 (3 \text{ H, s}) 1.64 - 1.70 (2 \text{ H, m}) 1.57 (2 \text{ H, s}). \]

\[ \delta_{\text{C}} (100 \text{ MHz, CDCl}_3), 167.8, 141.7, 138.4, 135.2, 130.9, 35.0, \]
34.9, 34.8, 34.8, 29.9, 26.0, 25.7, 21.8, 21.1, 20.3, 18.8. m/z (ESI+) 468 (11%, [M+Na]+), 357 (100%); HRMS calculated for C_{19}H_{29}^{127}INO_S: 468.0828 [M+Na]⁺, found 468.0842. \( \nu_{\text{max}} \) (thin film)/cm⁻¹, 3009, 2933, 1601, 1455, 1322, 1141, 853, 646.

(\( S \))-N-(3-(6-Bromobenzo[d][1,3]dioxol-5-yl)propylidene)-2,4,6-trimethylbenzenesulfinamide (9a)

General procedure D was followed to give 9a as a colourless oil (0.07 g, 0.17 mmol, 44%). \( \delta_H \) (100 MHz, CDCl₃), 8.35 (1H, t, \( J \) 4.5 Hz), 6.99 (1H, s), 6.86 (2H, d, \( J \) 0.5 Hz), 6.69 (1H, s), 5.95 (2H, s), 2.95 - 3.02 (2H, m), 2.77 - 2.86 (2H, m), 2.45 (6H, s), 2.29 (3H, s). \( \delta_C \) (75 MHz, CDCl₃), 166.5, 147.4, 141.6, 138.3, 130.8, 112.8, 110.0, 101.6, 86.1, 36.0, 31.9, 21.1, 18.7. m/z (ESI+) 422 (95.3%, [M+H]⁺), 444 (48.0%, [M+Na]⁺); HRMS calculated for C_{19}H_{20}^{79}BrNO_S: 422.0420 [M+H]⁺, found 422.0420. \( \nu_{\text{max}} \) (CHCl₃)/cm⁻¹, 3063, 2967, 2360, 1620, 1477.

(\( S \))-N-(3-(3-Bromothiophen-2-yl)propylidene)-2,4,6-trimethylbenzenesulfinamide (9b)

General procedure D was followed and the product was purified by flash column chromatography on silica gel (9:1, petroleum ether/ethyl acetate) to give 9b as a yellow oil (0.15 g, 0.33 mmol, 43%). [\( \alpha \)]D = 159.16 (c 1.70, CH₂Cl₂, 22 °C), \( \delta_H \) (300 MHz, CDCl₃), 8.36 (1H, t, \( J \) 4 Hz), 7.12 (1H, d, \( J \) 5 Hz), 6.90 (1H, d, \( J \) 5 Hz), 6.84 - 6.87 (2H, m), 3.10 - 3.19 (2H, m), 2.83 - 2.94 (2H, m), 2.44 (6H, s), 2.29 (3H, s). \( \delta_C \) (75 MHz, CDCl₃), 180.0, 165.8, 141.7, 138.3, 137.0, 130.9, 130.0, 123.7, 109.4, 36.3, 24.9, 21.1, 18.8. m/z (ESI+) 384 (6%, [M+H]⁺), 408 (100%, [M+Na]⁺); HRMS calculated for C_{16}H_{18}^{79}BrNOS₂: 405.9905 [M+Na]⁺, found 405.9926. \( \nu_{\text{max}} \) (CHCl₃)/cm⁻¹, 3009, 2928, 1621, 1602, 1441, 1081, 855.

(\( S \))-N-((\( S \))-2,3-dihydro-1H-inden-1-yl)-2,4,6-trimethylbenzenesulfinamide (2c)

Electronic Supplementary Material (ESI) for Chemical Communications
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General procedure H was followed to give 2 as white solid (22 mg, 0.073 mmol, 61%). \([\alpha]_D = -70.51\) (c 0.235, CH\(_2\)Cl\(_2\)).

