Dirhodium Carboxylate Catalysts from 2-Fenchyloxy or 2-Menthyloxy Arylacetic Acids: Enantioselective C–H Insertion, Aromatic Addition and Oxonium Ylide Formation/Rearrangement

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1. Experimental Procedures

All solvents utilised in this work were distilled prior to use by the following methods: tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl; dichloromethane (DCM) was distilled from phosphorus pentoxide and, when used for rhodium catalysed C–H insertion reactions, the calcium hydride distilled DCM was deoxygenated using the freeze/thaw/pump method or was stored over 4 Å molecular sieves and deoxygenated by bubbling a stream of nitrogen through it; ethyl acetate was distilled from potassium carbonate; and hexane was distilled prior to use. All commercial reagents were used without further purification unless otherwise stated.

$^1$H (300 MHz) and $^{13}$C (75.5 MHz) NMR spectra were recorded on a 300 MHz NMR spectrometer. $^1$H (400 MHz) and $^{13}$C (100.6 MHz) NMR spectra were recorded on a 400 MHz NMR spectrometer. $^1$H (500 MHz) and $^{13}$C (125.8 MHz) NMR spectra were recorded on a 500 MHz NMR spectrometer. $^1$H (600 MHz) and $^{13}$C (150.9 MHz) NMR spectra were recorded on a 600 MHz NMR spectrometer. All spectra were recorded at 300 K in deuterated chloroform (CDCl$_3$) unless otherwise stated, using tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ$_H$ and δ$_C$) are reported in parts per million (ppm) relative to TMS, and coupling constants (J) are expressed in Hertz (Hz). Splitting patterns in $^1$H NMR spectra are designated as s (singlet), br (broad), bs (broad singlet), d (doublet), t (triplet), q (quartet), qu (quintet), dd (doublet of doublets), dt (doublet of triplets), dq (doublet of quartets), ddd (doublet of doublet of doublets), dddd (doublet of doublet of doublet of doublets), dt (doublet of triplets), ddt (doublet of doublet of triplets), td (triplet of doublets), tt (triplet of triplets), qd (quartet of doublets), and m (multiplet). $^{13}$C NMR spectra were calibrated using the solvent signal, i.e. CDCl$_3$: δ$_C$ 77.0 ppm. $^{19}$F NMR spectra chemical shifts (δ$_F$) are reported relative to hexafluorobenzene (C$_6$F$_6$), which shows a single resonance at ~163 ppm. For previously synthesised compounds, spectroscopic details were in agreement with reported values unless otherwise stated.

Infrared spectra were measured using a FTIR UATR2 spectrometer for characterisation of pure compounds. IR monitoring of reactions was conducted using a FTIR UATR2 spectrometer or by evaporation of a solution on sodium chloride plates and recording on a PerkinElmer Paragon 1000 FT-IR spectrometer.

All Celite® and activated charcoal filtrations were carried out in a sintered glass funnel using a tea spoon of both materials. Flash chromatography was carried out either manually or using automated chromatography. Automated chromatography was carried out using a Varian (971-FP) which is equipped with automated fraction collector and UV detector. In all cases, Kieselgel silica gel 60, 0.035–0.075 mm (Merck) was used. Thin layer chromatography (TLC) was carried out on pre-coated silica gel plates (Merck 60 PF254). Visualization was achieved by UV (254 nm) light absorption, and potassium permanganate staining.

The enantiopurity of chiral compounds was measured using chiral stationary phase high performance liquid chromatography (HPLC), carried out on a Lux® 3μm Amylose-1 purchased from Phenomenex, or a Chiralcel® OJ–H, Chiralcel® purchased from Daicel Chemical Industries Limited. Details of the column conditions and mobile phase employed are included in Table SI.6. HPLC analysis was performed on a Waters Alliance 2695 separations
module with a Waters Alliance 2996 Photodiode Array detector. Optical rotations were measured on an Autopol V Plus Automatic Polarimeter at 589 nm in a 10 cm cell; concentrations (c) are expressed in g/100 mL. \([\alpha]_D^T\) is the specific rotation of a compound and is expressed in units of 10\(^{-1}\) deg cm\(^2\) g\(^{-1}\).

The Microanalysis Laboratory, National University of Ireland, Cork, performed elemental analysis using an Exeter Analytical CE440 elemental analyser. Low resolution mass spectra (LRMS) was recorded on a Waters Quattro Micro triple quadrupole instrument in electrospray ionization (ESI) mode using 50% acetonitrile–water containing 0.1% formic acid as eluent. High resolution (precise) mass spectra (HRMS) was recorded on a Waters LCT Premier Tof LC-MS instrument in electrospray ionization (ESI) mode using 50% acetonitrile–water containing 0.1% formic acid as eluent. High resolution (precise) mass spectra (HRMS) were recorded on an Agilent 6530B Accurate Mass Q-TOF LC/MS instrument in electrospray ionization (ESI) mode using 50% acetonitrile–water containing 0.1% formic acid as eluent. High resolution (precise) mass spectra (HRMS) was also recorded on a Waters Vion IMS instrument (SAA055K) with Waters Acquity I-class UPLC in electrospray ionization (ESI) mode using 50% acetonitrile–water containing 0.1% formic acid as eluent and Leucine Enkephalin as reference solution. Samples prepared for either LRMS or HRMS by employing acetonitrile as solvent.

Melting points were obtained using a unimelt Thomas–Hoover capillary melting point apparatus and are uncorrected.

Single crystal X-ray analysis was conducted on either a Bruker APEX II DUO diffractometer (for 7b-d, 7f, 7h, 26a and 47) or a Bruke B8 Quest diffractometer (for 30a) using either monochromatic Mo K\(\alpha\) (\(\lambda = 0.7107 \text{ Å}\)) or Cu K\(\alpha\) (\(\lambda = 1.5418 \text{ Å}\)) radiation. All calculation and refinement were made using APEX software.\(^{[1]}\) Analysis was undertaken with SHELX suite of programs and diagrams prepared with Mercury 3.0.18.\(^{[2]}\)
2. Synthesis of Dirhodium Carboxylate Catalysts

![Scheme SI.1: An overview of the dirhodium carboxylate catalyst synthesis]

2.1 Phenylacetic acid synthesis

2-Phenylacetic acid\(^3\) (S1)

A solution of methyl 2-phenylacetate (10.00 g, 64 mmol) in methanol (60 mL) was treated with a solution of sodium hydroxide (5.1 g, 127 mmol) in water (40 mL) and heated to 70°C for 3 h. The resulting mixture was cooled, then concentrated under reduced pressure to remove the methanol. The residue was diluted with water (40 mL) and washed with diethyl ether (40 mL). The separated aqueous layer was acidified to pH 2 with 2M HCl and extracted with DCM (3 \times 80 mL). The combined organic extracts were washed with brine (100 mL), dried over MgSO\(_4\) and concentrated to give 2-phenylacetic acid S1 (8.50 g, 94%) as a white solid which was used without further purification. Spectroscopic characteristics were consistent with previously reported data.\(^3\) m.p. 75–77 °C (Lit. 75–77 °C );\(^3\) \(^1\)H NMR (300 MHz CDCl\(_3\)): \(\delta = 3.64\) (2H, s), 7.25–7.37 (5H, m), 10.13 (1H, bs); IR (neat): 3200–2500 (COOH), 1690 (CO), 1407, 1228, 1186, 698.
2.2 tert-Butyl ester synthesis

tert-Butyl 2-phenylacetate\(^[4]\) (S2)

A solution of oxalyl chloride (6.0 mL, 71 mmol) and 2-phenylacetic acid S1 (8.43 g, 62 mmol) in DCM (50 mL) was treated with catalytic DMF (1 mL) and stirred for 2 h at room temperature. The reaction mixture was concentrated under reduced pressure, the residue was diluted with DCM (30 mL) and tert-butanol (t-BuOH) (30 mL) and stirred at room temperature overnight. The reaction mixture was concentrated under reduced pressure and following purification by column chromatography on silica gel employing hexane/ethyl acetate (95:5) as the eluent, tert-butyl 2-phenylacetate S2 (8.85 g, 74%) was isolated as a clear oil. Spectroscopic characteristics were consistent with previously reported data.\(^[4]\) \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 1.43\) (9H, s), 3.52 (2H, s), 7.20–7.35 (5H, m); IR (neat): 2979, 1729 (C=O), 1367, 1134, 695.


tert-Butyl 2-(naphthalen-2-yl)acetate\(^[5]\) (S3)

Oxalyl chloride (4.1 mL, 49 mmol), 2-naphthaleneacetic acid (8.00 g, 43 mmol), DCM (50 mL), DMF (1 mL) and t-BuOH/DCM (30 mL/30 mL) were used following the procedure described for S2 to give, following column chromatography on silica gel employing hexane/ethyl acetate (93:7) as the eluent, tert-butyl 2-(naphthalen-2-yl)acetate S3 (8.81 g, 85%) as a yellow solid. Spectroscopic characteristics were consistent with previously reported data.\(^[5]\) m.p. 44–45 °C (Lit., 45–46 °C );\(^[6]\) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 1.44\) (9H, s), 3.68 (2H, s), 7.39–7.49 (3H, m), 7.71 (1H, s), 7.76–7.84 (3H, m); IR (neat): 2977, 1713 (C=O), 1268, 1131, 800, 746.


tert-Butyl 2-(naphthalen-1-yl)acetate\(^[7]\) (S4)

Oxalyl chloride (5.2 mL, 62 mmol), 1-naphthaleneacetic acid (10.00 g, 54 mmol), DCM (75 mL), DMF (1 mL) and t-BuOH/DCM (35 mL/35 mL) were used following the procedure described for S2 to give, following column chromatography on silica gel employing hexane/ethyl acetate (93:7) as the eluent, tert-butyl 1-naphthaleneacetate S4 (10.02 g, 78%) as pale yellow oil. Spectroscopic characteristics were consistent with previously reported data.\(^[7]\) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 1.41\) (9H, s), 3.97 (2H, s), 7.35–7.44 (2H, m), 7.44–7.56 (2H, m), 7.76 (1H, d, J 7.7), 7.84 (1H, d, J 7.5), 7.99 (1H, d, J 8.3); IR (neat): 2977, 1726 (C=O), 1367, 1134, 800.


tert-Butyl 2-(4-bromophenyl)acetate\(^[8]\) (S5)

Oxalyl chloride (5.4 mL, 64 mmol), 4-bromopheny lacetic acid (12.0 g, 27 mmol), DCM (100 mL), DMF (2 mL) and t-BuOH/DCM (40 mL/40 mL) were used following the procedure described for S2 to give, following column chromatography on silica gel employing hexane/ethyl acetate (95:5) as the eluent, tert-butyl 2-(4-bromophenyl)acetate S5 (12.57 g, 83%) as pale yellow oil. Spectroscopic characteristics were consistent with previously reported data.\(^[8]\) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 1.43\) (9H, s), 3.47 (2H, s), 7.14 (2H, d, J 8.3), 7.44 (2H, d, J 8.4); IR (neat): 2978, 1730 (CO), 1488, 1139, 1012, 803.
tert-Butyl 2-(4-methoxyphenyl)acetate\textsuperscript{[9]} (S6)

Oxalyl chloride (8.8 mL, 104 mmol), 4-methoxyphenylacetic acid (15 g, 90 mmol), DCM (125 mL), DMF (2 mL) and t-BuOH/DCM (50 mL/50 mL) were used following the procedure described for S2 to give, following column chromatography on silica gel employing hexane/ethyl acetate (95:5) as the eluent, tert-butyl 2-(4-methoxyphenyl)acetate S6 (15.0 g, 75%) as pale yellow oil. Spectroscopic characteristics were consistent with previously reported data.\textsuperscript{[9]} ¹H NMR (300 MHz, CDCl₃): δ= 1.43 (9H, s), 3.45 (2H, s), 3.78 (3H, s), 6.84 (2H, d, J 8.4), 7.18 (2H, d, J 8.6); IR (neat): 2978, 1726 (C=O), 1512, 1277, 1135, 820.

2.3 α-Diazo ester synthesis

**tert-Butyl 2-diazo-2-phenylacetate\textsuperscript{[10]} (6a)**

1,8-Diazabicycloundec-7-ene (DBU) (19.9 mL, 113 mmol) was added dropwise over 5 minutes to a solution of 4-acetamidobenzenesulfonyl azide (p-ABSA) (13.01 g, 54 mmol) and tert-butyl 2-phenylacetate S2 (8.68 g, 45 mmol) in DMSO (60 mL) at room temperature. After addition was complete, the solution was stirred at room temperature overnight. The reaction mixture was diluted with diethyl ether (60 mL) and water (60 mL) and the layers separated. The aqueous layer was extracted with diethyl ether (3 × 50 mL) and combined organic extracts were washed with water (50 mL), brine (50 mL), dried over MgSO₄ and concentrated under reduced pressure. The crude α-diazo ester was purified by column chromatography on silica gel employing hexane/ethyl acetate (98:2) as the eluent, to give α-diazo ester 6a (8.61 g, 88%) as a dark orange oil. Spectroscopic characteristics were consistent with previously reported data.\textsuperscript{[10]} ¹H NMR (300 MHz, CDCl₃): δ= 1.55 (9H, s), 7.12–7.19 (1H, m), 7.32–7.41 (2H, m), 7.43–7.49 (2H, m); IR (neat): 2978, 2078 (C=N₂), 1695 (C=O), 1139, 754.

**tert-Butyl 2-diazo-2-(naphthalen-2-yl)acetate\textsuperscript{[11]} (6b)**

p-ABSA (6.69 g, 27 mmol), tert-butyl 2-naphthaleneacetate S3 (4.5 g, 17 mmol), (DBU) (6.9 mL, 46 mmol) and DMSO (40 mL) were used following the procedure described for 6a to give, following column chromatography on silica gel employing hexane/ethyl acetate (97:3) as the eluent, α-diazo ester 6b (4.37 g, 88%) as an orange solid. Spectroscopic characteristics were consistent with previously reported data.\textsuperscript{[11]} m.p. 84–85 °C; ¹H NMR (400 MHz, CDCl₃): δ= 1.58 (9H, s), 7.38–7.55 (3H, m), 7.74–7.87 (3H, m), 8.02 (1H, s); IR (neat): 2977, 2080 (C=N₂), 1689 (CO), 1144, 1125, 733.
**SI-8**

**tert-Butyl 2-diazo-2-(naphthalen-1-yl)acetate (6c)**

![Chemical Structure](image)

- p-ABSA (6.20g, 26 mmol), tert-butyl 2-naphthaleneacetate S4 (5.00 g, 21 mmol), DBU (7.7 mL, 52 mmol) and DMSO (50 mL) were used following the procedure described for 6a to give, following column chromatography on silica gel employing hexane/ethyl acetate (97:3) as the eluent, α-diazo ester 6c (1.35 g, 64%) as an orange oil. 
  - $\delta$= 1.53 (9H, s), 7.46–7.65 (4H, m), 7.81–7.90 (3H, m); $^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta$= 28.4, 82.0, 122.6, 124.5, 125.6, 126.1, 126.7, 128.8, 129.37, 129.41, 131.5, 134.1, 165.6; IR (neat): 2977, 2078 (C$_2$N), 1694 (C=O), 1148, 1100, 771; HRMS (ESI-TOF): $m/z$ [M+H]$^+$ for C$_{16}$H$_{17}$N$_2$O$_2$, 269.1286, found 269.1290.

**tert-Butyl 2-(4-bromophenyl)-2-diazoacetate[11] (6d)**

- p-ABSA (13.17 g, 55 mmol), tert-butyl 2-(4-bromophenyl)acetate S5 (12.39 g, 46 mmol), DBU (16.9 mL, 114 mmol) and DMSO (100 mL) were used following the procedure described for 6a to give, following column chromatography on silica gel employing hexane/ethyl acetate (97:3) as the eluent, α-diazo ester 6d (12.46 g, 92%) as an orange solid. Spectroscopic characteristics were consistent with previously reported data.[11] m.p. 71–73 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$= 1.54 (9H, s), 7.35 (2H, d, $J$ 8.7), 7.47 (2H, d, $J$ 8.7); IR (neat): 2976, 2082 (C$_2$N), 1689 (CO), 1489, 1147, 1001, 809.

**tert-Butyl 2-(4-methoxyphenyl)-2-diazoacetate[12] (6e)**

- p-ABSA (19.45 g, 81 mmol), tert-butyl 2-(4-methoxyphenyl)acetate S6 (15.00 g, 68 mmol), DBU (25.2 mL, 169 mmol) and DMSO (120 mL) were used following the procedure described for 6a. Upon work up, ~1/3 of the original ester starting material was still present in the reaction product. The reaction product was re-dissolved in 120 mL DMSO with a further 0.66 equiv. of p-ABSA and 1 equiv. DBU and stirred at room temperature for a further 24h. Upon work-up, ~10% starting material remained and an additional 0.1 equiv ABSA and 0.15 equiv DBU were added and the reaction mixture stirred for 24h at room temperature. Column chromatography on silica gel employing hexane/ethyl acetate (95:5) as the eluent, gave α-diazo ester 6e (9.57 g, 57%) as an orange oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$= 1.54 (9H, s), 3.80 (3H, s), 6.93 (2H, d, $J$ 8.9), 7.37 (2H, d, $J$ 8.9); $^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta$= 28.4, 55.4, 81.9, 114.5, 117.6, 125.9, 157.8, 165.1; IR (neat): 2934, 2073 (CN$_2$), 1693 (CO), 1511, 1243, 1139, 1000, 825; HRMS (ESI-TOF): $m/z$ [M+H]$^+$ for C$_{13}$H$_{17}$N$_2$O$_3$, 249.1239, found 249.1235.
2.4 Fenchyloxy acetate synthesis

tert-Butyl (2S)-2-(1′′R,2′′R,4′′S)-fenchyloxy-2-phenylacetate (7a)

Rhodium(II) acetate (7.4 mg, 0.017 mmol) was added in one portion to a stirring solution of (1R)-endo-(+)-fenchyl alcohol (2.58 g, 17 mmol) and α-diazo ester 6a (4.00 g, 18 mmol) in DCM (70 mL). After the evolution of gas subsided, the solution was stirred for 2 h at room temperature and the reaction mixture was concentrated under reduced pressure to give compound 7a as an 83:17 [(2S)/(2R)] mixture of diastereomers. Purification of the crude product by column chromatography on silica gel employing hexane/ethyl acetate (98:2) as the eluent allowed partial fractionation of diastereomers but not complete separation (combined yield, 3.37 g, 70%). Sequential recrystallisations from acetonitrile gave (2S)-7a (0.56 g, 12%), a white crystalline solid, as a single isomer. The other isomer was not isolated in pure form. (2S)-7a, less polar isomer; m.p. 57–59 °C; Spec. Rot.: [α]_D^20 +54.9 (c 1.0, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ= 0.89–1.10 (11H, m, contains 2H, m and 3 × 3H, s at 1.00, 1.04, 1.06), 1.29–1.49 (11H, m, contains 9H, s at 1.39 and 2H, m), 1.61–1.66 (1H, m), 1.67–1.79, (1H, m), 1.80–1.93 (1H, m), 2.99 (1H, d, J 1.7), 4.76 (1H, s), 7.27–7.37 (3H, m), 7.41–7.49 (2H, m); ¹³C NMR (75.5 MHz, CDCl₃): δ= 20.2, 20.9, 26.0, 26.2, 28.0, 31.2, 39.9, 41.4, 48.6, 49.4, 81.3, 81.8, 91.2, 127.2, 128.0, 128.1, 137.9, 170.7; IR (neat): 2937, 1742 (CO), 1106, 700; HRMS (ESI-TOF): m/z [M+H]+ calcd for C₂₁H₂₃O₃, 345.2430, found 345.2436; Elemental Analysis: calcd (%) for C₂₁H₂₃O₃: C, 76.70; H, 9.36. Found: C, 76.76; H, 9.23.

A characteristic signal of the (2R)-S7 isomer is the 1H d of C(2′′′)H observed at 3.09 ppm, J 1.7, in the ¹H NMR spectrum of the crude product. The ratio of diastereomers was calculated based on this signal which occurs at 2.99 ppm for the (2S)-7a isomer and 3.09 ppm for the (2R)-S7 isomer.

tert-Butyl (2S)-2-(1′′R,2′′R,4′′S)-fenchyloxy-2-(naphthalen-2′-yl)acetate (7b)

Rhodium(II) acetate (5.8 mg, 0.013 mmol), (1R)-endo-(+)-fenchyl alcohol (2.04 g, 13 mmol), α-diazo ester 6b (3.90 g, 15 mmol) and DCM (70 mL) were used following the procedure described for 7a to give compound 7b as an 83:17 [(2S)/(2R)] mixture of diastereomers. Purification of the crude product by column chromatography on silica gel employing hexane/ethyl acetate (98:2) as the eluent allowed partial fractionation of diastereomers but not complete separation (combined yield, 3.78 g, 70%). Sequential recrystallisations from acetonitrile gave (2S)-7b (1.62 g, 31%), a white crystalline solid, as a single isomer. The other isomer was not isolated in pure form. (2S)-7b, less polar isomer; m.p. 113–114 °C; Spec. Rot.: [α]_D^20 +80.2 (c 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ= 0.92–1.15 (11H, m, contains 2H, m and 3 × 3H, s at 1.00, 1.07, 1.10), 1.33–1.45 (11H, m, contains 9H, s at 1.38 and 2H, m), 1.61–1.68 (1H, m), 1.70–1.80 (1H, m), 1.85–1.95 (1H, m), 3.04 (1H, d, J 1.7), 4.90 (1H, s), 7.42–7.51 (2H, m), 7.56–7.65 (1H, m), 7.78–7.87 (3H, m), 7.89 (1H, s); ¹³C NMR (100.6 MHz, CDCl₃): δ= 20.2, 20.9, 26.0, 26.2, 28.0, 31.3, 39.8, 41.4, 48.7, 49.3, 81.4, 81.8, 91.1, 125.1, 126.0, 126.7, 127.7, 127.9, 128.1, 133.1, 133.3, 135.3, 170.6; IR (neat): 2928, 1714 (CO), 1290, 1128, 477; HRMS (ESI-TOF): m/z [M+H]+ calcd for C₂₆H₃₅O₃, 395.2567, found 395.2586; Elemental Analysis: calcd (%) for C₂₆H₃₅O₃: C, 79.15; H, 8.69. Found: C, 79.03; H, 8.57.
A characteristic signal of the (2R)-S8 isomer is the 1H d of C(2")H observed at 3.14 ppm, J 1.7, in the ¹H NMR spectrum of the crude product. The ratio of diastereomers was calculated based on this signal which occurs at 3.04 ppm for the (2S)-7b isomer and 3.14 ppm for the (2R)-S8 isomer.

**tert-Butyl (2S)-2-(1"R,2"R,4"S)-fenchyloxy-2-(naphthalen-1'-yl)acetate (7c)**

Rhodium(II) acetate (4.9 mg, 0.010 mmol), (1R)-endo- (+)-fenchyl alcohol (1.57 g, 10 mmol), α-diazo ester 6c (3.00 g, 11 mmol) and DCM (50 mL) were used following the procedure described for 7a to give the compound 7c as a 47:53 [(2S)/(2R)] mixture of diastereomers. Purification of the crude product by column chromatography on silica gel employing hexane/ethyl acetate (98:2) as the eluent allowed partial fractionation of diastereomers but not complete separation (combined yield, 2.84 g, 72%). Sequential recrystallisations from acetonitrile gave (2S)-7c (1.13 g, 29%), a white crystalline solid, as a single isomer. The other isomer was not isolated in pure form. (2S)-7c, less polar isomer; m.p. 69–71 °C; Spec. Rot.: [α]D20 = −2.0 (c 1.0, CHCl3); ¹H NMR (400 MHz, CDCl3): δ= 0.80–0.96 (4H, m, contains 1H, m and 3H, s at 0.84), 1.00 (1H, d, J 10.1), 1.09, 1.14 (2 x 3H, s), 1.26–1.43 (11H, m, contains 9H, s at 1.30 and 2H, m), 1.63 (1H, apparent d, J 3.0), 1.69–1.79 (1H, m), 1.81–1.92 (1H, m), 3.07 (1H, d, J 1.4), 5.34 (1H, s), 7.42–7.55 (3H, m), 7.67 (1H, d, J 7.0), 7.78–7.88 (2H, m), 8.30 (1H, d, J 8.2) ¹³C NMR (100.6 MHz, CDCl3): δ= 20.1, 21.1, 26.0, 26.2, 27.9, 31.4, 39.9, 41.4, 48.7, 49.3, 80.2, 81.5, 96.1, 124.8, 125.2, 125.5, 125.9, 126.8, 128.5, 131.1, 133.8, 134.0, 170.6; IR (neat): 2952, 1743 (CO), 1368, 1151, 789; Elementary Analysis: calcd (%) for C29H34O3: C, 79.15; H, 8.69. Found: C, 79.34; H, 8.63.