\(\delta_H\) (400 MHz, CDCl\(_3\)), 7.36 (1H, d, \(J\ 6.7\) Hz), 7.16 - 7.31 (3H, m), 6.86 (2H, s), 4.96 (1H, q, \(J\ 7.4\) Hz), 4.35 (1H, d, \(J\ 7.6\) Hz), 2.95 - 3.05 (1H, m), 2.81 - 2.91 (1H, m), 2.66 - 2.75 (1H, m), 2.60 (6H, s), 2.29 (3H, s), 1.94 - 2.06 (1H, m). \(\delta_C\) (100 MHz, CDCl\(_3\)), 143.5, 143.0, 140.5, 138.3, 136.4, 130.8, 128.1, 126.6, 124.8, 62.1, 36.9, 30.3, 21.0, 19.6. m/z (ESI+)322 (100%, [M+Na]+), 363 (23.7%) HRMS calculated for C\(_{18}\)H\(_{21}\)NOS: 322.1236 [M+Na]+, found 322.1248.

\(\nu_{\text{max}}\) (CHCl\(_3\))/ cm\(^{-1}\), 3686, 2987, 1603, 1476, 1422, 1279, 1082.

\(\lambda_{\text{max}}\) 245 nm.

Crystal Data for C\(_{18}\)H\(_{21}\)NOS (\(M = 299.42\)): monoclinic, space group P2/\(1/c\) (no. 14), \(a = 4.60842(14)\) Å, \(b = 24.0504(8)\) Å, \(c = 14.1862(5)\) Å, \(\beta = 94.048(3)\)°, \(V = 1568.40(9)\) Å\(^3\), \(Z = 4\), \(T = 90(2)\) K, \(\mu(\text{Cu K}\alpha) = 1.805\) mm\(^{-1}\), \(D_{\text{calc}} = 1.268\) g/mm\(^3\), 20574 reflections measured (7.248 \(\leq 2\Theta \leq 154.822\)), 3291 unique (\(R_{\text{int}} = 0.0345\)) which were used in all calculations. The final \(R_1\) was 0.0334 (\(I > 2\sigma(I)\)) and \(wR_2\) was 0.0897 (all data).

\((R)-N-((S)-2,3-Dihydrobenzofuran-3-yl)-2,4,6-trimethylbenzenesulfinamide (5a)\)

General procedure G was followed to give 5a as a white solid (0.044 g, 0.15 mmol, 63%). \([\alpha]_D = +112.73\) (c 0.50, CH\(_2\)Cl\(_2\), 24 °C). \(\delta_H\) (400 MHz, CDCl\(_3\)), 7.36 (1H, d, \(J\ 7.5\) Hz) 7.23 (1H, ddd, \(J\ 8.0, 7.3, 1.2\) Hz) 6.89 - 6.98 (1H, m) 6.86 (2H, s) 5.18 - 5.26 (1H, m) 4.64 - 4.77 (1H, m) 4.41 - 4.53 (2H, m) 2.59 (6H, s) 2.29 (3H, s). \(\delta_C\) (100 MHz, CDCl\(_3\)), 160.0, 137.4, 136.7, 131.0, 130.4, 126.6, 125.8, 121.3, 121.1, 110.4, 78.3, 58.2, 21.0, 19.5. m/z (ESI+)324 (100%, [M+Na]+), 302 (17.5%, [M+H]+); HRMS calculated for C\(_{17}\)H\(_{19}\)NO\(_2\)S: 324.1029 [M+Na]+, found 324.1033.

\((R)-N-((R)-chroman-4-yl)-2,4,6-trimethylbenzenesulfinamide (5b)\)
General procedure G was followed to give 5b as a white solid (0.02 g, 0.053 mmol, 48%). 