A characteristic signal of the (2R)-S9 isomer is the 1H d of C(2")H observed at 3.26 ppm, J 1.4, in the ¹H NMR spectrum of the crude product. The ratio of diastereomers was calculated based on this signal which occurs at 3.07 ppm for the (2S)-7c isomer and 3.26 ppm for the (2R)-S9 isomer.

**tert-Butyl (2S)-2-(4'-bromophenyl)-2-(1"R,2"R,4"S)-fenchyloxyacetate (7d)**

Rhodium(II) acetate (8.5 mg, 0.019 mmol), (1R)-endo- (+)-fenchyl alcohol (2.95 g, 19 mmol), α-diazo ester 6d (6.00 g, 21 mmol) and DCM (70 mL) were used following the procedure described for 7a to give compound 7d as a 79:21 [(2S)/(2R)] mixture of diastereomers. Purification of the crude product by column chromatography on silica gel employing hexane/ethyl acetate (98:2) as the eluent allowed partial fractionation of diastereomers but not complete separation (combined yield, 6.35 g, 79%). Sequential recrystallisations from acetonitrile gave (2S)-7d (3.26 g, 37%), a white crystalline solid, as a single isomer. The other isomer was not isolated in pure form. (2S)-7d, less polar isomer; m.p. 100–102 °C; Spec. Rot.: [α]D20 = +48.3 (c 1.0, CHCl3); ¹H NMR (400 MHz, CDCl3): δ= 0.90–1.10 (11H, m, contains 2H, m and 3 x 3H, 2 x s, one at 1.00 and two at 1.04), 1.33–1.46 (11H, m, contains 9H, s at 1.38 and 2H, m), 1.60–1.66 (1H, m), 1.67–1.76 (1H, m), 1.77–1.87 (1H, m), 2.97 (1H, bs, J 1.5), 4.71 (1H, s), 7.33 (2H, d, J 8.4), 7.46 (2H, d, J 8.4); ¹³C NMR (100.6 MHz,
A characteristic signal of the (2R)-S11 isomer is the 1H d of C(2′′)H observed at 3.05 ppm, J 1.4, in the ¹H NMR spectrum of the crude product. The ratio of diastereomers was calculated based on this signal which occurs at 2.96 ppm for the (2S)-7e isomer and 3.05 ppm for the (2R)-S11 isomer.

2.5 Menthyloxy acetate synthesis

**tert-Butyl (2S)-2-(1″R,2″R,4″S)-fenchyloxy-2-(4′-methoxyphenyl)acetate (7e)**

Rhodium(II) acetate (7.6 mg, 0.017 mmol), (1R)-endo-(+) -fenchyl alcohol (2.66 g, 17 mmol), α-diazo ester 6e (4.50 g, 18 mmol) and DCM (50 mL) were used following the procedure described for 7a to give compound 7e as a 83:17 [(2S)/(2R)] mixture of diastereomers. Purification of the mixture by column chromatography on silica gel employing hexane/ethyl acetate (95:5) as the eluent allowed partial fractionation of diastereomers but not complete separation (combined yield, 5.06 g, 80%). Sequential recrystallisations from acetonitrile gave (2S)-7e (2.32 g, 36%), a white crystalline solid, as a single isomer. (2S)-7e, less polar isomer; m.p. 66–68 °C; Spec. Rot.: [α]_D^20 = +60.4 (c 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ= 0.87–1.07 (11H, m, contains 2H, m and 3 × 3H, s at 0.99, 1.03 and 1.04), 1.31–1.46 (11H, m, contains 9H, s at 1.39 and 2H, m), 1.59–1.64 (1H, m), 1.66–1.77 (1H, m), 1.79–1.91 (1H, m), 2.96 (1H, d, J 1.4), 3.80 (3H, s), 4.70 (1H, s), 7.86 (2H, d, J 8.7), 7.36 (2H, d, J 8.7); ¹³C NMR (100.6 MHz, CDCl₃): δ= 20.2, 20.8, 26.0, 26.2, 28.0, 31.2, 39.8, 41.4, 48.6, 49.3, 55.2, 81.1, 81.2, 90.8, 113.5, 128.6, 130.0, 159.4, 170.9; IR (neat): 2946, 1714 (C=O), 1239, 1095, 847; Elemental Analysis: calcd (%) for C₂₃H₃₄O₄: C, 73.76; H, 9.15. Found: C, 73.84; H, 9.00.

A characteristic signal of the (2R)-S11 isomer is the 1H d of C(2′′″)H observed at 3.05 ppm, J 1.4, in the ¹H NMR spectrum of the crude product. The ratio of diastereomers was calculated based on this signal which occurs at 2.96 ppm for the (2S)-7e isomer and 3.05 ppm for the (2R)-S11 isomer.

**tert-Butyl (2S)-2-(1″R,2″R,4″S)-menthyloxy-2-phenylacetate (7f)**

Rhodium(II) acetate (10.6 mg, 0.026 mmol), (-)-menthol (3.76 g, 24 mmol) and α-diazo ester 6a (5.75 g, 26 mmol) and DCM (80 mL) were used following the procedure for 7a to give compound 7f as a 77:23 [(2S)/(2R)] mixture of diastereomers. Purification of the mixture by column chromatography on silica gel employing hexane/ethyl acetate (98:2) as the eluent allowed partial separation of isomers but not complete separation (combined yield, 6.93 g, 83%). Sequential recrystallisations from acetonitrile gave (2S)-7f (3.35 g, 40%), a white crystalline solid, as a single isomer. (2S)-7f, less polar isomer; m.p. 75–77 °C; Spec. Rot.: [α]_D^20 = −61.6 (c 1.0, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ= 0.79–1.08 (12H, m, which contains, 3H, m, 3H,
d, J 6.9 at 0.85, 3H, d, J 6.8 at 0.89 and 3H, d, J 7.1 at 0.94), 1.23–1.46 (11H, m, contains 2H, m, and 9H, s at 1.39), 1.58–1.71 (2H, m), 2.01–2.13 (1H, m), 2.44–2.61 (1H, m), 3.31 (1H, td, J 10.5, 4.2), 4.94 (1H, s), 7.23–7.37 (3H, m), 7.42–7.50 (2H, m); 13C NMR (75.5 MHz, CDCl3): δ= 16.4, 21.2, 22.3, 23.2, 25.2, 27.9, 31.5, 34.5, 40.4, 48.4, 78.5, 78.6, 81.4, 126.9, 128.0, 128.3, 138.3, 170.8; IR (neat): 2958, 1734 (C=O), 1146, 1097, 701; Elemental Analysis: calcd (%) for C22H34O3: C, 76.26; H, 9.89. Found: 76.45; H, 9.80.

**tert-Butyl (2R)-2-(1”R,2”S,5”R)-menthylloxy-2-phenylacetate (S12)**

(2R)-S12, more polar isomer (0.65 g, 8%), m.p. 80–81 °C; Spec. Rot.: [α]D20 = −137.3 (c 1.0, CHCl3); 1H NMR (400 MHz, CDCl3): δ= 0.49 (3H, d, J 6.9), 0.78–0.96 (8H, m, contains 2H, m and 3H, d, J 7.0 at 0.85 and 3H, d, J 7.0 at 0.92), 1.02 (1H, q, J 11.1), 1.23–1.45 (11H, m), 1.55–1.70 (2H, m), 2.07–2.17 (1H, m), 2.22–2.35 (1H, m), 3.09 (1H, td, J 10.5, 4.1), 4.83 (1H, s), 7.28–7.37 (3H, m), 7.39–7.47 (2H, m); 13C NMR (100.5 MHz, CDCl3): δ= 15.6, 21.1, 22.4, 22.9, 29.1, 27.9, 31.6, 34.4, 40.5, 48.1, 78.2, 79.2, 81.3, 127.4, 128.1, 128.3, 137.7, 171.0; IR (neat): 2959, 2930, 1735 (C=O), 1151, 1049, 697; Elemental Analysis: calcd (%) for C22H34O3: C, 76.26; H, 9.89. Found C, 75.95; H, 9.75.

**tert-Butyl (2S)-(1”R,2”S,5”R)-menthylloxy-2-(naphthalen-2-yl)acetate[13] (7g)**

Rhodium(II) acetate (10.5 mg, 0.024 mmol), (−)-menthol (3.71 g, 24 mmol) and α-diazo ester 6b (7.00 g, 26 mmol) and DCM (60 mL) were used following the procedure for 7a to give compound 7g as a 76:24 [(2S)/(2R)] mixture of diastereomers. Purification of the mixture by column chromatography on silica gel employing hexane/ethyl acetate (98:2) as the eluent allowed partial separation of isomers (combined yield, 7.16 g, 75%). Sequential recrystallisations from acetonitrile gave (2S)-7g (2.35, 29%), a white crystalline solid, as a single isomer. (2S)-7g, less polar isomer; m.p. 77–79 °C; Spec. Rot.: [α]D20 = −33.1 (c 1.0, CHCl3); 1H NMR (400 MHz, CDCl3): δ= 0.78–1.08 (12H, m, contains 3H, m, 2 x overlapping 3H, d, J ~7.0, at 0.87 and 0.88 and 3H, d, J 7.1 at 0.96), 1.26–1.46 (11H, m, contains 2H, m and 9H, s at 1.36), 1.60–1.72 (2H, m), 2.08 (1H, bd, J 11.6), 2.51–2.65 (1H, m), 3.36 (1H, td, J 10.5, 4.1), 5.10 (1H, s), 7.42–7.51 (2H, m), 7.60 (1H, dd, J 8.5, 1.4), 7.77–7.89 (3H, m), 7.92 (1H, s); 13C NMR (100.6 MHz, CDCl3): δ= 15.6, 21.3, 22.2, 23.2, 25.3, 28.0, 31.6, 34.5, 40.5, 48.4, 78.9, 79.0, 81.6, 124.8, 125.99, 126.06, 126.1, 127.7, 128.0, 128.2, 133.21, 133.23, 135.8, 170.8; IR (neat): 2953, 1737 (CO), 1147, 1095, 760; Elemental Analysis: calcd (%) for C26H36O3: C, 78.75; H, 9.15. Found: 78.75; H, 9.08.
**SUPPORTING INFORMATION**

**tert-Butyl (2R)-(1"R,2"S,5"R)-menthloxy-2-(naphthalen-2-yl)acetate**

(2R)-S13, more polar, minor isomer, white solid (0.52, 5%); m.p. 92–93 °C; Spec. Rot.: [α]_D^20 = −156.1 (c 1.0, CHCl₃); ^1H NMR (400 MHz, CDCl₃): δ = 0.46 (3H, d, J 6.9), 0.75–0.99 [8H, m, contains 2H, m, 3H, d, J 7.1 at 0.86 and 3H, d, J 6.5 at 0.93], 1.05 (1H, q, J 11.1), 1.21–1.49 (11H, m, contains 2H, m and 9H, s at 1.37), 1.54–1.67 (2H, m), 2.18 (1H, bd, J 11.7), 2.29–2.43 (1H, m), 3.13 (1H, td, J 10.5, 4.1), 5.02 (1H, s), 7.43–7.53 (2H, m), 7.57 (1H, dd, J 8.5, 1.4), 7.78–7.93 (3H, m), 7.89 (1H, s); ^13C NMR (100.6 MHz, CDCl₃): δ = 15.7, 21.1, 22.4, 22.9, 25.1, 27.9, 31.6, 34.4, 40.4, 48.1, 78.0, 79.2, 81.5, 125.1, 126.0, 126.1, 126.8, 127.8, 128.1, 128.14, 133.3, 135.1, 170.9; IR (neat): 2920, 1732 (C=O), 1148, 1084, 817; HRMS (ESI-TOF): m/z [M+H]^+ calcd for C₂₆H₄₀O₃Br, 425.1689, found 425.1684; Elemental Analysis: calcd (%) for C₂₆H₃₆O₃: C, 78.75; H, 9.15. Found: C, 78.64; H, 9.06.

**tert-Butyl (2S)-2-(4'-bromophenyl)-2-(1"R,2"S,5"R)-menthloxyacetate (7h)**

Rhodium(II) acetate (8.8 mg, 0.020 mmol), (−)-menthol (3.19 g, 20 mmol) and α-diazo ester 6d (6.10 g, 21 mmol) and DCM (60 mL) were used following the procedure for 7a to give compound 7h as a 87:13 [(2S)/(2R)] mixture of diastereomers. Purification of the mixture by column chromatography on silica gel employing hexane/ethyl acetate (98:2) as the eluent allowed partial separation of isomers (combined yield, 6.89 g, 81%). Sequential recrystallisations from acetonitrile gave (2S)-7h (3.93 g, 44%), a white crystalline solid, as a single isomer. The other isomer was not isolated in pure form. (2S)-7h, less polar isomer; m.p. 100–102 °C; Spec. Rot.: [α]_D^20 = −45.7 (c 1.0, CHCl₃); ^1H NMR (400 MHz, CDCl₃): δ = 0.76–1.07 (12H, m, contains, 3H, m, 3H, d, J 6.9 at 0.84, 3H, d, J 6.5 at 0.89 and 3H, d, J 7.1 at 0.94), 1.26–1.44 (11H, m, contains 2H, m and 9H, s at 1.39), 1.60–1.71 (2H, m), 2.03 (1H, bd, J 12.0), 2.42–2.57 (1H, m), 3.30 (1H, td, J 10.5, 4.1), 4.89 (1H, s), 7.31–7.37 (2H, m), 7.42–7.49 (2H, m); ^13C NMR (100.6 MHz, CDCl₃): δ = 16.3, 21.2, 22.3, 23.1, 25.3, 27.9, 31.5, 34.4, 40.3, 48.4, 78.0, 78.8, 81.7, 122.1, 128.6, 131.4, 137.4, 170.3; IR (neat): 2929, 1737 (C=O), 1144, 1096, 780; HRMS (ESI-TOF): m/z [M+H]^+ calcd for C₂₂H₃₄O₄Br, 425.169, found 425.1684; Elemental Analysis: calcd (%) for C₂₂H₃₄O₄Br: C, 62.12; H, 7.82. Found: C, 62.19; H, 7.75.

A characteristic signal of the (2R)-S14 isomer is the 1H triplet of doublets of C(1")H, J 10.5, 4.1, observed at 3.08 ppm in the ¹H NMR spectrum of the crude product. The ratio of diastereomers was calculated based on this signal which occurs at 3.30 ppm for the (2S)-7h isomer and 3.08 ppm for the (2R)-S14 isomer.
2.6 Carboxylic acid synthesis

(2S)-2-(1′″R,2″R,4″S)-Fenchyloxy-2-phenylacetic acid (8a)

Trifluoroacetic acid (TFA) (1.5 mL) was added to a stirring solution of (2S)-7a (0.50 g, 1.7 mmol) in DCM (5mL). The solution was stirred for 2 h at room temperature and then concentrated under reduced pressure to give the crude product. Following purification by column chromatography on silica gel employing hexane/ethyl acetate (99:1) as eluent, the pure acid 8a (0.44 g, 90%) was isolated as a white solid. m.p. 113–115 °C; Spec. Rot.: \([\alpha]_{D}^{20} = +137.5 \text{ (c 0.75, CHCl}_{3}\)); \(^1\text{H NMR (400 MHz, CDCl}_{3}\)): \(\delta = 0.91 \text{ (3H, s), 0.98–1.11 \text{ (8H, m, contains 2H, m and 2 × overlapping 3H, s at 1.04), 1.34–1.51 \text{ (2H, m), 1.64–1.68 \text{ (1H, m), 1.69–1.80 \text{ (2H, m), 3.08 \text{ (1H, finely split s, J 1.3), 4.88 \text{ (1H, s), 7.32–7.44 \text{ (5H, m), ~9.30 \text{ (1H, bs); 13C NMR (100.6 MHz, CDCl}_{3}\}): \(5 = 19.8, 20.9, 26.0, 26.07, 31.4, 39.6, 41.3, 48.7, 49.1, 80.5, 91.0, 127.7, 128.6, 129.0, 135.8, 172.9; IR (neat): 3400–2500 (COOH), 2951, 1721 \text{ (CO), 1455, 1114, 1099, 697; Elemental Analysis: calcd (%) for C_{18}H_{24}O_3: C, 74.97; H, 8.39. Found: 74.97; H, 8.38.}

(2S)-2-(1″R,2″R,4″S)-Fenchyloxy-2-(naphthalen-2″-yl)acetic acid (8b)

TFA (1 mL), (2S)-7b (0.15 g, 0.38 mmol) in DCM (5mL) were used following the procedure for 8a to give, following column chromatography on silica gel employing hexane/ethyl acetate (95:5) as the eluent, the acid 8b (95 mg, 74%) as a clear, viscous oil. Spec. Rot.: \([\alpha]_{D}^{20} = +130.9 \text{ (c 1.2, CHCl}_{3}\)); \(^1\text{H NMR (400 MHz, CDCl}_{3}\)): \(\delta = 0.81–1.13 \text{ (11H, m, contains 2H, m, 3 × 3H, s at 0.92, 1.05 and 1.08), 1.31–1.48 \text{ (2H, m), 1.61–1.68 \text{ (1H, m), 1.69–1.88 \text{ (2H, m), 3.10 \text{ (1H, bs), 5.04 \text{ (1H, s), 7.42–7.58 \text{ (3H, m), 7.77–7.90 \text{ (4H, m), ~9.21 \text{ (1H, bs); 13C NMR (100.6 MHz, CDCl}_{3}\): \(5 = 19.9, 20.9, 26.0, 26.07, 31.4, 39.6, 41.3, 48.7, 49.1, 80.7, 91.0, 124.7, 126.4, 126.6, 127.6, 127.8, 128.1, 128.6, 133.0, 133.4, 133.6, 174.3; IR (neat): 3300–2400 (COOH), 2950, 1717 \text{ (CO), 1112, 1101, 774, 732; HRMS (ESI-TOF): m/z [M+H]^{+} \text{ calcld for C}_{22}H_{22}O_{3}: 339.1960, found 339.1960.}

(2S)-2-(1″R,2″R,4″S)-Fenchyloxy-2-(naphthalen-1″-yl)acetic acid (8c)

TFA (1 mL), (2S)-7c (0.15 g, 0.38 mmol) and DCM (2.5mL) were used following the procedure for 8a to give, following column chromatography on silica gel employing hexane/ethyl acetate (95:5) as the eluent, the acid 8c (0.12 g, 93%) as a clear, viscous oil. Spec. Rot.: \([\alpha]_{D}^{20} = 170.2 \text{ (c 1.5, CHCl}_{3}\)); \(^1\text{H NMR (400 MHz, CDCl}_{3}\)): \(\delta = 0.71 \text{ (3H, s), 0.77–1.17 (8H, m, contains 2H, m and 2 × 3H, s at 1.06, 1.12), 1.19–1.47 \text{ (2H, m), 1.61–1.67 \text{ (1H, m), 1.68–1.83 \text{ (2H, m), 3.10 \text{ (1H, finely split s, J 1.2), 5.44 \text{ (1H, s), 7.41–7.53 \text{ (3H, m), 7.59 \text{ (1H, d, J 6.7), 7.81–7.88 \text{ (2H, m), 8.15 \text{ (1H, d, J 7.9), ~9.88 \text{ (1H, bs); 13C NMR (100.6 MHz, CDCl}_{3}\): \(5 = 19.7, 21.1, 26.0, 26.1, 31.5, 39.8, 41.3, 48.7, 49.1, 79.3, 91.6, 124.2, 125.0, 126.0, 126.6, 127.7, 128.8, 129.7, 131.1, 132.0, 134.0, 174.4; IR (neat): 3500–2600 (COOH), 2950, 1717 \text{ (CO), 1111, 1101, 774; Elemental Analysis: calcld (%) for C}_{22}H_{24}O_{3}: C, 78.07; H, 7.56. Found: 77.93; H, 7.56.}
**SUPPORTING INFORMATION**

(2S)-2-(4’-Bromophenyl)-2-(1”R,2”R,4”S)-fenchlyoxyacetic acid (8d)

TFA (2 mL), (2S)-7d (0.25 g, 0.59 mmol) and DCM (5 mL) were used following the procedure for 8a to give, following column chromatography on silica gel employing hexane/ethyl acetate (95:5) as the eluent, the acid 8d (0.16 g, 74%) as a white solid. m.p. 65–68 °C; Spec. Rot.: [α]_D^{25} = +98.1 (c 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 0.95 (3H, s), 0.98–1.09 (8H, m, contains 2H, m and 2 × overlapping 3H, s at 1.02), 1.35–1.48 (2H, m), 1.62–1.68 (1H, m), 1.68–1.82 (2H, m), 3.02 (1H, finely split s, J 1.1), 4.84 (1H, s), 7.31 (2H, d, J 8.4), 7.49 (2H, d, J 8.4), -9.20 (1H); ¹³C NMR (100.6 MHz, CDCl₃): δ = 20.0, 20.9, 26.0, 26.1, 31.3, 39.7, 41.3, 48.6, 49.2, 80.0, 91.5, 123.1, 129.2, 131.8, 135.2, 174.8; IR (neat): 3300-2400 (COOH), 2950, 1722 (CO), 1094, 816;

**Elemental Analysis:** calcd (%) for C₁₈H₂₃O₃Br: C, 58.86; H, 6.31. Found: 58.92; H, 6.27.

(2S)-2-(1”R,2”R,4”S)-Fenchlyoxy-2-(4’-methoxy)phenylacetic acid (8e)

A solution of (2S)-7e (0.60 g, 1.6 mmol) in methanol (15 mL) was treated with sodium hydroxide (0.64 g, 16 mmol) and heated under reflux for 4 h. The resulting mixture was cooled, then concentrated under reduced pressure to remove the methanol. The residue was dissolved in DCM (30 mL) and washed with 2M HCl (30 mL). The combined organic extracts were washed with brine (50 mL), dried over MgSO₄ and concentrated to give compound 8e (0.47 g, 92%), a white solid, as a 95:5 [(2S):2R] mixture of diastereomers which was used without further purification. m.p. 90–93 °C; Spec. Rot.: [α]_D^{25} = +133.6 (c 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 0.91 (3H, s), 0.99–1.12 (8H, m, contains 2H, m and 2 × 3H, s, at 1.02, 1.033), 1.33–1.50 (2H, m), 1.62–1.68 (1H, m), 1.68–1.80 (2H, m), 3.06 (1H, finely split s, J 1.2), 3.81 (3H, s), 4.82 (1H, s), 6.89 (2H, d, J 8.6), 7.32 (2H, d, J 8.6), COOH not observed; ¹³C NMR (100.6 MHz, CDCl₃): δ = 19.8, 20.9, 26.05, 26.08, 31.4, 39.5, 41.3, 48.7, 49.0, 55.3, 80.0, 90.5, 114.0, 127.9, 129.1, 160.1, 173.5; IR (neat): 3500–2300 (COOH), 2951, 1721 (CO), 1512, 1033, 829; **Elemental Analysis:** calcd (%) for C₁₉H₂₅O₃: C, 71.67; H, 8.23. Found C, 71.40; H, 8.09.

A characteristic signal of the (2R)-S15 isomer is the 1H, finely split singlet of C(2)H, J 1.2 observed at 3.12 ppm in the ¹H NMR spectrum of the crude product. The ratio of diastereomers was calculated based on this signal which occurs at 3.06 ppm for the (2S)-8e isomer and 3.12 ppm for the (2R)-S15 isomer.

(2S)-2-(1”R,2”S,5”R)-Menthyloxy-2-phenylacetic acid (8f)

TFA (5 mL), (2S)-7f (2.00 g, 5.8 mmol) and DCM (5mL) were used following the procedure for 8a to give compound 8f (1.61 g, quantitative) as a white solid which was used without further purification. m.p. 96–98 °C; Spec. Rot.: [α]_D^{20} = −14.05 (c 1.0, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ = 0.73–1.06 (12H, m, contains, 3H, m, 3H, d, J 6.6 at 0.81, 3H, d, J 7.0 at 0.85 and 3H, d, J 7.0 at 0.94), 1.18–1.45 (2H, m), 1.58–1.73 (2H, m), 1.90 (1H, bd, J 12.1), 2.28–2.47 (1H, m), 3.36 (1H, td, J 10.5, 4.2), 5.04 (1H, s), 7.29–7.41 (3H, m), 7.42–7.50 (2H, m), 9.01 (1H, bs); ¹³C NMR (75.5 MHz, CDCl₃): δ = 16.0, 21.2, 22.2, 23.0, 25.5, 31.5,
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34.3, 40.7, 48.6, 78.3, 79.5, 127.1, 128.6, 128.7, 137.0, 175.6; IR (neat): 3400–3000 (COOH), 2932, 1721 (CO), 1694, 1105, 1095, 696; Elemental Analysis: calcd (%) for C_{18}H_{26}O_{3}: C, 74.45; H, 9.02, found: C, 74.55; H, 8.99.

(2S)-2-(1''R,2''S,5''R)-Menthlyoxy-2-(naphthalen-2''-yl)acetic acid (8g)

TFA (5 mL), (2S)-7g (0.90 g, 2.5 mmol) and DCM (5mL) were used following the procedure for 8a to give compound 8g (0.71 g, quantitative) as an off white foamy solid which was used without further purification. m.p. 112–115 °C; Spec. Rot.: [α]_D^20 = 19.25 (c 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ= 0.73–1.05 (12H, m, contains, 3H, m, 3H, d, J 6.5 at 0.81, 3H, d, J 6.9 at 0.85, and 3H, d, J 7.0 at 0.96), 1.18–1.34 (1H, m), 1.34–1.48 (1H, m), 1.57–1.71 (2H, m), 1.91 (1H, bd, J 11.9), 2.34–2.48 (1H, m), 3.40 (1H, td, J 10.5, 4.1), 5.19 (1H, s), 7.44–7.52 (2H, m), 7.57 (1H, dd, J 8.5, 1.4), 7.77–7.87 (3H, m), 7.91 (1H, s), 8.57 (1H, bs); ^13C NMR (100.6 MHz, CDCl_3): δ= 16.0, 21.3, 22.2, 22.9, 25.5, 31.5, 34.3, 40.9, 48.6, 78.7, 79.8, 124.5, 126.3, 126.4, 126.6, 127.7, 128.2, 128.5, 133.1, 133.5, 134.4, 175.3; IR (neat): 3500–2200 (COOH), 2921, 1718 (CO), 1487, 1011, 813; Elemental Analysis: calcd (%) for C_{22}H_{28}O_{3}: C, 77.61; H, 8.29. Found: C, 77.62; H, 8.19.

(2S)-2-(4'-Bromophenyl)-2-(1''R,2''S,5''R)-menthlyoxyacetic acid (8h)

TFA (2.5 mL), (2S)-7h (0.60 g, 1.4 mmol) and DCM (5mL) were used following the procedure for 8a to give, following column chromatography on silica gel employing hexane/ethyl acetate (95:5) as the eluent, the acid 8h (0.36 g, 70%) as a colourless oily solid. Spec. Rot.: [α]_D^20 = −9.1 (c 1.7, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ= 0.71–1.04 (12H, m, contains, 3H, m, 3H, d, J 6.8 at 0.79, 3H, d, J 6.6 at 0.86 and 3H, d, J 7.0 at 0.93), 1.22–1.40 (2H, m), 1.58–1.71 (2H, m), 1.93 (1H, bd, J 11.6), 2.31–2.47 (1H, m), 3.34 (1H, td, J 10.5, 4.1), 5.01 (1H, s), 7.34 (2H, d, J 8.4), 7.47 (2H, d, J 8.3), 11.10 (1H, bs); ^13C NMR (100.6 MHz, CDCl_3): δ= 16.0, 21.2, 22.3, 23.0, 25.3, 31.5, 34.3, 40.5, 48.5, 77.4, 79.4, 122.8, 128.8, 131.7, 136.2, 176.5; IR (neat): 3500–2200 (COOH), 2921, 1718 (CO), 1487, 1011, 813; Elemental Analysis: calcd (%) for C_{18}H_{25}O_{3}Br: 58.54; H, 6.82. Found: 58.21; H, 6.97.

2.7 Dirhodium carboxylate synthesis

Sodium rhodium carbonate [Na_4Rh_2(CO_3)_4·2.5H_2O]^{14} (S16)

Rhodium acetate dimer (1.50 g, 3.4 mmol) in aqueous sodium carbonate (2M, 25 mL) was heated under reflux for 1 h. The resulting mixture was cooled to room temperature, filtered and washed with water (20 mL), methanol (20 mL) and diethyl ether (20 mL) to give the sodium salt of rhodium carbonate S16 (1.92 g, 97%) as a blue purple solid.

*Note: Four ligands surround the dirhodium unit throughout with just one shown for clarity.
SUPPORTING INFORMATION

**Dirhodium tetrakis [(2S)-2-(1′′R,2′′R,4′′S)-fenchyloxy-2-phenylacetate] (2S-FPA) (9a)**

Sodium rhodium carbonate [Na₄Rh₂(CO₃)₄·2.5H₂O] S16 (98 mg, 0.17 mmol) and (2S)-8a (0.39 g, 1.3 mmol) were added to water (20 mL) and refluxed overnight. The solution was cooled, extracted with DCM (3 × 30 mL) and the combined organic extracts were washed with saturated sodium bicarbonate solution (2 × 30 mL), brine (30 mL), dried over MgSO₄ and concentrated. Following purification by column chromatography on silica gel employing hexane/ethyl acetate (92:8) as the eluent, the rhodium complex 9a (70 mg, 31%) was isolated as a green oil.

**1H NMR (400 MHz, CDCl₃):** δ = 0.79–0.99 (11H, m, contains 2H, m, 3H, s at 0.81, 3H, s at 0.85 and 3H, s at 0.94), 1.22–1.38 (2H, m), 1.55–1.61 (1H, m), 1.63–1.79 (2H, m), 2.49 (1H, bs), 4.44 (1H, s), 7.11–7.26 (5H, m); **13C NMR (100.6 MHz, CDCl₃):** δ = 20.1, 20.9, 26.1, 26.2, 30.9, 39.8, 41.1, 48.5, 49.4, 82.0, 91.5, 126.8, 127.6, 128.0, 138.3, 191.7; **IR (neat):** 2947, 2869, 1689 (weak), 1602 (strong), 1400, 1129, 733.

Ethyl acetate (1.4 mol/Rh dimer) and water (0.8 mol/Rh dimer) were observed in the NMR spectra of compound 9a as axial ligands; ethyl acetate: δ_H 1.29 (t), 2.04 (s), 4.22 (q); δ_C 14.2, 20.9, 60.9, 173.0; H₂O: δ_H 2.25.

**Dirhodium tetrakis [(2S)-2-(1′′R,2′′R,4′′S)-fenchyloxy-2-(naphthalen-2′-yl)acetate] (2S-F-2′-NA) (9b)**

Sodium rhodium carbonate S16 (0.24 g, 0.41 mmol), 8b (1.10 g, 3.3 mmol) and water (50 mL) were used following the procedure for 9a to give, following purification by column chromatography on silica gel employing hexane/ethyl acetate (92:8) as the eluent, the rhodium complex 9b (0.50 g, 79%) as a green foamy solid. **Spec. Rot.:** [α]D₂₀ = +59.8 (c 0.2, CHCl₃); **1H NMR (400 MHz, CDCl₃):** δ = 0.64 (3H, s), 0.73–0.97 (8H, m, contains 2H, m and 2 x 3H, s at 0.89, 0.91), 1.06–1.13 (1H, m), 1.24–1.36 (1H, m), 1.52–1.57 (1H, m), 1.62–1.73 (2H, m), 2.45 (1H, bs), 4.47 (1H, s), 7.16 (1H, dd, J 8.6, 1.2), 7.39–7.52 (3H, m), 7.57 (1H, d, J 8.6), 7.69–7.77 (2H, m); **13C NMR (100.6 MHz, CDCl₃):** δ = 19.9, 20.9, 26.1, 31.0, 39.8, 41.0, 48.5, 49.2, 82.1, 91.6, 124.4, 125.89, 125.94, 126.1, 127.6, 128.2, 132.9, 135.5, 191.7; **IR (neat):** 2927, 1685 (weak), 1605 (strong), 1402, 1014, 756; **HRMS (ESI-TOF):** m/z [M+CH₃CN+H₂O+H]⁺ calcd for C₉₀H₁₀₆NO₁₃Rh₂, 1614.5769, found 1614.4830.

Ethyl acetate (0.8 mol/Rh dimer) and water (2 mol/Rh dimer) were observed in the NMR spectra of compound 9b as axial ligands; ethyl acetate: δ_H 1.27 (t), 2.04 (s), 4.17 (q); δ_C 14.2, 21.0, 60.7; H₂O: δ_H 1.85.
SUPPORTING INFORMATION

**Dirhodium tetrakis [(2S)-2-(1″R,2″R,4″S)-fenchyloxy-2-(naphthalen-1′-yl)acetate] (2S-F-1‘-NA) (9c)**

Sodium rhodium carbonate S16 (37 mg, 0.06 mmol), 8c (0.17 g, 0.51 mmol) in water (10 mL) were used following the procedure for 9a to give, after purification by column chromatography on silica gel employing hexane/ethyl acetate (92:8) as the eluent, the rhodium complex 9c (70 mg, 31%) as a green oil. Spec. Rot.: \([\alpha]_{D}^{20} = +92.6 \ (c \ 0.29, \ CHCl_3)\); \(^1H\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 0.67–0.93 \ (7H, m, \text{contains } 1H, m, 3H, s \text{ at } 0.73 \text{ and } 3H, s \text{ at } 0.86), 0.94–0.99 \ (1H, m), 1.07 \ (3H, s), 1.21–1.41 \ (2H, m), 1.50–1.70 \ (3H, m), 2.71 \ (1H, bs), 4.74 \ (1H, s), 7.15 \ (1H, d, J 6.9), 7.33 \ (2H, t, J 7.6), 7.42 \ (1H, t, J 7.6), 7.65 \ (1H, d, J 8.5), 7.75 \ (1H, d, J 8.1), 7.81 \ (1H, d, J 8.0); \(^{13}C\) NMR (100.6 MHz, CDCl\(_3\)): \(\delta = 20.0, 21.0, 26.0, 26.1, 31.2, 40.0, 41.2, 48.6, 49.3, 79.2, 93.0, 124.7, 125.1, 125.3, 125.8, 125.9, 128.28, 128.31, 131.0, 133.6, 134.9, 191.1; IR (neat): 2947, 2869, 1684 (weak), 1605 (strong), 1388, 1118, 773; HRMS (ESI-TOF): m/z [M+CH\(_3\)CN+H\(_2\)O\]^+ calcd for C\(_90\)H\(_{105}\)NO\(_{13}\)Rh\(_2\), 1613.5691, found 1613.5752.

Ethyl acetate (1.4 mol/Rh dimer) and water (0.9 mol/Rh dimer) were observed in the NMR spectra of compound 9c as axial ligands; ethyl acetate: \(\delta_H = 0.80–1.03 \ (11H, m, \text{contains } 2H, m, 3 \times 3H, s, \text{one at } 0.84 \text{ and two at } 0.91), 1.22–1.41 \ (2H, m), 1.56–1.77 \ (3H, m), 2.46 \ (1H, d, J 1.4), 4.40 \ (1H, s), 7.06 \ (2H, d, J 8.4), 7.36 \ (2H, d, J 8.5); IR (neat): 2948, 2858, 1685 (weak), 1605 (strong), 1386, 1129, 1010, 770.

**Dirhodium tetrakis [(2S)-2-(4′-bromophenyl)-2-(1″R,2″R,4″S)-fenchyloxyacetate] (2S-FBrPA) (9d)**

Sodium rhodium carbonate S16 (0.26 g, 0.45 mmol), 8d (1.33 g, 3.6 mmol) in water (50 mL) were used following the procedure for 9a to give, after purification by column chromatography on silica gel employing hexane/ethyl acetate (92:8) as the eluent, the rhodium complex 9d (0.47 g, 62%) as a green solid. Spec. Rot.: \([\alpha]_{D}^{20} = +17.6 \ (c \ 0.21, \ CHCl_3)\); \(^1H\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 0.80–1.03 \ (11H, m, \text{contains } 2H, m, 3 \times 3H, s, \text{one at } 0.84 \text{ and two at } 0.91), 1.22–1.41 \ (2H, m), 1.56–1.77 \ (3H, m), 2.46 \ (1H, d, J 1.4), 4.40 \ (1H, s), 7.06 \ (2H, d, J 8.4), 7.36 \ (2H, d, J 8.5); \(^{13}C\) NMR (100.6 MHz, CDCl\(_3\)): \(\delta = 20.1, 20.9, 26.0, 26.1, 31.0, 39.8, 41.0, 48.4, 49.3, 81.2, 92.0, 121.8, 128.4, 131.2, 137.0, 191.3; IR (neat): 2948, 2858, 1685 (weak), 1604 (strong), 1386, 1129, 1010, 770.

Ethyl acetate (0.4 mol/Rh dimer) and water (1.8 mol/Rh dimer) were observed in the NMR spectra of compound 9d as axial ligands; ethyl acetate: \(\delta_H = 1.30 \ (t), 2.06 \ (s), 4.23 \ (q); \delta_C = 14.2, 21.0, 60.9; H_2O: \delta_H = 2.16.\)
Dirhodium tetrakis [(2S)-2-(1"R,2"R,4"S)-fenchyloxy-2-(4'-methoxyphenyl)acetate] (2S-FMeOPA) (9e)

Sodium rhodium carbonate S16 (84 mg, 0.14 mmol), 8e (0.37 g, 1.15 mmol) in water (20 mL) were used following the procedure for 9a to give, after purification by column chromatography on silica gel employing hexane/ethyl acetate (90:10) as the eluent, the rhodium complex 9e (85 mg, 40%) as a green oil. Spec. Rot.: [α]$_D^{20}$ = +45.4 (c 0.23, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): δ = 0.78–1.00 (11H, m, contains 2H, m, 3×3H, s at 0.83, 0.91 and 0.93), 1.24–1.37 (2H, m), 1.53–1.61 (1H, m), 1.62–1.78 (2H, m), 2.48 (1H, bs), 3.75 (3H, s), 4.43 (1H, s), 6.76 (2H, d, J 8.6), 7.12 (2H, d, J 8.7); $^{13}$C NMR (100.6 MHz, CDCl$_3$): δ = 20.0, 20.9, 26.1, 26.2, 30.9, 39.8, 41.1, 48.5, 49.3, 55.1, 81.4, 91.3, 113.3, 128.0, 130.5, 158.9, 191.7; IR (neat): 2949, 2869, 1691 (weak), 1604 (strong), 1511, 1247, 1100; HRMS (ESI-TOF): m/z [M+CH$_3$CN+H$_2$O+H]$^+$ calcd for C$_{78}$H$_{105}$NO$_{17}$Rh$_2$, 1534.5565, found 1534.4889.

Ethyl acetate (1.4 mol/Rh dimer) and water (0.9 mol/Rh dimer) were observed in the NMR spectra of compound 9e as axial ligands; ethyl acetate: δ$_H$ 1.30 (t), 2.07 (s), 4.24 (q); δ$_C$ 14.2, 21.0, 61.0, 173.1; H$_2$O: δ$_H$ 2.59.

Dirhodium tetrakis [(2S)-2-(1"R,2"S,5"R)-menthylxylo-2-phenylacetate] (2S-MPA) (9f)

Sodium rhodium carbonate S16 (0.12 g, 0.2 mmol), 8f (0.47 g, 1.6 mmol) in water (25 mL) were used following the procedure for 9a to give, after purification by column chromatography on silica gel employing hexane/ethyl acetate (90:10) as the eluent, the rhodium complex 9f (0.11 g, 40%) as a foamy green solid. Spec. Rot.: [α]$_D^{20}$ = −41.8 (c 0.2, CHCl$_3$); $^1$H NMR (300 MHz, CDCl$_3$): δ = 0.65 (1H, q, J 11.1), 0.73–0.99 (11H, m, contains, 2H, m, 3H, d, J 6.9 at 0.77, 3H, d, J 6.5 at 0.82 and 3H, d, J 7.0 at 0.91), 1.10–1.24 (2H, m), 1.53–1.66 (2H, m), 1.72–1.83 (1H, m), 2.35–2.49 (1H, m), 2.89 (1H, td, J 10.3, 3.9), 4.53 (1H, s), 7.07–7.14 (2H, m), 7.17–7.24 (3H, m); $^{13}$C NMR (75.5 MHz, CDCl$_3$): δ = 16.5, 21.3, 22.3, 23.1, 24.9, 31.3, 34.5, 40.3, 48.6, 78.2, 78.6, 126.9, 127.6, 128.1, 139.1, 191.6; IR (neat): 2922, 1602, 1398, 1099, 754; HRMS (ESI-TOF): m/z [M+CH$_3$CN+H$_2$O+H]$^+$ calcd for C$_{74}$H$_{106}$NO$_{13}$Rh$_2$, 1422.6068, found 1422.6068.

Ethyl acetate (0.8 mol/Rh dimer) and water (1.2 mol/Rh dimer) were observed in the NMR spectra of compound 9f as axial ligands; ethyl acetate: δ$_H$ 1.28 (t), 2.07 (s), 4.19 (q); δ$_C$ 14.2, 21.0, 60.8, 172.5; H$_2$O: δ$_H$ 2.81.
SUPPORTING INFORMATION

Dirhodium tetrakis [(2S)-2-(1”R,2”S,5”R)-menthloxy-2-(naphthalen-2’-yl)acetate]
(2S-M-2'NA) (9g)

Sodium rhodium carbonate S16 (0.11 g, 0.18 mmol), 8g (0.50 g, 1.4 mmol) in water (20 mL) were used following the procedure for 9a to give, after purification by column chromatography on silica gel employing hexane/ethyl acetate (92:8) as the eluent, the rhodium complex 9g (55 mg, 29%) as a green oil. Spec. Rot.:  \([\alpha]^D_{20} = -9.5 \ (c \ 0.2, CHCl_3)\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 0.56 \ (1H, q, J_{11.2}), 0.65 - 0.99 \ (11H, m, contains, 2H, m, 3H, d, J 6.4 at 0.72, 3H, d, J 6.8 at 0.75, and 3H, d, J 7.0 at 0.91), 1.11 - 1.34 \ (2H, m), 1.45 - 1.67 \ (3H, m), 2.37 - 2.50 \ (1H, m), 2.79 \ (1H, td, J 10.3, 3.9), 4.52 \ (1H, s), 7.09 \ (1H, dd, J 8.5, 1.2), 7.39 - 7.48 \ (3H, m), 7.52 \ (1H, d, J 8.5), 7.72 \ (2H, d, J 7.8); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)): \(\delta = 16.5, 21.3, 22.3, 23.1, 24.9, 31.2, 34.4, 40.4, 48.5, 78.8, 79.3, 124.6, 125.8, 125.88, 125.89, 125.97, 127.64, 128.2, 132.9, 133.0, 136.5, 191.6; IR (neat): 2923, 1688 (weak), 1608 (strong), 1401, 1106, 758; HRMS (ESI-TOF): m/z [M+CH\(_3\)CN+H\(_2\)O+H\]^+ calcd for C\(_{90}H\(_{114}\)N\(_8\)O\(_{13}\)Rh\(_2\), 1622.6395, found 1622.6412.

Ethyl acetate (0.7 mol/Rh dimer) and water (1.2 mol/Rh dimer) were observed in the NMR spectra of compound 9g as axial ligands; ethyl acetate: \(\delta_H 1.28 \ (t), 2.02 \ (s), 4.19 \ (q); \delta_C 14.2, 21.0, 60.6; H\(_2\)O: \(\delta_H 2.49\).

Dirhodium tetrakis [(2S)-2-(4’-bromophenyl)-2-(1”R,2”S,5”R)-menthloxyacetate]
(2S-MBrPA) (9h)

Sodium rhodium carbonate S16 (58 mg, 0.10 mmol), 8h (0.29 g, 0.79 mmol) in water (15 mL) were used following the procedure for 9a to give, after purification by column chromatography on silica gel employing hexane/ethyl acetate (95:5) as the eluent, the rhodium complex 9h (73 mg, 50%) as a green solid. Spec. Rot.:  \([\alpha]^D_{20} = -23.0 \ (c \ 0.12, CHCl_3); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 0.71 - 1.04 \ (12H, m, contains, 3H, m, 3H, d, J 6.8 at 0.72, 3H, d, J 6.4 at 0.75, and 3H, d, J 7.0 at 0.93), 1.11 - 1.35 \ (2H, m), 1.55 - 1.66 \ (2H, m), 1.68 - 1.97 \ (1H, m), 2.31 - 2.44 \ (1H, m), 2.86 \ (1H, td, J 10.3, 3.8), 4.45 \ (1H, s), 6.99 \ (2H, d, J 8.3), 7.35 \ (2H, d, J 8.4); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)): \(\delta = 16.5, 21.2, 22.3, 23.1, 25.0, 31.4, 34.4, 40.4, 48.5, 77.8, 79.4, 121.7, 128.5, 131.2, 138.0, 191.3; IR (neat): 2952, 2921, 1604, 1388, 1011, 772; HRMS (ESI-TOF): m/z [M+CH\(_3\)CN+H\(_2\)O]^+ calcd for C\(_{74}H\(_{101}\)Br\(_4\)NO\(_{18}\)Rh\(_2\), 1737.2070, found 1737.2301.

Ethyl acetate (0.2 mol/Rh dimer) and water (0.8 mol/Rh dimer) were observed in the NMR spectra of compound 9h as axial ligands; ethyl acetate: \(\delta_H 1.30 \ (t), 2.04 \ (s), 4.21 \ (q); \delta_C 14.2, 20.9, 60.9, 173.0; H\(_2\)O: \(\delta_H 2.49\).
3. Synthesis of 2,3-dihydrobenzofurans

3.1 Ester Synthesis

**Methyl 2-(2-(benzyloxy)phenyl)acetate**\(^{[15]}\) (S17)

![Methyl 2-(2-(benzyloxy)phenyl)acetate](image)

Concentrated sulfuric acid (1 mL) was added to a stirring solution of 2-(2-(benzyloxy)phenyl)acetic acid (4.70 g, 19.39 mmol) in methanol (50 mL) and the reaction mixture was heated under reflux for 3 h. The reaction mixture was cooled to room temperature followed by addition of anhydrous sodium bicarbonate (1.5 g). The mixture was filtered and concentrated under reduced pressure to afford methyl 2-(2-(benzyloxy)phenyl)acetate S17 (4.65 g, quantitative) as a pale yellow oil which was used without further purification. Spectroscopic characteristics were consistent with previously reported data.\(^{[15]}\)

\[\text{H NMR (300 MHz, CDCl}_3\text{): } \delta = 3.63 (3H, s), 3.69 (2H, s), 5.08 (2H, s), 6.87–6.98 (2H, m), 7.18–7.45 (7H, m); \text{IR (neat): } 2950, 1736 (C=O), 1244, 1156, 1015, 750, 696.\]

**Benzyl 2-(2-(benzyloxy)phenyl)acetate**\(^{[16]}\) (S18)

![Benzyl 2-(2-(benzyloxy)phenyl)acetate](image)

Anhydrous potassium carbonate (10.60 g, 77 mmol) was added in one portion to a stirring solution of 2-(2-hydroxyphenyl)acetic acid (5.0 g, 33.0 mmol) in \(N,N\)-dimethylformamide (75 mL) at room temperature. Neat benzyl bromide (7.8 mL, 66 mmol) was added dropwise to the reaction mixture followed by stirring at room temperature for 24 h. The reaction mixture was diluted with ether (100 mL) and water (50 mL), followed by gradual addition of aqueous hydrochloric acid (2.0 M, 100 mL). The layers were separated and the aqueous layer was extracted using ether (3 × 100 mL). The combined organic extracts were washed with aqueous hydrochloric acid (2.0 M, 2 × 75 mL), water (75 mL) and brine (75 mL), dried using magnesium sulfate and concentrated under reduced pressure to give the crude dibenzylated ester as a pale pink solid. The crude product was recrystallized from hot acetonitrile to give the purified dibenzylated ester S18 (8.02 g, 73%) as a white solid. Spectroscopic characteristics were consistent with previously reported data.\(^{[16]}\)

\[\text{m.p. } 72–75 \degree C (\text{Lit. } 74.4–74.6 \degree C); \text{H NMR (400 MHz, CDCl}_3\text{): } \delta = 3.73 (2H, s), 5.04 (2H, s), 5.08 (2H, s), 6.88–6.97 (2H, m), 7.18–7.42 (12H, m); \text{IR (neat): } 1735 (\text{CO}), 1173, 1013, 728.\]
3.2 α-Diazo ester synthesis

Methyl 2-(2-(benzyl oxy)phenyl)-2-diazoacetate[17] (10)

\[
\text{N}_2\quad \text{CO}_2\text{Me}
\]

\[
\begin{align*}
p-\text{ABSA} & (7.26\, \text{g}, 30\, \text{mmol}), \text{methyl 2-}(2-\text{(benzyl oxy)phenyl})\text{-acetate S17} & (2.56\, \text{g}, 10\, \text{mmol}), \text{DBU} \\
& (6.25\, \text{mL}, 42\, \text{mmol}) \text{ and DMSO} & (30\, \text{mL}) \text{ were used following the procedure described for 6a to}
\end{align*}
\]

give, following column chromatography on silica gel employing hexane/ethyl acetate (90:10) as the eluent, to give α-diazo ester 10 (2.71 g, 80%) as a yellow oil. Spectroscopic characteristics were consistent with previously reported data.[17] ^1H NMR (400 MHz, CDCl3): ‚δ= 3.82 (3H, s), 5.10 (2H, s), 6.97 (1H, d, J 8.2), 7.03 (1H, t, J 7.6), 7.18–7.27 (1H, m), 7.29–7.44 (5H, m), 7.57 (1H, dd, J 7.8, 1.4); ^13C NMR (100.6 MHz, CDCl3): ‚δ= 52.0, 59.8, 70.7, 112.2, 114.0, 121.5, 127.5, 128.1, 128.6, 130.4, 136.3, 154.7, 166.7; IR (neat): 2951, 2093 (CN₂), 1694 (CO), 1247, 745, 696.