$[\alpha]_D = +133.27$ (c 0.56, CH$_2$Cl$_2$, 24 °C). $\delta_H$ (400 MHz, CDCl$_3$), 7.30 - 7.34 (1 H, m) 7.14 - 7.20 (1 H, m) 6.79 - 6.94 (4 H, m) 4.65 - 4.72 (1 H, m) 4.41 (1 H, d, $J = 8.8$ Hz) 4.22 - 4.28 (2 H, m) 2.61 (6 H, s) 2.34 - 2.45 (1 H, m) 2.29 (3 H, s) 2.08 - 2.19 (1 H, m). $\delta_C$ (100 MHz, CDCl$_3$), 148.8, 136.5, 130.9, 129.8, 128.3, 122.8, 120.5, 117.1, 110.0, 62.9, 50.5, 31.7, 21.0, 19.6. m/z (ESI+)338 (100%, [M+Na]$^+$), 316 (39.4%, [M+H]$^+$); HRMS calculated for C$_{18}$H$_{22}$NO$_2$: 316.1366 [M+H]$^+$, found 316.1379.

υ$_{max}$ (CHCl$_3$/ cm$^{-1}$), 3341, 3005, 2928, 1603, 1584, 1244, 1074.

Crystal Data for C$_{18}$H$_{21}$NO$_2$S (M=315.42): orthorhombic, space group P2$_1$2$_1$2$_1$ (no. 19), a = 4.5824(3) Å, b = 15.4160(11) Å, c = 22.7652(14) Å, V = 1608.19(19) Å$^3$, Z = 4, T = 90(2) K, $\mu$(Cu Kα) = 1.836 mm$^{-1}$, Dcalc = 1.303 g/mm$^3$, 11325 reflections measured (6.924 ≤ 2Θ ≤ 149.17), 3213 unique ($R_{int}$ = 0.0431) which were used in all calculations. The final $R_1$ was 0.0309 (I > 2σ(I)) and $wR_2$ was 0.0815 (all data).

(R)-2,4,6-Trimethyl-N-((S)-spiro[4.5]decan-2-yl)benzenesulfinamid e (8b)

Crystal Data for C$_{19}$H$_{29}$NOS (M=319.49): trigonal, space group P3$_1$ (no. 144), a = 20.64863(14) Å, c = 11.23270(10) Å, V = 4147.60(7) Å$^3$, Z = 9, T = 120(2) K, $\mu$(Cu 21
Kα) = 1.557 mm⁻¹, Dcalc = 1.151 g/mm³, 71755 reflections measured (4.942 ≤ 2Θ ≤ 156.834), 11429 unique (Rint = 0.0286) which were used in all calculations. The final R₁ was 0.0432 (I > 2σ(I)) and wR₂ was 0.1251 (all data).

(S)-N-Allyl-4-methyl-N-(2-(2,4,6-trimethylphenylsulfinamido)ethyl)benzenesulfonamide (8a)

General procedure G was followed to give 8a as a colourless oil (39 mg, 0.09 mmol, 51%). 

δH (400 MHz, CDCl₃): 7.60 - 7.77 (2 H, m), 7.28 - 7.37 (2 H, m), 6.83 - 6.88 (2 H, m), 5.51 - 5.77 (1 H, m), 5.09 - 5.25 (2 H, m), 4.53 (1 H, t, J 5.6 Hz), 3.69 - 3.89 (2 H, m), 3.21 - 3.41 (4 H, m), 2.53 - 2.60 (6 H, m), 2.43 (3 H, d, J 5.5 Hz), 2.26 - 2.32 (3 H, m). δC (100 MHz, CDCl₃): 143.6, 140.7, 136.8, 133.1, 132.8, 130.9, 129.8, 127.3, 127.2, 119.5, 51.6, 48.0, 43.0, 21.5, 21.0, 19.5. m/z (ESI+) 421 (47.2%, [M+H]+), 443 (100%, [M+Na]+); HRMS calculated for C₂₁H₁₈N₂O₃S₂: 443.1434 [M+Na]+, found 443.1433.