Benzyl 2-(2-(benzyl oxy)phenyl)-2-diazoacetate (12)

\[
\text{N}_2\quad \text{CO}_2\text{Bn}
\]

\[
\begin{align*}
p-\text{ABSA} & (2.17\, \text{g}, 9\, \text{mmol}), \text{benzyl 2-}(2-\text{(benzyl oxy)phenyl})\text{-acetate S18} & (1.38\, \text{g}, 4.2 \text{mmol}), \text{DBU} \\
& (2.0\, \text{mL}, 14\, \text{mmol}) \text{ and DMSO} & (20\, \text{mL}) \text{ were used following the procedure described for 6a to give, following column chromatography on silica gel employing hexane/ethyl acetate (90:10) as the eluent, α-diazo ester 12 (1.25 g, 83%) as an yellow oil; ^1H NMR (400 MHz, CDCl3): ‚δ= 5.10 (2H, s), 5.28 (2H, s), 6.97 (1H, d, J 8.3), 7.03 (1H, td, J 7.6, 1.0), 7.20–7.24 (1H, m), 7.59 (1H, dd, J 7.7, 1.4); ^13C NMR (100.6 MHz, CDCl3): ‚δ= 59.9, 66.4, 70.7, 112.2, 114.0, 121.5, 127.6, 128.10, 128.15, 128.18, 128.56, 128.58, 128.61, 130.4, 136.1, 136.3, 154.7, 166.1; IR (neat): 2093 (CN₂), 1693 (CO), 1242, 1147, 1009, 741, 694; HRMS (ESI-TOF): m/z [M+H]+ calcd for C_{22}H_{19}N_{2}O_{3} 359.1396, found 359.1391.}
\end{align*}
\]

Isopropyl 2-(2-(benzyl oxy)phenyl)-2-diazoacetate (13)

\[
\text{N}_2\quad \text{CO}_2\text{Pr}
\]

\[
\begin{align*}
\text{Elemental sodium (0.14 g, 6 mmol) was added to IPA (20 mL) at 0 °C. The mixture was} \\
\text{removed from the ice bath and stirred at room temperature for 30 minutes. Benzyl 2-}(2-\text{(benzyl oxy)phenyl})\text{-2-diazoacetate 12 (0.1 g}, 2.8 \text{mmol}) \text{ was dissolved in IPA (20 mL) and added to the stirring sodium isoproproxide solution. The resulting solution was stirred at room temperature for 48 h then it was evaporated onto silica gel and following column chromatography on silica gel employing hexane/ethyl acetate (95:5) as the eluent, α-diazo ester 13 (0.49 g, 57%) was isolated as a yellow oil; ^1H NMR (400 MHz, CDCl3): ‚δ= 1.29, (6H, d, J 6.2), 5.10 (2H, s), 5.16 (1H, septet, J 6.3), 6.96 (1H, d, J 8.2), 7.03 (1H, t, J 7.0, with further unresolved splitting), 7.18–7.25 (1H, m), 7.30–7.47 (5H, m), 7.59 (1H, dd, J 7.8, 1.4); ^13C NMR (100.6 MHz, CDCl3): ‚δ= 22.1, 68.5, 70.7, 112.2, 114.3, 121.4, 127, 128, 128.3, 128.6, 130.3, 136.4, 154.6, 165.9; IR (neat): 2093 (CN₂), 1692 (CO), 1244, 1003, 746, 696; HRMS (ESI-TOF): m/z [M+H]+ calcd for C_{18}H_{19}N_{2}O_{3} 311.1396, found 311.1390.}
\end{align*}
\]
3.3 Rhodium Catalysed C–H Insertion Reactions - 2,3-Dihydrobenzofuran Synthesis

Table SI.1: Investigation of reaction conditions on the cyclisation of 10

| Entry | Solvent | Atmospheric Conditions | Temperature (°C) | 11a:11b:S19
|-------|---------|------------------------|-----------------|------------------|
| 1     | toluene | under N₂                | rt              | 53:32:15<sup>c</sup> |
| 2     | DCM     | under N₂                | rt              | 1.3:0.7:98<sup>d</sup> |
| 3     | toluene | under N₂                | −60→rt<sup>e</sup> | 0.8:0.8:98.4     |
| 4     | toluene | open to air             | rt              | 0.7:0.8:98.5     |
| 5     | toluene | Schlenk                 | rt              | 46:28:26         |
| 6     | toluene | degassed solvent, Schlenk | rt          | 60:35:5          |

<sup>a</sup>The general procedure for the Rh₂(OAc)₄ catalysed C–H insertion involved the dropwise addition of a solution of aryl diazoacetate (in 8 mL solvent) to a stirring suspension of rhodium acetate (in 3 mL solvent). Reactions were monitored by IR spectroscopy and were generally complete within 30 min. <sup>b</sup>The ratio of 11a:11b:S19 was determined by the relative integration of signals at δ<sub>H</sub> 6.12 (1H, d), 5.99 (1H, d) and 7.91 (1H, dd) ppm, respectively, in the <sup>1</sup>H NMR spectra of the crude reaction mixtures. <sup>c</sup>Experiment was repeated and the ratio of 11a:11b:S19 was 58:35:7. <sup>d</sup>Experiment was repeated and the ratio of 180a:180b:S19 was 2:1.5:96.5. <sup>e</sup>The reaction mixture was found to still contain aryldiazoacetate (by IR spectroscopy of a sample withdrawn) after 1.5 h stirring between −50 °C and −60 °C so was allowed to warm up to room temperature over 30 min.

Procedure A:

General procedure for rhodium catalysed C–H insertion reactions to afford 2,3-dihydrobenzofuran

A solution of α-diazoacetate (0.10 g, 1 equiv.) in HPLC grade toluene or freshly distilled DCM (8 mL, further degassed using freeze, pump, thaw technique) was added dropwise via syringe pump over ~30 min to a stirring solution of rhodium(II) catalyst (1 mol%) in HPLC grade toluene or freshly distilled DCM (3 mL). The reaction was carried out at 0–3 °C or −45 °C using Schlenk techniques. The mixture was stirred at this temperature for 30 minutes after addition was complete. The mixture was then concentrated under reduced pressure to provide the crude product(s), a <sup>1</sup>H NMR spectrum obtained and following column chromatography on silica gel (25 g) employing hexane/ethyl acetate (99:1) as the eluent, both isomers of the dihydrobenzofuran were isolated. The less polar trans isomers were isolated as colourless oils while the more polar cis isomers were found to be white solids.
3-Methoxycarbonyl-2-phenyl-2,3-dihydrobenzofuran\textsuperscript{[17]} (11)

The title compound was prepared according to Procedure A from methyl 2-(2-(benzyloxy)phenyl)-2-diazoacetate 10 (100 mg, 0.35 mmol) and Rh\textsubscript{2}(2S-M-2′-NA)\textsubscript{4} 9g (6 mg, 1 mol%) in toluene (11 mL) at −45 °C.

\((2R,3R)\)-trans-3-Methoxycarbonyl-2-phenyl-2,3-dihydrobenzofuran\textsuperscript{[17]} (11a)

Spectroscopic characteristics were consistent with previously reported data.\textsuperscript{[17]} 11a, Colourless oil (45.2 mg, 50%); Spec. Rot.: \(\text{[}\alpha\text{]}_{D}^{21} = -67.6 (c 1.39, \text{CHCl}_3)\) [lit. \(\text{[}\alpha\text{]}_{D}^{21} = -58.2 (c 1.12, \text{CHCl}_3)\)] for 80% ee of (2\(R\),3\(R\))-11a; HPLC: 86% ee (determined by chiral phase HPLC, see Table SI.6 for HPLC conditions); \(\text{H}^1\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 3.82 (3\text{H, s}), 4.29 (1\text{H, d, J 7.4}), 6.12 (1\text{H, d, J 7.4}), 6.86 – 6.98 (2\text{H, m}), 7.20 – 7.29 (1\text{H, m}), 7.29 – 7.46 (6\text{H, m}); \text{IR (neat): 2922, 1736 (CO), 1478, 1234, 748.}\)

The preferred absolute configuration of 11a was determined to be (2\(R\),3\(R\)) by comparison of the recorded optical rotation values and HPLC data with literature reports.

\((2S,3R)\)-cis-3-Methoxycarbonyl-2-phenyl-2,3-dihydrobenzofuran\textsuperscript{[17]} (11b)

Spectroscopic characteristics were consistent with previously reported data.\textsuperscript{[17]} 11b, white solid (3.5 mg, 4%); m.p. 90 – 92 °C [lit. 90 – 91 °C]; Spec. Rot.: \(\text{[}\alpha\text{]}_{D}^{21} = -16.3 (c 0.01, \text{CHCl}_3)\) [lit. \(\text{[}\alpha\text{]}_{D}^{21} = +57.9 (c 1.00, \text{CHCl}_3)\)] for 70% ee of (2\(S\),3\(S\))-11b; HPLC: 18% ee (determined by chiral phase HPLC, see Table SI.6 for HPLC conditions); \(\text{H}^1\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 3.21 (3\text{H, s}), 4.62 (1\text{H, d, J 9.8}), 5.99 (1\text{H, d, J 9.8}), 6.91 – 7.00 (2\text{H, m}), 7.20 – 7.45 (7\text{H, m}); \text{IR (neat): 2980, 1727 (CO), 1480, 1104, 748.}\)

The preferred absolute configuration of 11b was determined to be (2\(S\),3\(R\)) by specific rotation and HPLC analysis following conversion to (2\(S\),3\(S\))-11a (vide infra).

Isomerization Reaction: Preparation of (2\(S\),3\(S\))-11a from (2\(S\),3\(R\))-11b

To a solution of 11b (8.9 mg, 0.035 mmol, 33% ee) in THF (0.8 mL) at −45 °C was added a solution of NaOMe in MeOH (0.1 M, 0.08 mL, 0.008 mmol, 0.44 eq). After 0.5 h of stirring at −45 °C, the reaction was quenched with saturated ammonium chloride solution (3 mL) and the whole mixture was extracted with EtOAc (3 x 6 mL). The combined organic extracts were washed with water (2 x 5 mL) and brine (2 x 5 mL), and dried over anhydrous MgSO\(_4\). Filtration and evaporation furnished the crude product (8.8 mg as colorless oil), \(\text{[}\alpha\text{]}_{D}^{20} = +13.90 (c 0.41, \text{CHCl}_3)\). The enantiomeric excess of 11a was determined to be 33% by chiral HPLC analysis (vide supra).
**SUPPORTING INFORMATION**

**Methyl 2-(2-(benzyloxy)phenyl)-2-oxoacetate[^18]** (S19)

Spectroscopic characteristics were consistent with previously reported data.[^18] White solid; m.p. 84–86 °C [Lit. 84–85 °C].[^18] ¹H NMR (400 MHz, CDCl₃): δ = 3.34 (3H, s), 5.08 (2H, s), 7.03–7.13 (2H, m), 7.32–7.47 (5H, m), 7.54–7.62 (1H, m), 7.91 (1H, dd, J 7.7, 1.4); ¹³C NMR (100.6 MHz, CDCl₃): δ = 51.9, 71.3, 112.8, 121.5, 122.8, 128.5, 128.6, 128.7, 131.0, 135.2, 136.3, 159.5, 165.5, 186.5; IR (neat): 1739 (CO), 1665, 1596 (CO), 1274, 1009, 751, 698; HRMS (ESI-TOF): m/z [M+H]⁺ calcd for C₂₈H₂₈O₄, 271.0970, found 287.0973.

**Table SI.2: Investigation of reaction conditions in the enantioselective cyclisation of 12**

| Entry | Catalyst     | Temp (°C) | 14a:14b:S20:S21 | Yieldc | Enantiopurityd,e |
|-------|--------------|-----------|-----------------|--------|-----------------|
| 1'    | Rh₂(S-PTTL)₄ 3 | -45       | 1.2:1.5:97.3:0   | -      | -               |
| 2'    | Rh₂(S-PTTL)₄ 3 | -20       | 0.7:1.3:5:93     | -      | -               |
| 3'    | Rh₂(S-PTTL)₄ 3 | -5        | 0.7:4.5:5.7:89.1 | -      | -               |
| 4     | Rh₂(S-PTTL)₄ 3 | 0–3       | 1:61.5:9:28.5g   | -69    | 98h             |
| 5     | Rh₂(S-PTTL)₄ 3 | 0–3       | 1:51.5:11:36i    | -55    | -               |
| 6     | Rh₂(2S-MPA)₄ 9f | -45       | 3:9.2:1:12:3:81.7i | 3      | 1               |
| 7     | Rh₂(2S-MPA)₄ 9f | 0–3       | 48.5:28:7:5:16j  | 18     | 78              |
| 8'    | Rh₂(2S-M-2'-NA)₄ 9g | -45 | 9:7:8:19:2:64j | -k     | -k              |
| 9     | Rh₂(2S-M-2'-NA)₄ 9g | 0–3       | 54.5:19.5:9:17m  | 26     | 8               |
| 10    | Rh₂(2S-F-1'-NA)₄ 9c | 0–3       | 5:9:7:4:13i      | 3      | 42              |
| 11    | Rh₂(2S-FBrPA)₄ 9d | 0–3       | 56:28:8:5:10.2i  | 27     | 10              |

[^18]: Reactions conducted using the general Procedure A for rhodium-catalysed C–H insertion reactions. The ratio of 14a:14b:S20:S21 was determined by the relative integration of signals at 6.13 (1H, d), 5.98 (1H, d), 7.93 (1H, dd) and 5.41 (1H, d), respectively, in the ¹H NMR spectra of the crude reaction mixtures. Isolated yield following column chromatography. Enantiopurity determined by chiral stationary phase HPLC (see Table SI.6 for further details). Stereochemical assignments made by analogy to 11a and 11b. Crude reaction mixture not purified. Crude reaction mixture contains ~10% unknown side-product. Stereochemistry assigned as 2R,3S by analogy to 11b. Crude reaction mixture contained ~5% unknown side-product. Crude reaction mixture contained ~40% unknown side-product. A sample of sufficient purity to allow accurate determination of enantiopurity was not isolated. Crude reaction mixture contained ~20% unknown side-product. Crude reaction mixture contained ~50% unknown side-product. Stereochemistry assigned as 2R,3R by analogy to 11a. Stereochemistry assigned as 2S,3R by analogy to 11b.
3-Benzyloxy carbonyl-2-phenyl-2,3-dihydrobenzofuran (14)

The title compound was prepared according to Procedure A from benzyl 2-(2-benzyloxyphenyl)-2-diazoacetate 12 (100 mg, 0.28 mmol) and Rh₂(2S-MPA)₄ 9f (4 mg, 1 mol%) in toluene (11 mL).

(2R,3R)-trans-3-Benzylcarbamoyl-2-phenyl-2,3-dihydrobenzofuran (14a)

Colourless oil (50 mg, 54%); Spec. Rot.: [α]₂⁰ = −76.2 (c 2.11, CHCl₃); HPLC: 79% ee (determined by chiral phase HPLC, see Table SI.6 for HPLC conditions); ¹H NMR (400 MHz, CDCl₃): δ = 4.32 (1H, d, J = 7.5), 5.20–5.29 (2H, fine AB q, J = 12.5), 6.13 (1H, d, J = 7.5), 6.86–6.95 (2H, m), 7.20–7.28 (1H, m), 7.28–7.43 (11H, m, ArH); ¹³C NMR (100.6 MHz, CDCl₃): δ = 55.9, 67.5, 85.5, 110.0, 121.0, 123.7, 125.3, 125.8, 128.3, 128.4, 128.5, 128.7, 128.8, 129.7, 135.4, 140.6, 159.4, 170.7; IR (neat): 3034, 1733 (CO), 1478, 1232, 748, 696; HRMS (ESI-TOF): m/z [M+H]+ calcd for C₂₂H₁₉O₃, 331.1334, found 331.1345.
(2S,3R)-cis-3-Benzylloxycarbonyl-2-phenyl-2,3-dihydrobenzofuran (14b)

White solid (15 mg, 16%); m.p. 89–90 °C; Spec. Rot.: [α]_D^20 = −10.4 (c 0.47, CHCl₃); HPLC: 22% ee (determined by chiral phase HPLC, see Table SI.6 for HPLC conditions); ^1H NMR (400 MHz, CDCl₃): δ = 4.50 (1H, d, J 12.2), 4.64 (1H, d, J 9.8), 4.71 (1H, d, J 12.3), 5.98 (1H, d, J 9.8), 6.90–7.03 (4H, m), 7.19–7.40 (10H, m); ^13C NMR (100.6 MHz, CDCl₃): δ = 53.8, 66.7, 85.7, 110.0, 121.3, 124.8, 125.9, 126.4, 128.17, 128.25, 128.28, 128.4, 129.7, 135.2, 137.0, 160.4, 169.8; IR (neat): 3033, 1733 (CO), 1478, 1150, 748, 696; HRMS (ESI-TOF): m/z [M+H]^+ calcd for C₂₂H₁₉O₃, 331.1334, found 331.1345.

Methyl 2-(2-(benzyl oxy)phenyl)-2-oxoacetate (S20)

^1H NMR (400 MHz, CDCl₃): δ = 4.78 (2H, s), 4.99 (2H, s), 6.99–7.04 (1H, m), 7.05–7.12 (1H, m), 7.16–7.43 (10H, m), 7.52–7.60 (1H, m), 7.93 (1H, dd, J 7.8, 1.5).

Benzyl 2-(2-(benzyl oxy)phenyl)-2-hydroxyacetate (S21)

^1H NMR (400 MHz, CDCl₃): δ = 3.60 (1H, d, J 6.2, appears reduced in a D₂O shake), 4.94–5.07 (2H, ABq, J 11.9), 5.08–5.18 (2H, ABq, J 12.4), 5.41 (1H, d, J 4.3), 6.89–7.01 (2H, m), 7.11–7.19 (2H, m), 7.22–7.39 (10H, m); ^13C NMR (100.6 MHz, CDCl₃): δ = 67.2, 70.2, 70.3, 112.3, 121.1, 127.2, 127.9, 128.0, 128.2, 128.5, 128.6, 129.5, 129.9, 135.4, 136.5, 156.2, 173.5; IR (neat): 3100–3600, 1733 (CO), 1492, 1453, 1242, 1246, 752, 696.

3-Isopropylloxycarbonyl-2-phenyl-2,3-dihydrobenzofuran (15)

The title compound was prepared according to Procedure A from isopropyl 2-(2-benzylox yphenyl)-2-diazoacetate 13 (100 mg, 0.32 mmol) and Rh₂(2S-MPA)_4 9f (4 mg, 1 mol%) in toluene (11 mL).

(2R,3R)-trans-3-Isopropylloxycarbonyl-2-phenyl-2,3-dihydrobenzofuran (15a)

Colourless oil (31.8 mg, 35%); Spec. Rot.: [α]_D^20 = −53.6 (c 1.20, CHCl₃); HPLC: 78% ee (determined by chiral phase HPLC, see Table SI.6 for HPLC conditions); ^1H NMR (400 MHz, CDCl₃): δ = 1.30 (3H, d, J 6.2), 1.31 (3H, d, J 6.2), 4.23 (1H, d, J 7.7), 5.13 (1H, septet, J 6.3), 6.11 (1H, d, J 7.7), 6.86–6.97 (2H, m), 7.18–7.28 (1H, m), 7.28–7.45 (6H, m); ^13C NMR (100.6 MHz, CDCl₃): δ = 21.86, 21.89, 55.9, 69.3, 85.5, 109.9, 120.9, 124.2, 125.0, 125.8, 128.3, 128.8, 129.6, 140.8, 159.3, 170.3; IR (neat): 2981, 1729 (CO), 1492, 1453, 1242, 1246, 752, 696; HRMS (ESI-TOF): m/z [M+H]^+ calcd for C₁₈H₁₉O₃, 283.1314, found 283.1310.
(2S,3R)-cis-3-Isopropyl oxycarbonyl-2-phenyl-2,3-dihydrobenzofuran (15b)

White solid (15.4 g, 17%); m.p. 56–58 °C; Spec. Rot.: $\alpha_{D}^{20} = -12.6 \ (c\ 0.12, \ CHCl_3)$; HPLC: 27% ee (determined by chiral phase HPLC, see Table SI.6 for HPLC conditions); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.67 (3H, d, J 6.2), 0.92 (3H, d, J 6.3), 4.52–4.63 (2H, m, contains 1H, septet), 5.97 (1H, d, J 9.9), 6.91–6.99 (2H, m), 7.21–7.42 (7H, m); $^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$ = 20.9, 21.4, 53.7, 68.5, 85.6, 109.9, 121.2, 125.1, 125.9, 126.6, 128.2, 128.3, 129.4, 137.3, 160.3, 169.4; IR (neat): 2984, 1727 (CO), 1480, 1101, 757, 695; HRMS (ESI-TOF): $m/z$ [M+H]$^+$ calcd for C$_{18}$H$_{19}$O$_3$, 283.1334, found 283.1310.
4. Synthesis of Thiopyran Dioxides

4.1 Preparation of α-Diazo-β-oxosulfone Compounds

Methyl 2-diazo-2-((4'-phenylbutyl)sulfonyl)acetate\textsuperscript{[19]} (16)

Potassium carbonate (3.07 g, 22.2 mmol) was added to a stirring solution of methyl 2-((4'-phenylbutyl)sulfonyl)acetate\textsuperscript{[19a]} (5.0 g, 18.5 mmol) in acetonitrile (100 mL) at room temperature. The reaction mixture was stirred for 10 min before being cooled to 0 °C while a solution of 4-acetamidobenzenesulfonyl azide (p-ABSA) (5.78 g, 24.0 mmol) in acetonitrile (50 mL) was added. The reaction mixture was stirred at 0 °C for 30 min, returned to room temperature and stirred overnight before the addition of a non-polar co-solvent, hexane (60 mL) and diethyl ether (30 mL), to precipitate sulfonamide salts. The reaction mixture was stirred for a further 15 minutes, concentrated under reduced pressure and dichloromethane was added in order to decant from the bulk sulfonamide salts. Purification by column chromatography on silica gel, using ethyl acetate/hexane (20:80 to 40:60) as eluent, gave pure methyl 2-diazo-2-((4'-phenylbutyl)sulfonyl)acetate 16 as a yellow oil (5.08 g, 93%). Spectroscopic characteristics were consistent with previously reported data\textsuperscript{[19]}. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta = 1.69\)–1.94 (4H, m), 2.65 (2H, t, \(J = 7.2\)), 3.34–3.43 (2H, m), 3.85 (3H, s), 7.11–7.23 (3H, m), 7.23–7.33 (2H, m); \textsuperscript{13}C NMR (75.5 MHz, CDCl\textsubscript{3}): \(\delta = 22.1, 29.6, 35.1, 53.0, 56.4, 72.8, 126.0, 128.2, 128.4, 141.0, 160.4\); IR (neat): 2125 (CN\textsubscript{2}), 1713 (CO), 1332, 1293, 1145, 1083 (SO\textsubscript{2}); HRMS (ESI-TOF): \(m/z [M+H]^+\) calcd for C\textsubscript{13}H\textsubscript{17}N\textsubscript{2}O\textsubscript{4}S, 297.0904, found 297.0907.

Methyl 2-diazo-2-((4'-(p-tolyl)butyl)sulfonyl)acetate\textsuperscript{[19]} (19)

The title compound was prepared using the procedure described for methyl 2-diazo-2-((4'-phenylbutyl)sulfonyl)acetate 16, using potassium carbonate (1.75 g, 12.7 mmol), methyl 2-((4'-phenylbutyl)sulfonyl)acetate\textsuperscript{[19a]} (3.0 g, 10.6 mmol) in acetonitrile (100 mL) and p-ABSA (3.30 g, 13.7 mmol) in acetonitrile (30 mL). The mixture was stirred at 0 °C for 30 min, returned to room temperature and stirred overnight. Purification by column chromatography on silica gel, using ethyl acetate/hexane (20:80) as eluent, gave the pure product methyl 2-diazo-2-((4'-(p-tolyl)butyl)sulfonyl)acetate 19 as a yellow oil (2.68 g, 82%) which solidified upon storage in the freezer. Spectroscopic characteristics were consistent with previously reported data\textsuperscript{[19]} m.p. 35–37 °C; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta = 1.66\)–1.91 (4H, m), 2.30 (3H, s), 2.60 (2H, t, \(J = 7.3\)), 3.32–3.42 (2H, m), 3.84 (3H, s), 7.03 (2H, apparent d, \(J = 8.0\)), 7.08 (2H, apparent d, \(J = 8.0\)); \textsuperscript{13}C NMR (75.5 MHz, CDCl\textsubscript{3}): \(\delta = 20.8, 22.0, 29.6, 34.5, 52.8, 56.3, 72.7, 128.0, 129.0, 135.3, 137.8, 160.3\); IR (neat): 2125 (CN\textsubscript{2}), 1713 (CO), 1333, 1293, 1145, 1082 (SO\textsubscript{2}).
Methyl 2-diazo-2-((4’-(4”-methoxyphenyl)butyl)sulfonyl)acetate[19] (20)

The title compound was prepared using the procedure described for methyl 2-diazo-2-((4’-phenylbutyl)sulfonyl)acetate 16, using potassium carbonate (1.66 g, 12.0 mmol), methyl 2-((4’-(4”-methoxyphenyl)butyl)sulfonyl)acetate[19a] (3.0 g, 10.0 mmol) in acetonitrile (100 mL) and p-ABSA (3.12 g, 13.0 mmol) in acetonitrile (30 mL). The mixture was stirred at 0 °C for 30 min, returned to room temperature and stirred overnight. Purification by column chromatography on silica gel, using ethyl acetate/hexane (20:80) as eluent, gave the pure product methyl 2-diazo-2-((4’-(4”-methoxyphenyl)butyl)sulfonyl)acetate 20 as a yellow solid (2.74 g, 84%). Spectroscopic characteristics were consistent with previously reported data.[19] m.p. 50–51 °C (lit. 49–51 °C).[19b] 

1H NMR (300 MHz, CDCl3): δ= 1.65–1.93 (4H, m), 2.59 (2H, t, J 7.3), 3.30–3.43 (2H, m), 3.78 (3H, s), 3.85 (3H, s), 6.82 (2H, apparent d, J 8.6), 7.07 (2H, apparent d, J 8.6); 13C NMR (75.5 MHz, CDCl3): δ= 22.0, 29.8, 34.2, 53.0, 55.2, 56.4, 72.8, 113.8, 129.1, 133.0, 157.9, 160.4; IR (neat): 2117 (CN2), 1724 (CO), 1331, 1299, 1147 (SO2).

Methyl 2-diazo-2-((4’-(4”-fluorophenyl)butyl)sulfonyl)acetate[19a] (21)

The title compound was prepared using the procedure described for methyl 2-diazo-2-((4’-phenylbutyl)sulfonyl)acetate 16, using potassium carbonate (1.81 g, 13.1 mmol), methyl 2-((4’-(4”-fluorophenyl)butyl)sulfonyl)acetate[19a] (3.15 g, 10.9 mmol) in acetonitrile (100 mL) and p-ABSA (3.41 g, 14.2 mmol) in acetonitrile (30 mL). The mixture was stirred at 0 °C for 30 min, returned to room temperature and stirred overnight. Purification by column chromatography on silica gel, using ethyl acetate/hexane (20:80) as eluent, gave the pure product methyl 2-diazo-2-((4’-(4”-fluorophenyl)butyl)sulfonyl)acetate 21 as a yellow oil (3.03 g, 88%). Spectroscopic characteristics were consistent with previously reported data.[19] m.p. 50–51 °C (lit. 49–51 °C).[19b] 

1H NMR (300 MHz, CDCl3): δ= 1.64–1.94 (4H, m), 2.63 (2H, t, J 7.3), 3.35–3.44 (2H, m), 3.86 (3H, s), 6.91–7.02 (2H, m), 7.06–7.16 (2H, m); 13C NMR (75.5 MHz, CDCl3): δ= 22.0, 29.7, 34.3, 53.0, 56.3, 72.8, 115.1 (d, 1JCF 21.2), 129.6 (d, 1JCF 7.9), 136.6 (d, 1JCF 3.3), 160.4, 161.3 (d, 1JCF 244.4); IR (neat): 2126 (CN2), 1713 (CO), 1333, 1294, 1216, 1145, 1083 (SO2).

2-Diazo-1-phenyl-2-((4’-phenylbutyl)sulfonyl)ethan-1-one[19] (22)

The title compound was prepared using the procedure described for methyl 2-diazo-2-((4’-phenylbutyl)sulfonyl)acetate 16, using potassium carbonate (1.57 g, 11.38 mmol), 1-phenyl-2-((4’-phenylbutyl)sulfonyl)ethan-1-one[19a] (3.0 g, 9.48 mmol) in acetonitrile (100 mL) and p-ABSA (2.96 g, 12.33 mmol) in acetonitrile (30 mL). The mixture was stirred at 0 °C for 30 min, returned to room temperature and stirred overnight. Purification by column chromatography on silica gel, using ethyl acetate/hexane (10:90–30:70) as eluent, gave the pure product 2-diazo-1-phenyl-2-((4’-phenylbutyl)sulfonyl)ethan-1-one 22 as a yellow solid (2.79 g, 86%). Spectroscopic characteristics were consistent with previously reported data.[19] m.p. 95–99 °C (lit. 97–99 °C).[19b] 

1H NMR (300 MHz, CDCl3): δ= 1.73–1.95 (4H, m), 2.66 (2H, t, J 7.2), 3.50–3.60 (2H, m), 7.10–7.21 (3H, m), 7.22–7.31 (2H, m), 7.45–7.54 (2H, m), 7.56–7.67 (3H, m); 13C NMR (75.5 MHz, CDCl3): δ= 22.1, 29.6, 35.1, 56.5, 80.1, 126.0, 127.3, 128.3, 128.4, 129.0, 133.3, 135.6, 141.0, 183.3; IR (neat): 2112 (CN2), 1647 (CO), 1327, 1282, 1224, 1137 (SO2).
The title compound was prepared using the procedure described for methyl 2-diazo-2-((4’-phenylbutyl)sulfonyl)acetate 16, using potassium carbonate (2.17 g, 15.7 mmol), benzyl 2-(dodecylsulfonyl)acetate[19a] (5.0 g, 13.1 mmol) in acetonitrile (100 mL) and p-ABSA (4.08 g, 17.0 mmol) in acetonitrile (50 mL). The mixture was stirred at 0 °C for 30 min, returned to room temperature and stirred overnight. Purification by column chromatography on silica gel, using ethyl acetate/hexane (20:80) as eluent, gave the pure product benzyl 2-diazo-2-(dodecylsulfonyl)acetate 23 as a yellow solid (4.19 g, 78%). Spectroscopic characteristics were consistent with previously reported data.[19b] m.p. 50–51 °C (lit. 48–50 °C)[19] \( ^1 \)H NMR (300 MHz, CDCl3): \( \delta = 0.83–0.94 \) (3H, apparent t), 1.19–1.45 (18H, m), 1.72–1.86 (2H, m), 3.30–3.39 (2H, m), 5.29 (2H, s), 7.37 (5H, s); \( ^{13} \)C NMR (75.5 MHz, CDCl3): \( \delta = 14.1, 22.6, 27.9, 28.9, 29.2, 29.3, 29.4, 29.52, 29.53, 31.8, 56.7, 67.8, 73.0, 128.4, 128.7, 128.8, 134.6, 160.0; IR (neat): 2124 (CN\(_2\)), 1720 (CO), 1330, 1288, 1142 (SO\(_2\)).

Methyl 2-((2’-cyclohexylethyl)sulfonyl)-2-diazoacetate[20] (24)

The title compound was prepared using the procedure described for methyl 2-diazo-2-((4’-phenylbutyl)sulfonyl)acetate 16, using potassium carbonate (1.85 g, 13.4 mmol), methyl 2-((2-cyclohexylethyl)sulfonyl) acetate[20] (3.03 g, 12.2 mmol) in acetonitrile (30 mL) and p-ABSA (2.93 g, 12.2 mmol) in acetonitrile (30 mL). The mixture was stirred at 0 °C for 30 min, returned to room temperature and stirred overnight. Purification by column chromatography on silica gel, using ethyl acetate/hexane (20:80) as eluent, gave pure methyl 2-((2’-cyclohexylethyl)sulfonyl)-2-diazoacetate 24 as a yellow oil (2.65 g, 79%). Spectroscopic characteristics were consistent with previously reported data.[20] \( ^1 \)H NMR (300 MHz, CDCl3): \( \delta = 0.84–1.05 \) (2H, m), 1.06–1.46 (4H, m), 1.58–1.81 (7H, m), 3.34–3.46 (2H, symmetrical m), 3.88 (3H, s); \( ^{13} \)C NMR (75.5 MHz, CDCl3): \( \delta = 25.9, 26.1, 29.5, 32.7, 36.4, 52.9, 54.6, 72.8, 160.4; IR (neat): 2124 (CN\(_2\)), 1713 (CO), 1331, 1294, 1144 (SO\(_2\)).
### 4.2 Rhodium Catalysed C–H Insertion Reactions – Thiopyran Dioxide synthesis

**Table SI.3:** Chiral rhodium(II) catalysis of α-diazo-β-oxosulfones 16, 19–23

![Rhodium Catalysed C–H Insertion Reactions – Thiopyran Dioxide synthesis](image)

| Entry | Diazo | R       | R’     | d.r. | A | % Yield | B | % Yield | C & D | % Yield | E | % Yield |
|-------|-------|---------|--------|------|---|---------|---|---------|-------|---------|---|---------|
| 1     | 16    | Ph      | OMe    | 90:10| 41 (92)<sup>b</sup> | 5 (4)<sup>i</sup> | 21 | 18a & b | S22   |
| 2<sup>a</sup> | 16    | Ph      | OMe    | 92:8 | 64 (92)<sup>b</sup> | 4 (6)<sup>i</sup> | 23 | 1       |       |
| 3     | 19    | p-MeC<sub>6</sub>H<sub>4</sub> | OMe    | 93:7 | 50 (89)<sup>b</sup> | 4 (11)<sup>i</sup> | 11 | 7       |       |
| 4     | 20    | p-OMeC<sub>6</sub>H<sub>4</sub> | OMe    | -<sup>k</sup> | 42 (51)<sup>b</sup> | 11 (9)<sup>i</sup> | 13 | 8       |       |
| 5     | 21    | p-FC<sub>6</sub>H<sub>4</sub> | OMe    | 89:11| 53 (90)<sup>b</sup> | 7 (6)<sup>i</sup> | 12 | 1       |       |
| 6<sup>f</sup> | 22    | Ph      | Ph     | -<sup>k</sup> | 1 (69)<sup>m</sup> | 2<sup>n</sup> (-) | 25<sup>n</sup> | -       |       |
| 7     | 23    | C<sub>6</sub>H<sub>17</sub> | OBn    | -<sup>k</sup> | 31 (56)<sup>b</sup> | -<sup>o</sup> | -<sup>o</sup> | -       |       |

<sup>a</sup>The relative ratio of C–H insertion products could not be determined due to overlapping signals in the <sup>1</sup>H NMR spectra of the crude product mixtures. The spectra for the samples were recorded in both CDCl<sub>3</sub> and in C<sub>6</sub>D<sub>6</sub> in an attempt to resolve signals.

<sup>b</sup>The diastereomeric ratio was determined by integration of the methyl signals in the <sup>1</sup>H NMR spectra of the crude product mixtures in C<sub>6</sub>D<sub>6</sub>.

<sup>c</sup>Isolated yield after column chromatography.

<sup>d</sup>The enantiomeric excess was measured by chiral-phase HPLC analysis (for full details see Table SI.6). The trans-sulfolane (C) and cis-sulfolane (D) were not isolated as pure compounds due to epimerisation of the cis-sulfolane (D) to the trans-sulfolane (C) during column chromatography on silica gel. The isolated yields of trans-sulfolane (C) are for samples which contain traces of the cis-sulfolane (C) (See Experimental for details). Clear baseline resolution of chiral HPLC peaks was difficult to achieve for the mixed sulfolane samples and therefore enantiomeric excess was unable to be determined for the trans-sulfolane (C) and cis-sulfolane (D). Reaction conducted on a 1 gram scale (3.5 mmol). The major enantiomer has a 2<sup>R</sup>,3<sup>S</sup> configuration. The major enantiomer has a 2<sup>R</sup>,3<sup>S</sup> configuration. The major enantiomer has a 2<sup>R</sup>,3<sup>R</sup> configuration. The major enantiomer has a 2<sup>R</sup>,3<sup>S</sup> configuration. The major enantiomer has a 2<sup>R</sup>,3<sup>R</sup> configuration. The major enantiomer has a 2<sup>R</sup>,3<sup>R</sup> configuration. The major enantiomer has a 2<sup>R</sup>,3<sup>S</sup> configuration. The major enantiomer has a 2<sup>R</sup>,3<sup>R</sup> configuration. The major enantiomer has a 2<sup>R</sup>,3<sup>S</sup> configuration. The major enantiomer has a 2<sup>R</sup>,3<sup>R</sup> configuration. The major enantiomer has a 2<sup>R</sup>,3<sup>S</sup> configuration. The major enantiomer has a 2<sup>R</sup>,3<sup>R</sup> configuration.

<sup>e</sup>Diastereomeric ratio was not determined due to overlapping signals in the <sup>1</sup>H NMR spectra of the crude product mixtures. Reaction conducted under reflux. Absolute configuration undertermined. Sample was not isolated pure. Conatianed unknown side-products. 29b and S30a & b were isolated in 42% yield as a combined mixture.
Table SI.4: Chiral rhodium(II) catalysis of α-diazo-β-oxosulfones 24

| Entry | Rhodium catalyst | Solvent | Temp (°C) | Time (h) | d.r. 30a:30b | 30a % Yield | % ee  | 30b % Yield | % ee  |
|-------|------------------|---------|-----------|---------|--------------|-------------|-------|-------------|-------|
| 1     | Rh$_2$(S-DOSP)$_4$ | CH$_2$Cl$_2$ | rt        | 0.5     | 96:4 | 64 (22)$^d$ | - |
| 2$^a$ | Rh$_2$(S-R-MEPY)$_4$ | CH$_2$Cl$_2$ | reflux    | 24      | -     | 0 (0) | 0 |
| 3     | Rh$_2$(S-PTTL)$_4$ | CH$_2$Cl$_2$ | rt        | 0.5     | 98:2 | 80 (36)$^d$ | - |
| 4     | Rh$_2$(S-PTPA)$_4$ | CH$_2$Cl$_2$ | rt        | 0.5     | 94:6 | 65 (25)$^d$ | - |
| 5     | Rh$_2$(S-TCPTTL)$_4$ | CH$_2$Cl$_2$ | rt        | 0.5     | 97:3 | 81 (10)$^d$ | - |
| 6     | Rh$_2$(2S-F-2ʹ-NA)$_4$ | CH$_2$Cl$_2$ | rt        | 2       | 94:6 | 67 (60)$^d$ | - |
| 7     | Rh$_2$(S-PTTL)$_4$ | toluene  | rt        | 0.5     | 97:3 | 63 (43)$^d$ | - |
| 8     | Rh$_2$(S-PTTL)$_4$ | toluene  | -20       | 2       | 97:3 | 62 (47)$^d$ | - |
| 9     | Rh$_2$(2S-F-2ʹ-NA)$_4$ | toluene  | -20       | 2       | 91:9 | 52 (62)$^d$ | - |
| 10    | Rh$_2$(2S-F-2ʹ-NA)$_4$ | toluene  | -70       | 2       | 91:9 | 56 (60)$^d$ | - |
| 11    | Rh$_2$(2S-FBrPA)$_4$ | CH$_2$Cl$_2$ | -20       | 18      | 88:12 | 82 (53)$^d$ | 12 (27)$^f$ |
| 12    | Rh$_2$(2S-MBrPA)$_4$ | CH$_2$Cl$_2$ | -20       | 18      | 92:8 | 88 (28)$^d$ | 6 (13)$^f$ |
| 13    | Rh$_2$(2S-F-2ʹ-NA)$_4$ | CH$_2$Cl$_2$ | -20       | 18      | 95:5 | 85 (84)$^d$ | - |
| 14$^g$ | Rh$_2$(2S-F-2ʹ-NA)$_4$ | CH$_2$Cl$_2$ | -20       | 18      | 96:4 | 91 (84)$^d$ | 2 (~0) |

$^a$Diastereomeric ratio was calculated from $^1$H NMR spectra of the crude product mixture. $^b$Isolated yield after column chromatography. $^c$The enantiomeric excess was measured by chiral-phase HPLC analysis (for full details see Table SI.6). $^d$Second peak in the HPLC trace. $^e$Only starting material (24) was evident in the $^1$H NMR spectrum of the crude product mixture. The major enantiomer has a (1S,4aS,8aR) configuration. $^f$Reaction conducted on a 2 mmol scale compared to 0.35–0.85 mmol for entry 1–13.
4.2.1. Cyclisation of α-diazo-β-oxosulfone 16

Methyl (2R,3S)-3-phenyltetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide (17a)

An oven dried 60 mL Schlenk tube (27 x 150 mm) containing 4Å molecular sieves (~ 600–800 mg) and a magnetic stir bar was flame dried and cooled under nitrogen. Rh₂(2S-F-2'-NA)₄ 9b (53.1 mg, 34.2 μmol) was charged as a solid to the Schlenk tube. Methyl 2-diazo-2-((4'-phenylbutylsulfonyl)acetate 16 (1.01 g, 3.42 mmol) was charged into a dry 25 mL roundbottom flask. The Schlenk tube and roundbottom flask were both placed under vacuum and back filled with nitrogen 3 times. The Rh₂(2S-F-2'-NA)₄ 9b was dissolved in deoxygenated dichloromethane (DCM, 5 ml), and the methyl 2-diazo-2-((4'-phenylbutylsulfonyl)acetate 16 was dissolved in deoxygenated DCM (20 ml). The Schlenk tube containing the rhodium solution was placed into an ethanol cooling bath set at −20 °C while stirring. Once the ethanol bath had stabilised at −20 °C, the diazo 16 solution was added dropwise over 240 minutes via syringe to the Schlenk tube using a syringe pump. The reaction solution was stirred overnight at −20 °C before warming to room temperature. The reaction solution was filtered through a short pad of Celite® and activated charcoal, and concentrated under reduced pressure to give the crude product, which was then analysed by ¹H NMR spectroscopy in CDCl₃ and in C₆D₆. The ¹H NMR in CDCl₃ showed that compound 17a was the major product, d at δH 4.16 (J 12.2), with minor compounds: 17b, s at δH 3.53, 18a, s at δH 3.74, 18b, s at δH 3.83 and S22, d at δH 6.55 (J 15.8). The ¹H NMR analysed in C₆D₆ allowed the determination of the thiopyran diastereomeric ratio (92:8 dr, 17a:17b, s at δH 3.06; s at δH 2.98) compared to overlapping peaks in the CDCl₃ ¹H NMR spectra. The crude product mixture, which was loaded using Celite®, was purified using column chromatography on silica gel, employing ethyl acetate/hexane (10:90 to 50:50) as eluent, and gave methyl (2R,3S)-3-phenyltetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide 17a (589 mg, 64%), methyl (2S,3S)-3-phenyltetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide 17b (41 mg, 4%), methyl (2'R,3'R)-3-benzyltetrahydrothiophene-2-carboxylate 1,1-dioxide 18a (208 mg, 23%), of which contains ~15% 18b, s at 3.83) and methyl 2-((4'-phenylbut-3'-en-1'-yl)sulfonyl)acetate S22 (8 mg, 1%). 18a or 18b were not isolated as single pure compounds, but as a mixture. An enriched 18b sample was obtained by taking the first few test tubes of the second least polar component, and an enriched 18a sample was obtained by taking the last few test tubes of the third least polar component. 17a, most polar component, white solid; m.p. 152–154 °C; Spec. Rot.: [α]D20 -34.9 (c 1.0, CH₂Cl₂); HPLC: 92% ee (determined by chiral phase HPLC, see Table SI.6 for HPLC conditions); ¹H NMR (300 MHz, CDCl₃): δ = 1.64–1.81 (1H, m), 2.03–2.14 (1H, m), 2.14–2.40 (2H, m), 3.02–3.15 (1H, m), 3.26 (1H, dt, J 14.2, 3.6, 3.6), 3.58 (3H, s), 3.64 (1H, td, J 12.4, 12.4, 3.3), 4.16 (1H, d, J 12.2), 7.15–7.36 (5H, m); ¹H NMR (300 MHz, C₆D₆): δ = 0.78–0.97 (1H, m), 1.04–1.16 (1H, m), 1.25–1.40 (1H, m), 1.64–1.82 (1H, m), 2.23 (1H, td, J 13.8, 13.8, 3.6), 2.43–2.53 (1H, m), 3.06 (3H, s), 3.57 (1H, td, J 12.4, 12.4, 3.4), 3.91 (1H, d, J 12.2), 6.87–7.12 (5H, m); ¹³C NMR (75.5 MHz, CDCl₃): δ = 23.2, 32.7, 45.5, 52.3, 53.1, 71.4, 127.2, 127.7, 129.0, 140.1, 163.1; IR (neat): 1732 (CO), 1320, 1293, 1142, 1124 (SO₂); HRMS (ESI-TOF): m/z [M+H]+ calcd (%) for C₁₄H₁₆O₃S: 269.0842, found 269.0845; Elemental Analysis: calcld (%) for C₁₄H₁₆O₃S: C, 58.19; H, 6.01, found: C, 58.41; H, 6.12.
Methyl (2S,3S)-3-phenyltetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide[17b]

Methyl (2S,3S)-3-phenyltetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide 17b (41 mg, 4%) was isolated as a white solid (least polar component). Spectroscopic characteristics were consistent with previously reported data.[19] m.p. 112–115 °C (lit 116–118 °C).[19b] 1H NMR (300 MHz, CDCl3): δ = 1.86 (1H, dq, J 14.0, 3.3, 3.3, 3.3), 2.11–2.36 (2H, m.), 2.61 (1H, dq, J 13.3, 13.3, 13.3, 4.0), 3.04 (1H, dq, J 14.1, 3.3, 3.3, 3.3), 3.53 (3H, s), 3.61–3.75 (2H, m), 3.99 (1H, dd, J 4.5, 2.9), 7.15–7.21 (2H, m), 7.23–7.37 (3H, m); 13C NMR (75.5 MHz, CDCl3): δ = 23.0, 23.7, 44.6, 47.9, 52.7, 70.5, 127.0, 127.9, 129.0, 139.6, 166.6; IR (neat): 1725 (CO), 1310, 1294, 1169, 1112 (SO2); HRMS (ESI-TOF): m/z [M+H]+ calcd for C13H17O2S, 269.0842, found 269.0839.

Methyl (2R,3R*)-3-benzyltetrahydrothiophene-2-carboxylate 1,1-dioxide (18a)

Methyl (2R,3R*)-3-benzyltetrahydrothiophene-2-carboxylate 1,1-dioxide 18a (208 mg, 23%), of which contains ~15% 18b, was isolated as a colourless oil (an enriched 18a sample was obtained by taking the last few test tubes of the third least polar component); 1H NMR (300 MHz, CDCl3): δ = 1.78–1.96 (1H, m), 2.21–2.34 (1H, m), 2.73 (1H, dd, J 13.5, 8.0), 2.91 (1H, dd, J 13.5, 6.4), 2.97–3.13 (2H, m), 3.27 (1H, dq, J 13.0, 7.2, 2.1), 3.66 (1H, d, J 9.8), 3.74 (3H, s), 7.09–7.19 (2H, m), 7.20–7.35 (3H, m); 13C NMR (75.5 MHz, CDCl3): δ = 26.2, 39.9, 41.6, 52.7, 53.3, 70.3, 127.0, 128.7, 129.1, 137.1, 165.5; IR (neat): 1739 (CO), 1315, 1268, 1168, 1119 (SO2); HRMS (ESI-TOF): m/z [M+H]+ calcd for C13H17O2S, 269.0842, found 269.0841.

Methyl (2S*,3R*)-3-benzyltetrahydrothiophene-2-carboxylate 1,1-dioxide (18b)

Methyl (2S*,3R*)-3-benzyltetrahydrothiophene-2-carboxylate 1,1-dioxide 18b was isolated as a mixture with 18a (an enriched 18b sample was obtained by taking the first few test tubes of the second least polar component); characteristic peaks of 18b: 1H NMR (300 MHz, CDCl3): δ = 3.38–3.51 (1H, m), 3.80 (1H, d, J 6.3), 3.83 (3H, s).