υmax (CHCl₃)/ cm⁻¹, 2927, 1693, 1495, 1455, 1347, 1155, 1093.

(R)-N-((R)-6,7-dihydro-5H-indeno[5,6-d][1,3]dioxol-5-yl)-2,4,6-trimethylbenzenesulfonamide (10a)

General procedure G was followed to give 10a as a white solid (11 mg, 0.03 mmol, 22%). δH (400 MHz, CDCl₃): 6.86 (2H, s), 6.80 (1H, s), 6.68 (1H, s), 5.92 (2H, d, J 0.7 Hz), 4.80 - 4.89 (1H, m), 4.29 (1H, d, J 9.8 Hz), 2.85 - 2.94 (1H, m), 2.63 - 2.81 (2H, m), 2.60 (6H, s), 2.29 (3H, s), 1.95 - 2.07 (1H, m). δC (100 MHz, CDCl₃): 148.0, 146.9, 140.5, 138.3, 136.4, 136.3, 136.2, 130.8, 105.1, 101.2, 62.1, 37.3, 30.2, 29.7, 21.0, 19.6. m/z (ESI+) 344 (27.3%, [M+H]⁺), 366 (100%, [M+Na]⁺); HRMS calculated for C₁₉H₁₈NO₃S: 366.1134 [M+Na]⁺, found 366.1133. υmax (CHCl₃)/ cm⁻¹, 3687, 3600, 3063, 3047, 2987, 1693, 1474.

(R)-N-((R)-5,6-Dihydro-4H-cyclopenta[b]thiophen-4-yl)-2,4,6-trimethylbenzenesulfonamide (10b)
General procedure G was followed to give 10b as a yellow solid (9.9 mg, 0.03 mmol, 25%).

[α]D = +100.06 (c 0.26, CH2Cl2, 22 °C). δH (300 MHz, CDCl3), 7.18 (1H, d, J 5 Hz), 6.92 (1H, d, J 5 Hz), 6.85 (2H, s), 4.86 - 4.95 (1H, m), 2.82 - 3.14 (2H, m), 2.57 (9H, s), 2.30 - 2.44 (2H, m), 2.28 (3H, s). δC (100 MHz, CDCl3), 140.6, 136.5, 130.8, 128.8, 127.1, 125.2, 124.0, 122.0, 57.7, 40.7, 27.1, 21.0, 19.5. m/z (ESI+) 239 (100%), 328 (78.8%, [M+Na]+); HRMS calculated for C16H19NOS2: 328.0800 [M+Na]+, found 328.0812.

Crystal Data for C16H19NOS2 (M = 305.44): monoclinic, space group C2 (no. 5), a = 15.1360(9) Å, b = 4.5783(3) Å, c = 23.0086(13) Å, β = 102.954(6)°, V = 1553.86(16) Å³, Z = 4, T = 120(2) K, μ(Cu Kα) = 3.055 mm⁻¹, Dcalc = 1.306 g/mm³, 10794 reflections measured (7.886 ≤ 2θ ≤ 157.094), 3267 unique (Rint = 0.0440) which were used in all calculations. The final R1 was 0.0481 (I > 2σ(I)) and wR2 was 0.1327 (all data).