Methyl 2-(((4'-phenylbut-3'-en-1'-yl)sulfonyl)acetate (S22)

Methyl 2-(((4'-phenylbut-3'-en-1'-yl)sulfonyl)acetate S22 (8 mg, 1%) was isolated as a mixture with 18a; colourless oil; 1H NMR (600 MHz, CDCl3): δ = 2.77–2.85 (2H, m), 3.40–3.46 (2H, m), 3.83 (3H, s), 4.00 (2H, s), 6.19 (1H, dt, J 15.8, 7.0, 7.0), 6.55 (1H, d, J 15.8), 7.22–7.39 (5H, m); 13C NMR (150.9 MHz, CDCl3): δ = 25.7, 53.0, 53.4, 57.7, 124.8, 126.2, 127.8, 128.7, 133.2, 136.5, 163.6; IR (neat): 1744 (CO), 1317, 1300, 1263, 1143, 1111 (SO2); HRMS (ESI-TOF): m/z [M+H]+ calcd for C13H17O2S, 269.0842, found 269.0838.
4.2.2. Cyclisation of α-diazo-β-oxosulphone 19

Methyl (2R,3S)-3-(p-tolyl)tetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide (25a)

The title compound was prepared following the procedure described for methyl (2R,3S)-3-phenyltetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide 17a using methyl 2-diazo-2-(4′-(4′-methylenephenyl)butylsulfonyl)acetate 19 (113 mg, 0.36 mmol), Rh₂(2S-F-2'-NA)₄ 9b (5.7 mg, 3.64 µmol) in deoxygenated DCM (15 mL). The diazo 19 solution was added dropwise over 120 minutes via syringe to the Schlenk tube using a syringe pump. The reaction solution was stirred overnight at −20 °C before warming to room temperature. The reaction solution was filtered through a short pad of Celite® and activated charcoal, and concentrated under reduced pressure to give the crude product, which was then analysed by ¹H NMR spectroscopy in CDCl₃ and in C₆D₆. The ¹H NMR in CDCl₃ showed that compound 25a was the major product, d at δH 4.16 (J 12.2), with minor compounds: 25b, s at δH 3.56, S23a, s at δH 3.76, S23b, s at δH 3.83 and S24, d at δH 6.51 (J 15.8). The ¹H NMR analysed in C₆D₆ allowed the determination of the thiopyran diastereomeric ratio (93:7 dr, 25a:25b, s at δH 3.10: s at δH 3.02) compared to overlapping peaks in the CDCl₃ ¹H NMR spectra. The crude product mixture, which was loaded using Celite®, was purified using column chromatography on silica gel, employing ethyl acetate/hexane (10:90 to 30:70) as eluent, and gave methyl (2R,3S)-3-(p-tolyl)tetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide 25a (51 mg, 50%), methyl (2R,3S)-3-(p-tolyl)tetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide 25b (4 mg, 4%), methyl (2R*,3R*)-3-(4′-methylbenzyl)tetrahydrothiophene-2-carboxylate 1,1-dioxide S23a (11 mg, 11%, of which contains <10% S23b, s at 3.83), and methyl 2-((4′-methylphenyl)but-3′-en-1′-yl)sulfonyl)acetate S24 (7 mg, 7%). S23a or S23b were not isolated as single pure compounds, but as a mixture. An enriched S23b sample was obtained by taking the first few test tubes of the second least polar component, and an enriched S23a sample was obtained by taking the last few test tubes of the third least polar component. 25a, most polar component, white solid; m.p. 150–151 °C; Spec. Rot.: [α]D ⁰ ~-41.1 (c 1.0, CH₂Cl₂); HPLC: 89% ee (determined by chiral phase HPLC, see Table S1.6 for HPLC conditions); ¹H NMR (300 MHz, CDCl₃): δ= 1.62–1.80 (1H, m), 1.98–2.11 (1H, m), 2.12–2.38 (5H, m containing s at 2.31), 3.02–3.16 (1H, m), 3.24 (1H, dt, J 14.2), 3.53–3.66 (4H, m containing s at 3.58), 4.16 (1H, d, J 12.2), 7.04–7.15 (4H); ¹H NMR (300 MHz, C₆D₆): δ= 0.94–1.11 (1H, m), 1.15–1.26 (1H, m), 1.36–1.46 (1H, m), 1.73–1.91 (1H, m), 2.04 (3H, s), 2.43 (1H, td, J 13.7, 3.6), 2.55–2.65 (1H, m), 3.10 (3H, s), 3.61 (1H, td, J 12.3, 3.3), 4.05 (1H, d, J 12.2), 6.91 (4H, s); ¹³C NMR (75.5 MHz, CDCl₃): δ= 21.0, 23.2, 32.7, 45.0, 52.2, 53.0, 71.4, 127.0, 129.5, 137.1, 137.3, 163.1; IR (neat): 1730 (CO), 1310, 1137, 1124 (SO₂); HRMS (ESI-TOF): m/z [M+H]+ calcd for C₁₄H₁₃O₃S: 283.0999, found 283.0996; Elemental Analysis: calcd (%) for C₁₄H₁₃O₃S: C, 59.55; H, 6.43, found: C, 59.55; H, 6.36;

Methyl (2R,3S)-3-(p-tolyl)tetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide (25b)

Methyl (2R,3S)-3-(p-tolyl)tetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide 25b (4 mg, 4%) was isolated as a white solid (least polar component). Spectroscopic characteristics were consistent with previously reported data.¹⁹ ¹H NMR (300 MHz, CDCl₃): δ= 1.83 (1H, dq, J 14.0, 3.4), 2.10–2.36 (5H, m containing s at 2.32), 2.58 (1H, qd, J 13.4, 4.1), 3.03 (1H, dq, J 14.0, 3.3), 3.53–3.74 (5H, m containing s at 3.56), 3.97 (1H, dd, J 4.5, 3.0), 7.06 (2H, d, J 8.2), 7.13 (2H, d, J 8.2); ¹H NMR (300 MHz, C₆D₆): δ= 1.21–1.32 (1H, m), 1.33–1.45 (1H, m), 1.65–1.84 (1H, m), 2.01
Methyl (2R*,3R*)-3-(4'-methylbenzyl)tetrahydrothiophene-2-carboxylate 1,1-dioxide (S23a)

Methyl (2R*,3R*)-3-(4'-methylbenzyl)tetrahydrothiophene-2-carboxylate 1,1-dioxide S23a (11 mg, 11%, containing <10% S23b, s at 3.83) as a white solid (an enriched S23a sample was obtained by taking the last few test tubes of the third least polar component); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 1.76\)–1.95 (1H, m), 2.20–2.37 (4H, h containing s at 2.32), 2.68 (1H, dd, J 13.5, 8.0), 2.88 (1H, dd, J 13.5, 6.3), 2.94–3.12 (2H, m), 3.26 (1H, qd, J 12.9, 7.2, 2.2), 3.65 (1H, d, J 9.8), 3.76 (3H, s, OCH\(_3\)), 7.03 (2H, d, J 8.1), 7.11 (2H, d, J 8.1); \(^13\)C NMR (300 MHz, CDCl\(_3\)): \(\delta = 0.99–1.17\) (1H, m), 1.26–1.42 (1H, m), 1.97–2.15 (4H, h containing s at 2.09), 2.20–2.33 (1H, m), 2.38–2.48 (2H, m), 2.66–2.83 (1H, m), 3.30 (3H, s), 3.48 (1H, d, J 9.8), 6.77 (2H, d, J 8.0), 6.91 (2H, d, J 8.0); \(^13\)C NMR (75.5 MHz, CDCl\(_3\)): \(\delta = 21.0, 26.1, 39.4, 41.6, 52.7, 53.3, 70.3, 129.0, 129.4, 134.0, 136.6, 165.5; IR (s): 1742, 1311, 1273, 1171, 1126, 1120; HRMS (ESI-Q-TOF): \(m/z [M+Na]^+\) calcd for C\(_{14}\)H\(_{15}\)O\(_3\)S\(_2\), 283.0999, found 283.1000.

Methyl (2R*,3S*)-3-(4'-methylbenzyl)tetrahydrothiophene-2-carboxylate 1,1-dioxide (S23b)

Methyl (2R*,3S*)-3-(4'-methylbenzyl)tetrahydrothiophene-2-carboxylate 1,1-dioxide S23b was isolated as a mixture with S23a (an enriched S23b sample was obtained by taking the first few test tubes of the second least polar component); characteristic peaks of S23b: \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 3.38–3.50\) (1H, m), 3.79 (1H, d, J 6.2), 3.83 (3H, s).

Methyl 2-((4'-p-tolyl)but-3'-en-1'-yl)sulfonyl)acetate (S24)

Methyl 2-((4'-p-tolyl)but-3'-en-1'-yl)sulfonyl)acetate S24 (7 mg, 7%) was isolated as a white solid; m.p. 91–93 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 2.33\) (3H, s), 2.72–2.84 (2H, m), 3.37–3.46 (2H, m), 3.82 (3H, s), 3.99 (2H, s), 6.12 (1H, dt, J 15.8, 7.0), 6.51 (1H, d, J 15.8), 7.12 (2H, d, J 8.1), 7.24 (2H, d, J 8.1); \(^13\)C NMR (300 MHz, CDCl\(_3\)): \(\delta = 2.10\) (3H, s), 2.40–2.53 (2H, m), 2.93–3.03 (2H, m), 3.18 (3H, s), 3.44 (2H, s), 5.76 (1H, dt, J 15.8, 7.0), 6.19 (1H, d, J 15.8), 6.96 (2H, d, J 8.0), 7.12 (2H, d, J 8.0); \(^13\)C NMR (75.5 MHz, CDCl\(_3\)): \(\delta = 21.2, 25.7, 53.1, 53.4, 57.7, 123.7, 126.1, 129.3, 133.0, 133.8, 137.6, 163.6; IR (s): 1753, 1745, 1300, 1260, 1144, 1110; HRMS (ESI-Q-TOF): \(m/z [M+Na]^+\) calcd for C\(_{14}\)H\(_{15}\)O\(_3\)S\(_2\), 283.0999, found 283.0997; Elemental Analysis: calcd (%) for C\(_{14}\)H\(_{15}\)O\(_3\)S\(_2\): C, 59.55; H, 6.43, found: C, 59.30; H, 6.38.
4.2.3. Cyclisation of α-diazo-β-oxosulfone 20

Methyl (2R,3S)-3-(4'-methoxyphenyl)tetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide[19b] (26a)

The title compound was prepared following the procedure described for methyl (2R,3S)-3-phenyltetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide 17a using methyl 2-diazo-2-(4'-((4''-methoxyphenyl)butylsulfonyl)acetate 20 (147.5 mg, 0.45 mmol), Rh2(2S-F-2'-NA)4 9b (7.0 mg, 4.52 μmol) in deoxygenated DCM (15 mL). The diazo 20 solution was added dropwise over 120 minutes via syringe to the Schlenk tube using a syringe pump. The reaction solution was stirred overnight at −20 °C before warming to room temperature. The reaction solution was filtered through a short pad of Celite® and activated charcoal, and concentrated under reduced pressure to give the crude product, which was then analysed by 1H NMR spectroscopy in CDCl3 and in C6D6. The 1H NMR in CDCl3 showed that compound 26a was the major product, d at δH 4.09 (J 12.1), with minor compounds: 26b, s at δH 3.56, S25b, s at δH 3.83, and S26, s at δH 3.80, also evident. No evidence of S25a. Both the CDCl3 and C6D6 1H NMR spectra contained overlapping peaks making it difficult to determine accurately the thiopyran diastereomeric ratio. The crude product mixture, which was loaded using Celite®, was purified using column chromatography on silica gel, employing ethyl acetate/hexane (20:80 to 40:60) as eluent, and gave methyl (2R,3S)-3-(4'-methoxyphenyl)tetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide 26a (56 mg, 42%), methyl (2S,3S)-3-(4'-methoxyphenyl)tetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide 26b (15 mg, 11%), methyl (2R,3R')-3-(4'-methoxybenzyl)tetrahydrothiophene-2-carboxylate 1,1-dioxide S25a (14 mg, 13%, of which contains ~20% S25b, s at 3.83), and methyl 2-(4'-(4'-methoxyphenyl)but-3'-en-1'-yl)sulfonyl)acetate S26 (11 mg, 8%). S25a or S25b were not isolated as single pure compounds, but as a mixture. An enriched S25b sample was obtained by taking the first few test tubes of the second least polar component, and an enriched S25a sample was obtained by taking the last few test tubes of the third least polar component. 26a, most polar component, white solid; m.p. 175–177 °C; Spec. Rot.: [α]D20 −19.4 (c 1.0, CH2Cl2); HPLC: 51% ee (determined by chiral phase HPLC, see Table S1.6 for HPLC conditions); 1H NMR (300 MHz, CDCl3); δ = 1.60–1.79 (1H, m), 2.00–2.11 (1H, m), 2.12–2.38 (2H, m), 2.99–3.13 (1H, m), 3.24 (1H, dt, J 14.3, 3.6), 3.52–3.65 (4H, m containing s at 3.59), 3.78 (3H, s), 4.09 (1H, d, J 12.1), 6.80–6.88 (2H, m), 7.08–7.15 (2H, m); 13C NMR (75.5 MHz, CDCl3); δ = 23.2, 32.7, 44.7, 52.2, 53.1, 55.2, 71.7, 114.3, 128.2, 132.1, 159.0, 163.1; IR (neat): 1726, 1325, 1257, 1140; HRMS (ESI-TOF): m/z [M+H]+ calcd for C14H16O2S: 299.0948, found 299.0946. Elemental Analysis: calcd (%) for C14H16O2S: C, 56.36; H, 6.08. Found: C, 56.11; H, 5.96.

Methyl (2S,3S)-3-(4'-methoxyphenyl)tetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide[19] (26b)

Methyl (2S,3S)-3-(4'-methoxyphenyl)tetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide 26b (14.8 mg, 11%) was isolated as a white solid (least polar component). Spectroscopic characteristics were consistent with previously reported data.[19] m.p. 110–113 °C (lit. 90–92 °C of a 91% ee 26b sample).[19b] 1H NMR (300 MHz, CDCl3); δ = 1.82 (1H, dq, J 14.0, 3.4), 2.09–2.34 (2H, m), 2.57 (1H, dq, J 13.3, 4.0), 3.03 (1H, dq, J 14.0, 3.3), 3.52–3.73 (5H, m containing s at 3.56), 3.79 (3H, s), 3.96 (1H, dd, J 4.5, 2.9), 6.81–6.90 (2H, m), 7.06–7.14 (2H, m); 13C NMR (75.5 MHz, CDCl3); δ = 23.0, 23.9, 43.8, 47.8, 52.7, 55.2, 70.6, 114.2, 128.0, 131.6,
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159.0, 166.6; IR (neat): 1723, 1324, 1249, 1172, 1117; HRMS (ESI-TOF): m/z [M+H]+ calcd for C\textsubscript{14}H\textsubscript{19}O\textsubscript{5}S, 299.0948, found 299.0952.

Methyl (2R*,3R*)-3-(4'-methoxybenzyl)tetrahydrothiophene-2-carboxylate 1,1-dioxide (S25a)

Methyl (2R*,3R*)-3-(4'-methoxybenzyl)tetrahydrothiophene-2-carboxylate 1,1-dioxide S25a (14 mg, 13%, of which contains ~20% S25b, s at 3.83) as a white solid (an enriched S25a sample was obtained by taking the last few test tubes of the third least polar component); m.p. 127–129 °C; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta = 1.77–1.94 \text{ (1H, m)}, 2.20–2.33 \text{ (1H, m)}, 2.68 \text{ (1H, dd, J 13.6, 7.9)}, 2.85 \text{ (1H, dd, J 13.6, 6.4)}, 2.93–3.13 \text{ (2H, m)}, 2.93–3.13 \text{ (2H, m)}, 3.38–3.50 \text{ (1H, m)}, 3.83 \text{ (3H, s)}.

Methyl (2R*,3S*)-3-(4'-methoxybenzyl)tetrahydrothiophene-2-carboxylate 1,1-dioxide (S25b)

Methyl (2R*,3S*)-3-(4'-methoxybenzyl)tetrahydrothiophene-2-carboxylate 1,1-dioxide S25b was isolated as a mixture with S25a (an enriched S25b sample was obtained by taking the first few test tubes of the second least polar component); characteristic peaks of S25b: \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta = 3.38–3.50 \text{ (1H, m)}, 3.83 \text{ (3H, s)}.

Methyl 2-((4'-4''-methoxyphenyl)but-3'-en-1'-yl)sulfonyl)acetate (S26)

Methyl 2-((4'-4''-methoxyphenyl)but-3'-en-1'-yl)sulfonyl)acetate S26 (11 mg, 8%) was isolated as a colourless oil; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta = 2.72–2.83 \text{ (2H, m)}, 3.36–3.46 \text{ (2H, m)}, 3.80 \text{ (3H, s)}, 3.82 \text{ (3H, s)}, 3.99 \text{ (2H, s)}, 6.03 \text{ (1H, dt, J 15.8, 7.0)}, 6.48 \text{ (1H, d, J 15.8)}, 6.81–6.88 \text{ (2H, m), 7.24–7.32 (2H, m)}; \textsuperscript{13}C NMR (75.5 MHz, CDCl\textsubscript{3}): \(\delta = 25.7, 53.1, 53.3, 55.3, 57.7, 114.1, 122.5, 127.4, 129.4, 132.5, 159.3, 163.6; \text{ IR (neat): 1728, 1306, 1243, 1101; HRMS (ESI-TOF): m/z [M+H]+ calcd for C\textsubscript{14}H\textsubscript{19}O\textsubscript{5}S, 299.0948, found 299.0945.
4.2.4. Cyclisation of α-diazo-β-oxosulfone 21

Methyl (2R,3S)-3-(4′-fluorophenyl)tetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide (27a)

The title compound was prepared following the procedure described for methyl (2R,3S)-3-phenyltetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide 17a using methyl 2-diazo-2-(4′-(4″-fluorophenyl)butylsulfonyl)acetate 21 (127.5 mg, 0.41 mmol), Rh2(2S-F-2′-NA)4 9b (6.3 mg, 4.06 pmol) in deoxygenated DCM (15 mL). The diazo 21 solution was added dropwise over 120 minutes via syringe to the Schlenk tube using a syringe pump. The reaction solution was stirred overnight at −20 °C before warming to room temperature. The reaction solution was filtered through a short pad of Celite® and activated charcoal, and concentrated under reduced pressure to give the crude product, which was then analysed by 1H NMR spectroscopy in CDCl3 and in C6D6. The 1H NMR in CDCl3 showed that compound 27a was the major product, d at δH 4.15 (J 12.2), with minor compounds: 27b, s at δH 3.56, S27a, s at δH 3.76, S27b, s at δH 3.83, and S28, dt at δH 6.10 (J 15.8, 7.0) also evident. The 1H NMR analysed in C6D6 allowed the determination of the thiopyran diastereomeric ratio (89:11 dr, 27a:27b) compared to overlapping peaks in the CDCl3 1H NMR spectra. The crude product mixture, which was loaded using Celite®, was purified using column chromatography on silica gel, employing ethyl acetate/hexane (15:85 to 50:50) as eluent, and gave methyl (2R,3S)-3-(4″-fluorophenyl)tetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide 27a (61 mg, 53%), methyl (2S,3S)-3-(4″-fluorophenyl)tetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide 27b (8 mg, 7%), methyl (2R′,3R′)-3-(4″-fluorobenzyl)tetrahydrothiophene-2-carboxylate 1,1-dioxide S27a (14 mg, 12%, of which contains <10% S27b, s at 3.83), and methyl 2-(4″-(4″-fluorophenyl)but-3′-en-1′-yl)sulfonyl)acetate S28 (1 mg, 1%). S27a or S27b were not isolated as single pure compounds, but as a mixture. An enriched S27b sample was obtained by taking the first few test tubes of the second least polar component, and an enriched S27a sample was obtained by taking the last few test tubes of the third least polar component. 27a, most polar component, white solid; m.p. 154–155 °C; Spec. Rot.: [α]20 −31.1 (c 1.0, CH2Cl2); HPLC: 90% ee (determined by chiral phase HPLC, see Table SI.6 for HPLC conditions); 1H NMR (300 MHz, CDCl3): δ= 1.62−1.80 (1H, m), 2.00−2.11 (1H, m), 2.14–2.39 (2H, m), 3.04–3.18 (1H, m), 3.26 (1H, dt, J 14.2, 3.7), 3.56–3.70 (4H, m containing s at 3.59), 4.15 (1H, d, J 12.2), 6.95–7.06 (2H, m), 7.14–7.23 (2H, m); 1H NMR (300 MHz, C6D6): δ= 0.73–0.90 (1H, m), 1.07–1.30 (2H, m), 1.64–1.82 (1H, m), 2.31 (1H, td, J 13.8, 3.6), 2.47–2.58 (1H, m), 3.07 (3H, s), 3.48 (1H, td, J 12.4, 3.4), 3.83 (1H, d, J 12.1), 6.71 (4H, d, J 7.0); 19F NMR (282.4 MHz, CDCl3): δ= −114.3 (1F, s); 13C NMR (75.5 MHz, CDCl3): δ= 23.1, 32.6, 44.7, 52.1, 53.1, 71.4, 115.8 (d, 2JCF 21.5), 128.8 (d, 3JCF 8.2), 135.9 (d, 4JCF 3.3), 162.0 (d, 1JCF 247.0), 163.0; IR (neat): 1727, 1312, 1291, 1122; HRMS (ESI-TOF): m/z [M+Na]+ calcd for C13H15FO3SNa, 309.0567, found 309.0564; Elemental Analysis: calcd (%) for C13H15FO3S: C, 54.53; H, 5.28; found: C, 54.60; H, 5.34.
Methyl (2S,3S)-3-(4′-fluorophenyl)tetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide (27b)

Methyl (2S,3S)-3-(4′-fluorophenyl)tetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide 27b (8 mg, 7%) was isolated as a white solid (least polar fraction). Spectroscopic characteristics were consistent with previously reported data.\(^[19a]\) m.p. 155–157 °C (lit 155–156 °C).\(^[19a]\) 1H NMR (300 MHz, CDCl\(_3\)):\(\delta= 1.84 (1H, d, J = 13.9, 3.4), 2.10–2.36 (2H, m), 2.58 (1H, qd, J = 13.3, 4.1), 3.05 (1H, d, J = 14.0, 3.3), 3.56 (3H, s, OCH\(_3\)), 3.60–3.73 (2H, m), 3.96 (1H, dd, J = 4.5, 2.9), 6.97–7.07 (2H, m), 7.12–7.21 (2H, m); 1H NMR (300 MHz, CDCl\(_3\)):\(\delta= 1.11 (1H, d, J = 13.9, 3.4), 1.28–1.41 (1H, m), 1.59–1.78 (1H, m), 2.18 (1H, qd, J = 13.5, 3.6), 2.40 (1H, d, J = 14.0, 3.3), 2.97 (3H, s), 3.21–3.39 (2H, m), 3.87 (1H, dd, J = 4.5, 2.9), 6.51–6.69 (4H, m); 19F NMR (282.4 MHz, CDCl\(_3\)):\(\delta= -114.1 (1F, s); 13C NMR (75.5 MHz, CDCl\(_3\)):\(\delta= 23.0, 23.9, 43.8, 47.8, 52.8, 70.5, 115.9 (d, \text{J}_{CF} 21.4), 128.6 (d, \text{J}_{CF} 8.0), 135.4 (d, \text{J}_{CF} 3.3), 162.2 (d, \text{J}_{CF} 247.2), 166.5; IR (neat): 1735, 1309, 1220, 1173, 1118; HRMS (ESI-TOF): \text{m/z} [M+Na]^+ \text{calcd for C}_{13}H_{15}FO_3SNa, 309.0567, found 309.0562.

Methyl (2R′,3R′)-3-(4′-fluorobenzyl)tetrahydrothiophene-2-carboxylate 1,1-dioxide (S27a)

Methyl (2R′,3R′)-3-(4′-fluorobenzyl)tetrahydrothiophene-2-carboxylate 1,1-dioxide S27a (14 mg, 12%, of which contains <10% S27b, s at 3.83) was isolated as an opaque oil (an enriched S27a sample was obtained by taking the last few test tubes of the third least polar component); 1H NMR (300 MHz, CDCl\(_3\)):\(\delta= 1.76–1.95 (1H, m), 2.20–2.33 (1H, m), 2.71 (1H, dd, J = 13.6, 8.0), 2.89 (1H, dd, J = 13.6, 6.5), 2.95–3.13 (2H, m), 3.28 (1H, qd, J = 13.0, 7.1, 2.1), 3.65 (1H, d, J = 9.8), 3.76 (3H, s), 6.95–7.05 (2H, m), 7.08–7.17 (2H, m); 1H NMR (300 MHz, CDCl\(_3\)):\(\delta= 0.89–1.08 (1H, m), 1.14–1.27 (1H, m), 1.87 (1H, dd, J = 13.4, 8.5), 2.19–2.33 (2H, m), 2.42 (1H, qd, J = 12.9, 7.2, 2.3), 2.53–2.69 (1H, m), 3.29 (3H, s), 3.39 (1H, d, J = 9.9), 6.51–6.60 (2H, m), 6.66–6.77 (2H, m); 19F NMR (282.4 MHz, CDCl\(_3\)):\(\delta= -115.6 (1F, s); 13C NMR (75.5 MHz, CDCl\(_3\)):\(\delta= 26.2, 39.2, 41.6, 52.6, 53.4, 70.2, 115.6 (d, \text{J}_{CF} 21.3), 130.5 (d, \text{J}_{CF} 8.0), 132.9 (d, \text{J}_{CF} 3.3), 161.9 (d, \text{J}_{CF} 245.4), 165.4; IR (neat): 1741, 1317, 1266, 1219, 1158, 1120; HRMS (ESI-TOF): \text{m/z} [M+Na]^+ \text{calcd for C}_{13}H_{15}FO_3SNa, 309.0567, found 309.0564.

Methyl (2R′,3S′)-3-(4′-fluorobenzyl)tetrahydrothiophene-2-carboxylate 1,1-dioxide (S27b)

Methyl (2R′,3S′)-3-(4′-fluorobenzyl)tetrahydrothiophene-2-carboxylate 1,1-dioxide S27b was isolated as a mixture with S27a (an enriched S27b sample was obtained by taking the first few test tubes of the second least polar component); characteristic peaks of S27b: 1H NMR (300 MHz, CDCl\(_3\)):\(3.39–3.50 (1H, m), 3.83 (3H, s, CH\(_3\)).\)
4.2.5. Cyclisation of α-diazo-β-oxosulfone 22

((2R,3S')-1,1-Dioido-3-phenyltetrahydro-2H-thiopyran-2-yl)(phenyl)methanone (28a)

An oven dried 60 mL Schlenk tube (27 x 150 mm) containing 4Å molecular sieves (~600–800 mg) and a magnetic stir bar was flame dried and cooled under nitrogen. Rh2(2S-F-2’-NA)4 9b (10.8 mg, 6.92 μmol) was charged as a solid to the Schlenk tube. 2-Diazo-1-phenyl-2-((4’-phenylbutyl)sulfonyl)ethan-1-one 22 (237 mg, 0.69 mmol) was charged into a dry 25 mL roundbottom flask. The Schlenk tube and roundbottom flask were both placed under vacuum and back filled with nitrogen 3 times. The Rh2(2S-F-2’-NA)4 9b was dissolved in deoxygenated DCM (5 ml), and the 2-diazo-1-phenyl-2-((4’-phenylbutyl)sulfonyl)ethan-1-one 22 was dissolved in deoxygenated DCM (10 ml). The Schlenk tube containing the rhodium solution was placed into an oil bath set at 55 °C. Once the rhodium solution began to reflux, the diazo solution 22 was added dropwise over 120 minutes via syringe to the Schlenk tube using a syringe pump. The reaction solution was stirred overnight while heating under reflux before cooling to room temperature. The reaction solution was filtered through a short pad of Celite® and activated charcoal, and concentrated under reduced pressure to give the crude product, which was then analysed by 1H NMR spectroscopy in CDCl3. The 1H NMR in CDCl3 showed that compound S29 was the major product, d at δH 4.62 (J 9.7) and d at δH 4.77 (J 6.6), with minor compound 28a, d at δH 5.26. The crude product mixture, which was loaded using Celite®, was purified using column chromatography on silica gel, employing ethyl acetate/hexane (10:90 to 40:60) as eluent, and gave ((2R,3S’)-1,1-dioido-3-phenyltetrahydro-2H-thiopyran-2-yl)(phenyl)methanone 28a (3 mg, 1%), ((2R,3R*)-1,1-dioido-3-phenyltetrahydro-2H-thiopyran-2-yl)(phenyl)methanone 28b (4 mg, 2%), ((2R*,3R*)-3-benzyl-1,1-diodotetrahydrothiophen-2-yl)(phenyl) methanone S29a (52 mg, 52% of which contains ~5% S29b, d at 4.77). 28a, most polar fraction, white solid; m.p. 244–245 °C; HPLC: 69% ee (determined by chiral phase HPLC, see Table S1.6 for HPLC conditions); Spec. Rot.: [α]D20 +25.50 (c 0.5, CH2Cl2); 1H NMR (600 MHz, CDCl3); δ= 1.77–1.89 (1H, m), 2.09–2.19 (1H, m), 2.20–2.29 (1H, m), 2.31–2.43 (1H, m), 3.21 (1H, td, J 14.0, 3.8), 3.32 (1H, dt, J 14.2, 3.5), 3.95 (1H, td, J 12.4, 3.3), 5.26 (1H, d, J 11.7), 7.09–7.22 (5H, m), 7.36–7.42 (2H, m), 7.49–7.55 (1H, m), 7.82–7.87 (2H, m); 13C NMR (150.9 MHz, CDCl3); δ= 23.3, 33.0, 45.5, 53.0, 70.9, 127.3, 127.4, 128.6, 128.86, 133.8, 137.7, 140.5, 189.1; IR (neat): 1671, 1322, 1291, 1139; HRMS (ESI-TOF): m/z [M+H]+ calcd for C19H19O3S, 315.1049, found 315.1052.
(2R*,3R*)-1,1-Dioxido-3-phenyltetrahydro-2H-thiopyran-2-yl)(phenyl)methanone\(^{[19]}\) (28b)

(2R*,3R*)-1,1-dioxido-3-phenyltetrahydro-2H-thiopyran-2-yl)(phenyl)methanone 28b (4 mg, 2\%) was isolated as an impure colourless oil (least polar fraction). Spectroscopic characteristics were consistent with previously reported data.\(^{[19]}\) \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ= 1.88 (1H, dq, J 14.0, 3.3), 2.20–2.42 (2H, m), 2.72 (1H, dq, J 13.5, 4.0), 3.09 (1H, dq, J 13.9, 3.2), 3.79–3.90 (2H, m), 5.07 (1H, dd, J 4.5, 2.8), 7.06–7.18 (5H, m), 7.20–7.30 (2H, m), 7.36–7.46 (3H, m); IR (neat): 1668, 1324, 1297, 1245, 1121; HRMS (ESI-TOF): \(m/z\) [M+H]\(^+\) calcd for C\(_{18}\)H\(_{19}\)O\(_3\)S, 315.1049, found 315.1053.

((2R*,3R*)-3-Benzyl-1,1-dioxidotetrahydrothiophen-2-yl)(phenyl)methanone (S29a)

((2R*,3R*)-3-Benzyl-1,1-dioxidotetrahydrothiophen-2-yl)(phenyl)methanone S29a (52 mg, 25\% of which contains ~5\% S29b, d at 4.77) was isolated as a white solid; m.p. 111–113 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ= 1.91–2.06 (1H, m), 2.27–2.39 (1H, m), 2.72 (1H, dd, J 13.4, 8.2), 2.88 (1H, dd, J 13.4, 6.1), 3.07–3.19 (1H, m), 3.28–3.48 (2H, m), 4.61 (1H, d, J 9.7), 7.08–7.29 (5H, m), 7.45–7.55 (2H, m), 7.58–7.66 (1H, m), 7.92–8.01 (2H, m); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)): δ= 26.2, 40.0, 41.5, 53.5, 71.0, 127.0, 128.7, 128.9, 129.0, 129.1, 134.3, 136.5, 137.4, 189.8; IR (neat): 1668, 1303, 1267, 1121; HRMS (ESI-TOF): \(m/z\) [M+H]\(^+\) calcd for C\(_{18}\)H\(_{19}\)O\(_3\)S, 315.1049, found 315.1049.

Only trace amount of the cis-sulfolane S29b was evident from a d at δ\(_H\) 4.77 (J 6.6)

4.2.6. Cyclisation of α-diazo-β-oxosulfone 23

Benzyl (2R,3R)-3-octyltetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide\(^{[19]}\) (29a)

The title compound was prepared following the procedure described for methyl (2R,3S)-3-phenyltetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide 17a using benzyl 2-diazo-2-(dodecylsulfonyl)acetate 23 (161 mg, 0.39 mmol), Rh\(_2\)(2S-F-2′-NA)\(_4\) 9b (6.1 mg, 3.94 μmol) in deoxygenated DCM (15 mL). The diazo 23 solution was added dropwise over 120 minutes via syringe to the Schlenk tube using a syringe pump. The reaction solution was stirred overnight at −20 °C before warming to room temperature. The reaction solution was filtered through a short pad of Celite\(^®\) and activated charcoal, and concentrated under reduced pressure to give the crude product, which was then analysed by \(^1\)H NMR spectroscopy in CDCl\(_3\) and in C\(_6\)D\(_6\). The \(^1\)H NMR in CDCl\(_3\) showed that compound 29a, d at δ\(_H\) 3.70 (J 10.5), and S30b, m at 3.37–3.50, were the major products, with the minor compound, 29b, m at δ\(_H\) 3.52–3.64, also evident. There was no evidence of S30a. Both the CDCl\(_3\) and C\(_6\)D\(_6\) \(^1\)H NMR spectra contained overlapping peaks making it difficult to determine accurately the thiopyran diastereomeric ratio. The crude product mixture, which was loaded using Celite\(^®\), was purified using column chromatography on silica gel, employing ethyl acetate/hexane (5:95 to 20:80) as eluent, and gave benzyl (2R*,3R*)-3-octyltetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide 29a (46 mg, 31\%), benzyl (2R,3S)-3-octyltetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide 29b (20 mg, 13\%), and benzyl (2R*,3R*)-3-nonyltetrahydrothiophene-2-carboxylate 1,1-dioxide S30a (44 mg, 29\%, of
which contains ~32% S30b, m at 3.37–3.50). S30a or S30b were not isolated as single pure compounds, but as a mixture. An enriched S30b sample was obtained by taking the first few test tubes of the second least polar component, and an enriched S30a sample was obtained by taking the last few test tubes of the second most polar component. 29a, most polar component, white solid. Spectroscopic characteristics were consistent with previously reported data.[19] m.p. 85–87 °C (lit. 86–88 °C);[19b] Spec. Rot.: [α]20 D = –14.3 (c 1.0, CH2Cl2); HPLC: 56% ee (determined by chiral phase HPLC, see Table SI.6 for HPLC conditions); 1H NMR (300 MHz, CDCl3): δ = 0.83–0.93 (3H, m), 1.07–1.38 (15H, m), 1.97–2.18 (3H, m), 2.34–2.50 (1H, m), 2.83–3.00 (1H, m), 3.19 (1H, dt, J 14.1, 4.2), 3.70 (1H, d, J 10.5), 5.27 (2H, s), 7.28–7.43 (5H, m); 13C NMR (75.5 MHz, CDCl3): δ = 14.0, 22.4, 22.6, 26.2, 28.3, 29.1, 29.30, 29.34, 31.8, 33.3, 38.9, 51.9, 67.9, 71.3, 128.4, 128.48, 128.54, 134.9, 164.0; IR (neat): 1727, 1302, 1129; HRMS (ESI-TOF): m/z [M+Na]+ calcd for C21H32O3SNa, 403.1914, found 403.1919; Elemental Analysis: calcd (%) for C21H32O3S: C, 66.28; H, 8.48. Found: C, 66.28; H, 8.41.

**Benzyl (2R,3S)-3-octyltetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide**[19] (29b)

Benzyl (2R,3S)-3-octyltetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide 29b (20 mg, 13%) was isolated as a colourless oil (least polar fraction). Spectroscopic characteristics were consistent with previously reported data.[19] HPLC: 53% ee (determined by chiral phase HPLC); Spec. Rot.: [α]20 D = –11.2 (c 1.0, CH2Cl2); 1H NMR (300 MHz, CDCl3): δ = 0.83–0.93 (3H, m), 1.09–1.35 (14H, m), 1.62 (1H, dq, J 14.1, 3.6), 1.70–1.86 (1H, m), 1.96–2.18 (2H, m), 2.27–2.42 (1H, m), 2.94 (1H, dq, J 13.9, 3.3), 3.52–3.64 (1H, m), 3.90 (1H, dd, J 4.5, 2.9), 5.14 (1H, d, J 12.1), 5.31 (1H, d, J 12.1), 7.36 (5H, br s); 13C NMR (75.5 MHz, CDCl3): δ = 14.1, 22.6, 23.0, 25.0, 26.5, 29.2, 29.3, 31.8, 34.1, 39.6, 48.2, 67.8, 68.5, 128.5, 128.7, 134.8, 166.1; IR (neat): 1727, 1322, 1172, 1118; HRMS (ESI-TOF): m/z [M+H]+ calcd for C21H33O3S, 381.2094, found 381.2094.

**Benzyl (2R*,3R*)-3-nonyltetrahydrothiophene-2-carboxylate 1,1-dioxide (S30a)**

Benzyl (2R*,3R*)-3-nonyltetrahydrothiophene-2-carboxylate 1,1-dioxide S30a (44 mg, 29%, of which contains ~32% S30b, m at 3.36–3.50) was isolated as a colourless oil (an enriched S30a sample was obtained by taking the last few test tubes of the second most polar component); 1H NMR (300 MHz, CDCl3): δ = 0.82–0.94 (3H, m), 1.15–1.35 (14H, m), 1.38–1.61 (2H, m), 1.71–1.90 (1H, m), 2.30–2.43 (1H, m), 2.70–2.86 (1H, m), 3.09 (1H, td, J 12.8, 6.9), 3.26 (1H, qd, J 12.9, 6.9, 1.9), 3.61 (1H, d, J 9.4), 5.23 (1H, d, J 12.3), 5.30 (1H, d, J 12.3), 7.29–7.43 (5H, m); 13C NMR (75.5 MHz, CDCl3): δ = 14.1, 22.7, 26.6, 26.8, 29.2, 29.4, 29.5, 31.8, 34.4, 40.2, 52.7, 68.3, 71.0, 128.4, 128.55, 128.6, 134.9, 165.5; IR (neat): 1740, 1308, 1267, 1179, 1114; HRMS (ESI-TOF): m/z [M+H]+ calcd for C21H33O3S, 381.2094, found 381.2092.
**SUPPORTING INFORMATION**

**Benzyl (2R*,3S*)-3-nonyltetrahydrothiophene-2-carboxylate 1,1-dioxide (S30b)**

Benzyl (2R*,3S*)-3-nonyltetrahydrothiophene-2-carboxylate 1,1-dioxide **S30b** was isolated as a mixture with **S30a** (an enriched **S30b** sample was obtained by taking the first few test tubes of the second least polar component); characteristic peaks of **S30b**: 1H NMR (300 MHz, CDCl₃): δ = 3.37–3.50 (1H, m); 13C NMR (75.5 MHz, CDCl₃): δ = 27.6, 31.5, 40.0, 51.5, 67.7, 67.8, 165.2.

### 4.2.7. Cyclisation of α-diazo-β-oxosulfone 24

**Methyl (1R,4aS,8aR)-octahydro-1H-isothiochromene-1-carboxylate 2,2-dioxide**

The title compound was prepared following the procedure described for methyl (2R,3S)-3-phenyltetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide **17a** using methyl 2-((2′-cyclohexylethyl)sulfonyl)-2-diazoacetate **24** (534 mg, 1.95 mmol), Rh₂(2S-F-2′-NA)₉ **9b** (30.3 mg, 19.5 μmol) in deoxygenated DCM (15 mL). The diazo **24** solution was added dropwise over 120 minutes via syringe to the Schlenk tube using a syringe pump. The reaction solution was stirred overnight at ~20 °C before warming to room temperature. The reaction solution was filtered through a short pad of Celite® and activated charcoal, and concentrated under reduced pressure to give the crude product, which was then analysed by 1H NMR spectroscopy in CDCl₃. The 1H NMR in CDCl₃ showed very efficient C–H insertion in the synthesis of **30**, with a thiopyran diastereomeric ratio (96:4 dr, **30a:30b**, s at δH 3.85: m at δH 3.58–3.77). The crude product mixture, which was loaded using Celite®, was purified using column chromatography on silica gel, employing ethyl acetate/hexane (30:70) as eluent, and gave methyl (1R,4aS,8aR)-octahydro-1H-isothiochromene-1-carboxylate 2,2-dioxide **30a** (436 mg, 91%), and methyl (1R*,4aR*,8aS*)-octahydro-1H-isothiochromene-1-carboxylate 2,2-dioxide **30b** (10 mg, 2%); **30a**, most polar component, white solid; m.p. 163–164 °C (lit. 163–164 °C)[20] Spec. Rot.: [α]D²⁰ = −22.6 (c 1.0, CH₂Cl₂); HPLC: 84% ee (determined by chiral phase HPLC, see Table SI.6 for HPLC conditions); 1H NMR (300 MHz, CDCl₃): δ = 0.96–1.39 (5H, m), 1.58–1.86 (4H, m), 1.90–2.03 (2H, m), 2.13 (1H, qd, J 11.7, 3.2), 2.93–3.22 (2H, m), 3.63 (1H, d, J 11.7), 3.85 (3H, s); 13C NMR (75.5 MHz, CDCl₃): δ = 24.9, 25.6, 30.75, 30.83, 32.7, 40.5, 42.9, 52.4, 53.2, 71.2, 164.0; IR (neat): 1733, 1291, 1127; HRMS (ESI-TOF): m/z [M+H]+ calcd for C₁₁H₁₉O₂S 247.0993, found 247.0995.

**Elemental Analysis**: calcd (%) for C₁₁H₁₉O₂S: C, 53.64; H, 7.25. Found: C, 53.55; H, 7.25.

**Methyl (1R*,4aR*,8aS*)-octahydro-1H-isothiochromene-1-carboxylate 2,2-dioxide**

Methyl (1R*,4aR*,8aS*)-octahydro-1H-isothiochromene-1-carboxylate 2,2-dioxide **30b** (10 mg, 2%) was isolated as a white solid (least polar component); HPLC: 0% ee (determined by chiral phase HPLC, see Table SI.6 for HPLC conditions); 1H NMR (300 MHz, CDCl₃): δ = 0.92–1.11 (2H, m), 1.14–1.36 (2H, m), 1.62–2.14 (8H, m), 2.96 (1H, dq, J 14.0, 3.2), 3.58–3.77 (2H, m containing dd, J 4.6, 3.1), 3.80 (3H, s); 13C NMR (75.5 MHz, CDCl₃): δ = 25.4, 25.5, 30.9, 31.1, 32.9, 33.6, 43.0, 48.5, 52.8, 68.9, 166.9; IR (neat): 1731,1315, 1288, 1229, 1167, 1109; HRMS
(ESI-TOF): \( m/z \ [M+H]^+ \) calcd for \( \text{C}_{11}\text{H}_{18}\text{O}_4\text{S} \) 247.1004; found 247.1008; **Elemental Analysis**: calcd (%) for \( \text{C}_{11}\text{H}_{18}\text{O}_4\text{S} \): C, 53.64; H, 7.37. Found: C, 53.46; H, 7.37.
5. Synthesis of α-diazoacetamides

Procedure B

A 100 ml three-neck round-bottom flask was charged with water (10 ml), dichloromethane (5 ml) and sodium azide (5.5 eq.). The flask was cooled to 0 °C, after which trifluoromethanesulfonyl anhydride (1.1 eq.) was slowly added via syringe over 15 minutes while vigorously stirring the solution. The resulting solution was vigorously stirred at 0 °C for two hours after which the layers were separated. The aqueous layer was extracted with dichloromethane (5 ml) and the combined organic layer was washed with aqueous sodium carbonate (10 ml, 10%) and dried with magnesium sulfate. The dried solution of triflyl azide was added slowly to a solution of the relevant α-cyanoacetamide (1.0 eq) and triethylamine (1.1 eq.) in dichloromethane (30 ml for 10 mmol scale of α-cyanoacetamide) while stirring at 0 °C. The solution was allowed to slowly reach room temperature and reaction progression was monitored by IR spectroscopy. After complete disappearance of the azide stretch (~2100 cm\(^{-1}\)), the solution was carefully concentrated under reduced pressure. The desired α-cyano-α-diazoacetamide was afforded following purification by flash chromatography on silica gel using hexane:ethyl acetate (80:20) as eluent.\[21\]

Note: The resonance for the diazo carbon is a weak signal in the \(^{13}\)C NMR spectra and often is not observed for the derivatives across the series.

\[21\] N,N-Dibenzyl-2-cyano-2-diazoacetamide\[21\] (31)

This title compound was prepared according to Procedure B from N,N-(dibenzyl)-2-cyanoacetamide (2.84 g, 10.80 mmol), sodium azide (6.60 g, 100 mmol), trifluoromethanesulfonic anhydride (1.9 mL, 11.2 mmol) and triethylamine (1.70 mL, 12.0 mmol). The crude product was purified by flash chromatography on silica gel with hexane:ethyl acetate as eluent. Spectroscopic characteristics were consistent with previously reported data.\[21\] Yellow oil, 2.05 g (66%); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 4.59 \text{ (4H, s)}\), 7.19–7.38 (10H, m); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)): \(\delta = 50.3, 109.7, 127.7, 128.1, 128.9, 135.5, 159.9\); IR (neat): 2214, 2117, 1626.

\[21\] N-(tert-Butyl)-2-cyano-2-diazo-N-(4′-fluorobenzyl)acetamide\[21\] (33)

This title compound was prepared according to Procedure B from N-(tert-butyl)-2-cyano-N-(4′-fluorobenzyl)acetamide (3.12 g, 12.5 mmol), sodium azide (5.581 g, 85.80 mmol), trifluoromethanesulfonic anhydride (2.30 mL, 14.0 mmol) and triethylamine (1.80 mL, 13.0 mmol). The crude product was purified by flash chromatography on silica gel with hexane:ethyl acetate as eluent. Spectroscopic characteristics were consistent with previously reported data.\[21\] Yellow crystals, 2.22 g (65%); m.p. 105–107 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 1.42 \text{ (9H, s)}\), 4.67 (2H, s), 7.01–7.11 (2H, m), 7.13–7.22 (2H, m); \(^{19}\)F NMR (376.5 MHz, CDCl\(_3\)): \(\delta = -114.9\); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)): \(\delta = 28.5, 49.1, 60.4, 109.8, 115.7 (J_{CF} 21.7), 127.6 (J_{CF} 8.1), 134.1 (J_{CF} 3.2), 160.9, 162.0 (J_{CF} 246.0);\) IR (neat): 2213 (CN), 2121 (CN\(_2\)), 1626 (CO).
**SUPPORTING INFORMATION**

**N-(tert-Butyl)-2-cyano-2-diazo-N-(4′-bromobenzyl)acetamide**[21] (34)  
This title compound was prepared according to *Procedure B* from *N-(tert-butyl)-2-cyano-N-(4′-bromobenzyl)acetamide* (2.07 g, 6.700 mmol), sodium azide (2.60 g, 40.0 mmol), trifluoromethanesulfonic anhydride (1.2 mL, 7.0 mmol) and triethylamine (0.98 mL, 7.00 mmol). The crude product was purified by flash chromatography on silica gel with hexane:ethyl acetate as eluent. Spectroscopic characteristics were consistent with previously reported data.[21] Yellow crystals, 2.03 g (90%); m.p. 109–111 °C (Lit.[21] 109–112 °C); ^1^H NMR (400 MHz, CDCl$_3$): δ= 1.41 (9H, s), 4.65 (2H, s), 7.10 (2H, d, J 8.4), 7.50 (2H, d, J 8.4); ^1^C NMR (100.6 MHz, CDCl$_3$): δ= 28.5, 49.3, 54.8, 60.4, 109.7, 121.3, 127.7, 131.9, 137.6, 160.9; IR (neat): 2213, 2119, 1634.

**N-(tert-Butyl)-2-cyano-2-diazo-N-(4′-chlorobenzyl)acetamide**[21] (35)  
This compound was prepared according to *Procedure B* from *N-(tert-butyl)-2-cyano-N-(4′-chlorobenzyl)acetamide* (2.50 g, 9.40 mmol), sodium azide (5.37 g, 83.0 mmol), trifluoromethanesulfonic anhydride (1.63 mL, 10.0 mmol) and triethylamine (1.35 mL, 10.0 mmol). The crude product was purified by flash chromatography on silica gel with hexane:ethyl acetate as eluent. Spectroscopic characteristics were consistent with previously reported data.[21] Yellow crystals, 1.76 g (64%); m.p. 108–110 °C (Lit.[21] 109–113 °C); ^1^H NMR (400 MHz, CDCl$_3$): δ= 1.41 (9H, s), 4.67 (2H, s), 7.16 (2H, d, J 8.4), 7.34 (2H, d, J 8.4); ^1^C NMR (100.6 MHz, CDCl$_3$): δ= 28.5, 49.2, 54.8, 60.4, 109.7, 127.4, 128.9, 133.2, 137.1, 160.9; IR (neat): 2213, 2118, 1634.

**N-(tert-Butyl)-2-cyano-2-diazo-N-(2′,6′-dichlorobenzyl)acetamide** (36)  
This title compound was prepared according to *Procedure B* from *N-(tert-butyl)-2-cyano-N-(2′,6′-dichlorobenzyl)acetamide* (2.41 g, 8.10 mmol), sodium azide (4.00 g, 62.0 mmol), trifluoromethanesulfonic anhydride (1.41 mL, 8.50 mmol) and triethylamine (0.85 mL, 8.50 mmol). The crude product was purified by flash chromatography on silica gel with hexane:ethyl acetate as eluent. Yellow crystals, 2.50 g (94%); m.p. 109–110 °C; ^1^H NMR (400 MHz, CDCl$_3$): δ= 1.33 (9H, s), 4.92 (2H, s), 7.17–7.24 (1H, m), 7.34 (2H, d, J 8.0); ^1^C NMR (100.6 MHz, CDCl$_3$): δ= 28.3, 48.1, 59.9, 110.0, 129.5, 129.6, 132.3, 135.8, 162.9; IR (neat): 2214, 2118, 1642; HRMS (ESI-TOF): m/z [M+Na]$^+$ calcd for C$_{15}$H$_{14}$Cl$_2$N$_2$ONa 347.0437, found 347.0439.