(S)-2,3-Dihydrobenzofuran-3-amine hydrochloride (6)

Sulfinamide 5a (0.023 g, 0.075 mmol) was dissolved in dry dioxane (2 mL) and a 4 M hydrochloride solution in dioxane was added. The reaction mixture was stirred for 2 hours at room temperature. The product was collected by filtration to give 6 as a white powder (0.013 g, 0.074 mmol, 98%). m.p. = 241-243 °C. [α]D = +9.12 (c 0.20, MeOH, 20 °C), δH (400 MHz, D2O), 7.52 (1H, d, J 8 Hz), 7.37 - 7.43 (1H, m), 7.03 - 7.09 (1H, m), 6.98 (1H, d, J 8 Hz), 5.09 (1H, dd, J 7 and 3 Hz), 4.61 - 4.73 (2H, m). δC (100 MHz, D2O), 131.9, 125.9, 121.9, 110.6, 73.9, 52.2. vmax (CHCl3)/ cm⁻¹, 3045, 2853, 2360, 2340, 1598, 1490. m/z (ESI+)226 (100%), 158 (21.5%, [M+Na]+); HRMS calculated for C8H9NO: 158.0576 [M+Na]+, found 158.0585.
NMR spectrum
3-(6-bromo-1,3-benzodioxol-5-yl)prop-2-enoate (A3)
3-(6-bromo-1,3-benzodioxol-5-yl)propan-1-ol (B3)
3-(2-bromophenyl)propanal (C1)
3-(2-iodophenyl)propanal (C2)
3-(6-bromo-1,3-benzodioxol-5-yl)propanal (C3)

![Chemical structure and NMR spectrum of 3-(6-bromo-1,3-benzodioxol-5-yl)propanal (C3)](image-url)
1-(but-3-en-1-yloxy)-2-iodobenzene (D2)
2-(2-iodophenoxy)acetaldehyde (E1)

Chemical Shift (ppm)
Synthesis of 3-(2-iodophenoxy)propanal (E2)

Chemical Shift (ppm)
3-(3-bromothiophen-2-yl)propan-1-ol (L)
3-(3-bromothiophen-2-yl)propanal (M)
(S)-N-(3-(2-Bromophenyl)propyldene)-2-methylpropane-2-sulfinamide (1a)
(S)-N-(3-(2-Iodophenyl)propylidene)-2-methylpropane-2-sulfinamide (1b)
(S)-[3-(2-iodophenyl)propylidene]-2,4,6-trimethylbenzenesulfinamide (1c)
(S)-N-(2-(2-iodophenoxy)ethylidene)-2,4,6-trimethylbenzenesulfinamide (4a)
(S)-N-(3-(2-iodophenoxy)propyldene)-2,4,6-trimethylbenzenesulfinamide (4b)
(S)-N-(3-iodopropyl)-N-(2-((mesitylsulfinyl)imino)ethyl)-4-methylbenzenesulfonamide (7a)
(S)-N-(3-(1-(iodomethyl)cyclohexyl)propyldiene)-2,4,6-trimethylbenzenesulfinamide (7b)
(S)-N-(3-(3-Bromothiophen-2-yl)propylidene)-2,4,6-trimethylbenzenesulfinamide (9b)
(S)-N-((S)-2,3-dihydro-1H-inden-1-yl)-2,4,6-trimethylbenzenesulfinamide (2)
(S)-N-((R)-2,3-dihydrobenzofuran-3-yl)-2,4,6-trimethylbenzenesulfinamide (5a)
(R)-N-((R)-chroman-4-yl)-2,4,6-trimethylbenzenesulfinamide (5b)
(S)-N-allyl-4-methyl-N-(2-(2,4,6-trimethylphenylsulfinamido)ethyl)benzenesulfonamide (8a)

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Chemical Shift (ppm)
(S)-N-((R)-spiro[4.5]decan-2-2,4,6-trimethylbenzenesulfinamide (8b)
(R)-(6,7-dihydro-5H-indeno[5,6-d][1,3]dioxol-5-yl)-2,4,6-trimethylbenzenesulfinamide (10a)
(R)-N-((R)-5,6-Dihydro-4H-cyclopenta[b]thiophen-4-yl)-2,4,6-trimethylbenzenesulfinamide (10b)
(S)-2,3-dihydrobenzofuran-3-amine hydrochloride (6)

Water

Chemical Shift (ppm)

Electronic Supplementary Material (ESI) for Chemical Communications
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References