**N-(tert-Butyl)-2-cyano-2-diazo-N-(4′-methylbenzyl)acetamide**[21] (37)  
This title compound was prepared according to *Procedure B* from *N-(tert-butyl)-2-cyano-N-(4′-methylbenzyl)acetamide* (1.72 g, 7.00 mmol), sodium azide (2.60 g, 40.0 mmol), trifluoromethanesulfonic anhydride (1.3 mL, 7.2 mmol) and triethylamine (1.00 mL, 7.20 mmol). The crude product was purified by flash chromatography on silica gel with hexane:ethyl acetate as eluent. Spectroscopic characteristics were consistent with previously reported data.[21] Yellow crystals, 1.56 g (83%); m.p. 86–88 °C.
SUPPORTING INFORMATION

(Lit.,[21] 85–86 °C); 1H NMR (400 MHz, CDCl3): δ = 1.42 (9H, s), 2.34 (3H, s), 4.67 (2H, s), 7.09 (2H, d, J 8.1), 7.17 (2H, d, J 8.0); 13C NMR (100.6 MHz, CDCl3): δ = 21.1, 28.5, 49.7, 60.3, 109.9, 125.9, 129.4, 135.3, 137.1, 160.9; IR (neat): 2213, 2117, 1634.

N-(tert-Butyl)-2-cyano-2-diazo-N-(3′,5′-dimethylbenzyl)acetamide (38)

This title compound was prepared according to Procedure B from N-(tert-butyl)-2-cyano-N-(3′,5′-dimethylbenzyl)acetamide (2.78 g, 10.8 mmol), sodium azide (6.00 g, 92.0 mmol), trifluoromethanesulfonic anhydride (1.90 mL, 11.2 mmol) and triethylamine (1.60 mL, 11.2 mmol). Purified by flash chromatography on silica gel with hexane:ethyl acetate as eluent. Yellow crystals, 1.79 g (58%); m.p. 105–107 °C; 1H NMR (400 MHz, CDCl3): δ = 1.42 (9H, s), 2.31 (6H, s), 4.64 (2H, s), 6.79 (2H, s), 6.90 (1H, s); 13C NMR (100.6 MHz, CDCl3): δ = 21.4, 28.5, 49.7, 60.3, 109.9, 123.8, 129.1, 138.2, 138.3, 160.9; IR (neat): 2213, 2119, 1634; HRMS (ESI-TOF): m/z [M+Na]⁺ calcld for C₁₆H₂₈N₄O₃Na 307.1529, found 307.1533.

N-(tert-Butyl)-2-cyano-2-diazo-N-(2′,4′,6′-trimethylbenzyl)acetamide (39)

This title compound was prepared according to Procedure B from N-(tert-butyl)-2-cyano-N-(2′,4′,6′-trimethylbenzyl)acetamide (1.78 g, 6.50 mmol), sodium azide (3.60 g, 55.0 mmol), trifluoromethanesulfonic anhydride (1.10 mL, 6.80 mmol) and triethylamine (0.95 mL, 6.80 mmol). The crude product was purified by flash chromatography on silica gel with hexane:ethyl acetate as eluent. Yellow crystals, 1.18 g (61%); m.p. 91–92 °C; 1H NMR (400 MHz, CDCl3): δ = 1.31 (9H, s), 2.26 (3H, s), 2.32 (6H, s), 4.64 (2H, s), 6.82 (2H, s); 13C NMR (100.6 MHz, CDCl3): δ = 20.7, 20.8, 28.2, 47.8, 59.9, 109.8, 130.3, 131.0, 136.8, 137.2, 163.1; IR (neat): 2215, 2119, 1635; HRMS (ESI-TOF): m/z [M+Na]⁺ calcld for C₁₇H₂₉N₄O₃Na 321.1685, found 321.1685.

N-Benzyl-N-(tert-butyl)-2-cyano-2-diazoacetamide[21] (40)

This title compound was prepared according to Procedure B from N-(tert-butyl)-2-cyano-N-(benzyl)acetamide (2.04 g, 8.90 mmol), sodium azide (3.65 g, 60.80 mmol), trifluoromethanesulfonic anhydride (1.5 mL, 9.5 mmol) and triethylamine (1.3 mL, 9.5 mmol). The crude product was purified by flash chromatography on silica gel with hexane:ethyl acetate as eluent. Spectroscopic characteristics were consistent with previously reported data.[21] Yellow crystals, 1.65 g (72%); m.p. 88–92 °C (Lit.,[21] 89–91 °C); 1H NMR (400 MHz, CDCl3): δ = 1.43 (9H, s), 4.71 (2H, s), 7.18–7.42 (5H, m); 13C NMR (100.6 MHz, CDCl3): δ = 28.5, 49.7, 60.3, 109.8, 126.0, 127.5, 128.7, 138.4, 160.9; IR (neat): 2214, 2121, 1634.
This title compound was prepared according to Procedure B from N-(tert-butyl)-2-cyano-N(4'-nitrobenzyl)acetamide (2.89 g, 10.5 mmol), sodium azide (6.00 g, 92.0 mmol), trifluoromethanesulfonic anhydride (1.85 mL, 11.0 mmol) and triethylamine (1.50 mL, 11.0 mmol). This crude product was purified by flash chromatography on silica gel with hexane:ethyl acetate as eluent. Spectroscopic characteristics were consistent with previously reported data.[21] Yellow crystals, 1.570 g (50%); m.p. 125–127 °C (Lit.[21] 122–124 °C); 1H NMR (400 MHz, CDCl3): δ = 1.43 (9H, s), 4.80 (2H, s), 7.43 (2H, d, J 8.8), 8.23–8.28 (2H, m); 13C NMR (100.6 MHz, CDCl3): δ = 28.4, 49.4, 54.8, 60.6, 109.6, 124.0, 126.8, 146.3, 147.3, 161.1; IR (neat): 2214, 2125, 1719, 1636.

This title compound was prepared according to Procedure B from N-(tert-butyl)-2-cyano-N(4'-carbomethoxybenzyl)acetamide (0.79 g, 2.70 mmol), sodium azide (1.17 g, 18.0 mmol), trifluoromethanesulfonic anhydride (0.50 mL, 3.0 mmol) and triethylamine (0.43 mL, 3.0 mmol). The crude product was purified by flash chromatography on silica gel with hexane:ethyl acetate as eluent. Spectroscopic characteristics were consistent with previously reported data.[21] Yellow crystals, 1.86 g (81%); m.p. 88–91 °C (Lit.[21] 90–93 °C); 1H NMR (400 MHz, CDCl3): δ = 1.42 (9H, s), 3.92 (3H, s), 4.75 (2H, s), 7.31 (2H, d, J 8.2), 8.05 (2H, d, J 8.3); 13C NMR (100.6 MHz, CDCl3): δ = 28.5, 49.7, 52.2, 60.5, 109.6, 126.0, 129.4, 130.1, 143.8, 161.0, 166.8; IR (neat): 2214, 2125, 1719, 1636.

This title compound was prepared according to Procedure B from N-(tert-butyl)-2-cyano-N(4'-trifluoromethylbenzyl)acetamide (2.00 g, 6.70 mmol), sodium azide (2.60 g, 40.8 mmol), trifluoromethanesulfonic anhydride (1.2 mL, 7.0 mmol) and triethylamine (0.98 mL, 7.00 mmol). The crude product was purified by flash chromatography on silica gel with hexane:ethyl acetate as eluent. Spectroscopic characteristics were consistent with previously reported data.[21] Yellow crystals, 1.95 g (90%); m.p. 68–69 °C (Lit.[21] 65–67 °C); 1H NMR (400 MHz, CDCl3): δ = 1.43 (9H, s), 4.76 (2H, s), 7.35 (2H, d, J 8.3), 7.64 (2H, d, J 8.3); 19F NMR (376.5 MHz, CDCl3): δ = −62.5; 13C NMR (100.6 MHz, CDCl3): δ = 28.5, 49.4, 60.5, 109.6, 124.0 (q, JCF 272.0), 125.8 (q, JCF 3.8), 126.3, 129.8 (q, JCF 32.6), 142.7, 161.0; IR (neat): 2214, 2122, 1640.
This title compound was prepared according to Procedure B from N-(tert-buty1)-2-cyano-N-(4'-cyanobenzyl) acetamide (3.19 g, 12.5 mmol), sodium azide (5.58 g, 85.80 mmol), trifluoromethanesulfonic anhydride (2.30 mL, 14.0 mmol) and triethylamine (1.80 mL, 13.0 mmol). The crude product was purified by flash chromatography on silica gel with hexane:ethyl acetate as eluent. Yellow crystals, 1.99 g (57%); m.p. 148–150 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 1.42 (9H, s), 4.75 (2H, s), 7.36 (2H, d, J 7.8), 7.69 (2H, d, J 8.1); $^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$ = 28.5, 49.5, 60.6, 109.6, 111.5, 118.5, 126.7, 132.6, 144.2, 161.1; IR (neat): 2228, 2214, 2123, 1638; HRMS (ESI-TOF): $m/z$ [M+H]$^+$ calcd for C$_{15}$H$_{16}$N$_5$O 304.1169, found 304.1172.

This title compound was prepared according to Procedure B from N-(tert-buty1)-2-cyano-N-(4'-methoxybenzyl) acetamide (3.27 g, 12.50 mmol), sodium azide (5.58 g, 85.8 mmol), trifluoromethanesulfonic anhydride (2.20 mL, 13.0 mmol) and triethylamine (1.82 mL, 13.0 mmol). The crude product was purified by flash chromatography on silica gel with hexane:ethyl acetate as eluent. Spectroscopic characteristics were consistent with previously reported data. Yellow crystals, 2.72 g (76%); m.p. 108–111 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 1.41 (9H, s), 3.81 (3H, s), 4.65 (2H, s), 6.90 (2H, d, J 8.6), 7.12 (2H, d, J 8.5); $^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$ = 28.5, 49.2, 55.3, 60.2, 109.9, 114.1, 127.2, 130.2, 158.9, 160.8; IR (neat): 2213, 2120, 1633.
6. Aromatic Addition

Table SI.5: Aromatic addition catalyst screen of \( \alpha \)-cyano-\( \alpha \)-diazoacetamide 31

| Entry | Catalyst\(^a\) | Time (h) | 32 Yield (%\(^b\)) | 32 % ee\(^c\) |
|-------|----------------|----------|---------------------|----------------|
| 1\(^d\) | Rh\(_2\)(OAc)\(_4\) | 1.0 | 90                | -              |
| 2     | Rh\(_2\)(2S-F-2'-NA)\(_4\) 9b | 1.5 | 85 | 67              |
| 3     | Rh\(_2\)(2S-MBrPA)\(_4\) 9h | 1.5 | 84 | 53              |
| 4     | Rh\(_2\)(2S-M-2'-NA)\(_4\) 9g | 1.5 | 87 | 51              |
| 5     | Rh\(_2\)(2S-FBrPA)\(_4\) 9d | 1.5 | 88 | 59              |
| 6     | Rh\(_2\)(2S-FOMePA)\(_4\) 9e | 1.5 | 90 | 73              |
| 7\(^d,e\) | Rh\(_2\)(2S-FOMePA)\(_4\) 9e | 12.0 | 75 | 60              |
| 8     | Rh\(_2\)(2S-F-1'-NA)\(_4\) 9c | 1.5 | 87 | 62              |
| 9     | Rh\(_2\)(S-DOSP)\(_4\) 2 | 1.5 | 80 | 17              |
| 10    | Rh\(_2\)(S-PTTL)\(_4\) 3 | 1.5 | 85 | 11\(^f\)        |
| 11    | Rh\(_2\)(S-TCPPTTL)\(_4\) 4 | 1.5 | 80 | 14              |
| 12    | Rh\(_2\)(S-TFPTTL)\(_4\)  | 1.5 | 82 | 32\(^f\)        |
| 13    | CuPF\(_6\)-((R,R)-Ph-BOX) | 12 | 88 | 36              |

\(^a\) 1.0 mol\% of catalyst. \(^b\) Purified by flash chromatography. \(^c\) Enantiomeric excess determined by chiral HPLC analysis; dextrorotatory (+), 1\(S\) enantiomer predominates in each case, unless otherwise stated. \(^d\) Reaction performed at room temperature. \(^e\) Toluene used as solvent. \(^f\) Levorotatory (–), 1\(R\) enantiomer
Figure SI.2: Graph of time, yield and enantiopurity versus temperature for the Rh₂(2S-F-2'-NA)₄ 9b catalysed transformation of α-cyano-α-diazoacetamide 31.

Scheme SI.2: Impact of catalyst loading on the aromatic addition of affording α-cyano-α-diazoacetamide 33.

1.20 mol%[Rh] 83%, 87% ee
0.60 mol%[Rh] 83%, 87% ee
0.20 mol%[Rh] 85%, 87% ee
0.05 mol%[Rh] 91%, 88% ee
Table SI.6: Rhodium acetate catalyzed aromatic addition reactions of α-cyano-α-diazoacetamides 31, 33–45 \[a\]

\[
\begin{align*}
31, 33–45 & \xrightarrow{\text{Rh}_2(OAc)_4 (1 \text{ mol%})} 32, 46–58
\end{align*}
\]

| Compounds | Yield |
|-----------|-------|
| 46        | 92%   |
| 47        | 80%   |
| 48        | 80%   |
| 49        | 98%   |
| 50        | 76%   |
| 51        | 78%   |
| 52        | 86%   |
| 53        | 83%   |
| 32        | 90%   |
| 54        | 75%   |
| 55        | 77%   |
| 56        | 82%   |
| 57        | 95%   |
| 58        | 89%   |

\[a\]Isolated yields after chromatography.

**Procedure C**

A round bottom flask was charged with dichloromethane (35 mL) and Rh\(_2\)(2S-FOMePA)\(_4\) 9e (1.0 mol%). The flask was cooled to 0 °C, after which a solution of α-diazoacetamide (0.100 g) in CH\(_2\)Cl\(_2\) (15 mL) was added over the course of 15 minutes. The reaction progress was monitored by IR spectroscopy. Following complete disappearance of the diazo stretch (2119–2129 cm\(^{-1}\)), the solution was concentrated under reduced pressure and the resulting residue was purified by silica gel chromatography using hexane:ethyl acetate (75:25) as eluent.
9-Aza-9-benzyl-1(S)-cyanobicyclo[5.3.0]deca-2,4,6-trien-10-one[21] (32)

This title compound was prepared according to Procedure C from N,N-dibenzyl-α-cyano-α-diazoacetamide (0.10 g, 0.38 mmol) and Rh₂(2S-FOMePA)₄ 9e (5.0 mg, 1.0 mol%) in dichloromethane (50 mL). Colourless crystals (0.080 g, 90%). Spectroscopic characteristics were consistent with previously reported data.[21] m.p. 172–174 °C (Lit.,[21] 172–174 °C); Spec. Rot.: [α]₀⁺¹⁺36.00 (c 0.200, CHCl₃); HPLC: 73% ee (determined by chiral phase HPLC, see Table S1.6 for HPLC conditions); ¹H NMR (400 MHz, CDCl₃): δ= 3.93 (1H, d, J 14.9), 4.16 (1H, d, J 14.9) 4.59 (2H, s), 5.14 (1H, d, J 8.8), 6.28–6.37 (1H, m), 6.40–6.49 (1H, m), 6.68–6.77 (2H, m), 7.22–7.41 (5H); ¹³C NMR (100.6 MHz, CDCl₃): δ= 41.9, 47.3, 49.7, 107.3 br, 113.0 br, 114.1, 122.6, 128.3, 129.6, 130.3, 128.5, 129.1, 134.9, 167.4; IR (neat): 2238, 1704.

9-Aza-9-tert-butyl-1(S)-cyano-4-fluorobicyclo[5.3.0]deca-2,4,6-trien-10-one[21] (46)

This title compound was prepared according to Procedure C from N-(tert-butyl)-2-cyano-2-diazo-N-(4’-fluorobenzyl) acetamide (0.10 g, 0.39 mmol) and Rh₂(2S-FOMePA)₄ 9e (5.0 mg, 1.0 mol%) in dichloromethane (50 mL). Spectroscopic characteristics were consistent with previously reported data.[21] Colourless crystals (0.075 g, 83%); m.p. 175–177 °C (Lit.,[21] 177–178 °C); Spec. Rot.: [α]₀⁺¹⁺119.67 (c 0.300, CHCl₃); HPLC: 88% ee (determined by chiral phase HPLC, see Table S1.6 for HPLC conditions); ¹H NMR (400 MHz, CDCl₃): δ= 1.48 (9H, s), 4.19 (1H, d, J 15.3), 4.43 (1H, d, J 15.3), 5.44 (1H, dd, J 9.7, 4.9), 6.34–6.44 (2H, m), 6.51 (1H, dd, J 16.0, 7.7); ¹³C NMR (100.6 MHz, CDCl₃): δ= 27.4, 45.5, 48.7, 55.7, 112.0 (²JCF 28.7), 114.5, 115.7 br, 117.0 br, 120.0 (d, ³JCF 11.3), 122.7 (d, ²JCF 35.7) 161.0 (d, ¹JCF 248.6) 166.2; ¹⁹F NMR (376.5 MHz, CDCl₃): δ= –97.5; IR (neat): 2239, 1704.

9-Aza-9-tert-butyl-1(S)-cyano-4-bromobicyclo[5.3.0]deca-2,4,6-trien-10-one[21] (47)

This title compound was prepared according to Procedure C from N-(tert-butyl)-2-cyano-2-diazo-N-(4’-bromobenzyl) acetamide (0.10 g, 0.33 mmol) and Rh₂(2S-FOMePA)₄ 9e (5.0 mg, 1.0 mol%) in dichloromethane (50 mL). Spectroscopic characteristics were consistent with previously reported data.[21] Colourless crystals (0.089 g, 72%); m.p. 167–169 °C (Lit.,[21] 169–171 °C); Spec. Rot.: [α]₀⁺¹⁺148.58 (c 0.140, CHCl₃); HPLC: 85% ee (determined by chiral phase HPLC, see Table S1.6 for HPLC conditions); ¹H NMR (400 MHz, CDCl₃): δ= 1.47 (9H, s), 4.15 (1H, d, J 15.4), 4.36 (1H, dd, J 15.3, 1.1), 5.14 (1H, d, J 9.3), 6.23 (1H, d, J 7.1), 6.57 (1H, d J 9.4), 7.12 (1H, d, J 7.1); ¹³C NMR (100.6 MHz, CDCl₃): δ= 27.4, 44.1 br, 48.7, 55.7, 111.9 br, 114.1, 117.5 br, 122.0, 124.2, 131.9, 132.1, 166.2; IR (neat): 2238, 1702.
SUPPORTING INFORMATION

9-Aza-9-tert-butyl-1(S)-cyano-4-chlorobicyclo[5.3.0]deca-2,4,6-trien-10-one\[^{21}\] (48)

This title compound was prepared according to Procedure C from N-(tert-butyl)-2-cyano-2-diazo-N-(4'-chlorobenzyl)acetamide (0.10 g, 0.38 mmol) and Rh₂(2SFOMePA)₄ \(9e\) (5.0 mg, 1.0 mol%) in dichloromethane (50 mL). Spectroscopic characteristics were consistent with previously reported data.\[^{21}\] Colourless crystals (0.079 g, 83%); \textbf{m.p.} 172–175 °C (Lit.,\[^{21}\] 178–179 °C); \textbf{Spec. Rot.: }[\alpha]_{D}^{20} +152.50 (c 0.080, CHCl₃); \textbf{HPLC: }84% ee (determined by chiral phase HPLC, see \textbf{Table SI.6} for HPLC conditions); \textbf{1H NMR (400 MHz, CDCl₃): }\(\delta = 1.47\) (9H, s), 4.17 (1H, d, J 15.2), 4.38 (1H, dd, J 15.2, 1.4), 5.19 (1H, d, J 9.3), 6.30–6.35 (1H, m), 6.43 (1H, dd, J 9.3, 1.0), 6.88 (1H, d, J 7.1); \textbf{13C NMR (100.6 MHz, CDCl₃): }\(\delta = 27.4, 43.7, 48.8, 55.7, 110.7\) br, 114.1, 115.5 br, 121.4, 128.7, 129.6, 135.2, 166.2; \textbf{IR (neat): }2237, 1703.

9-Aza-9-tert-butyl-1(R)-cyano-2,6-dichlorobicyclo[5.3.0]deca-2,4,6-trien-10-one (49)

This title compound was prepared according to Procedure C from N-(tert-butyl)-2-cyano-2-diazo-N-(2',6'-dichlorobenzyl) acetamide (0.10 g, 0.34 mmol) and Rh₂(2SFOMePA)₄ \(9e\) (5.0 mg, 1.0 mol%) in dichloromethane (50 mL). White crystals (0.099 g, 98%); \textbf{m.p.} 122–124 °C; \textbf{Spec. Rot.: }[\alpha]_{D}^{20} +157.50 (c 0.080, CHCl₃); \textbf{HPLC: }83% ee (determined by chiral phase HPLC, see \textbf{Table SI.6} for HPLC conditions); \textbf{1H NMR (400 MHz, CDCl₃): }\(\delta = 1.52\) (9H, s), 4.23 (1H, d, J 16.6), 4.38 (1H, d, J 16.5), 6.63 (1H, d, J 6.7), 6.67–6.74 (1H, 6.82 (1H, d, J 11.4); \textbf{13C NMR (100.6 MHz, CDCl₃): }\(\delta = 27.4, 48.7, 51.0, 56.3, 112.5, 117.4, 119.0, 126.2, 127.5, 129.6, 130.0, 162.9; \textbf{IR (neat): }2242, 1715; \textbf{HRMS (ESI-TOF): }m/z [M+H]\(^+\) calcd for C₁₅H₁₅Cl₃N₂O, 297.0556, found 297.0559.

9-Aza-9-tert-butyl-1(S)-cyano-4-methylbicyclo[5.3.0]deca-2,4,6-trien-10-one\[^{21}\] (50)

This title compound was prepared according to Procedure C from N-(tert-butyl)-2-cyano-2-diazo-N-(4'-methylbenzyl) acetamide (0.10 g, 0.41 mmol) and Rh₂(2SFOMePA)₄ \(9e\) (5.0 mg, 1.0 mol%) in dichloromethane (50 mL). Spectroscopic characteristics were consistent with previously reported data.\[^{21}\] Colourless crystals (0.086 g, 89%); \textbf{m.p.} 133–135 °C (Lit.,\[^{21}\] 132–133 °C); \textbf{Spec. Rot.: }[\alpha]_{D}^{20} +144.00 (c 0.100, CHCl₃); \textbf{HPLC: }87% ee (determined by chiral phase HPLC, see \textbf{Table SI.6} for HPLC conditions); \textbf{1H NMR (400 MHz, CDCl₃): }\(\delta = 1.45\) (9H, s), 2.11 (3H, s), 4.03 (1H, d, J 14.0), 4.25 (1H, d, J 14.0), 4.65 br (1H, d, J 8.2), 6.17 (1H, d, J 8.3), 6.22 (1H, d, J 7.2), 6.46 (1H, d, J 7.2); \textbf{13C NMR (100.6 MHz, CDCl₃): }\(\delta = 23.7, 27.4, 38.6\) br, 49.0, 55.2, 96.2 br, 114.5, 122.1, 127.8, 128.1, 138.9, 167.4; \textbf{IR (neat): }2238, 1702.

\textit{Note: Resonance for C(2) not detected due to signal broadening}
9-Aza-9-tert-butyl-1(S)-cyano-3,5-dimethylbicyclo[5.3.0]deca-2,4,6-trien-10-one\(^{[21]}\) (51)

This title compound was prepared according to Procedure C from \(N\)-(tert-butyl)-2-cyano-2-diazoo-\(N\)-(3',5'-dimethylbenzyl) acetamide (0.10 g, 0.39 mmol) and \(\text{Rh}_2(2\text{S}-\text{FOMePA})_4\) 9e (5.0 mg, 1.0 mol%) in dichloromethane (50 mL). Spectroscopic characteristics were consistent with previously reported data.\(^{[21]}\) Colourless crystals (0.080 g, 88%); m.p. 191–192 °C; Spec. Rot.: \([\alpha]_D^{20} +261.50\) (c 0.100, CHCl\(_3\)); HPLC: 68% ee (determined by chiral phase HPLC, see Table SI.6 for HPLC conditions); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta=\) 1.41 (9H, s), 2.00, 2.02 (2 × 3H, 2 × s), 3.38 (1H, br s), 3.73 (1H, d, J 12.2), 3.93 (1H, d, J 12.1), 5.77 (1H, s), 6.17 (1H, s); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)): \(\delta=\) 22.5, 22.6, 27.5, 49.8, 54.9, 113.4, 117.8, 128.1, 134.2, 136.3, 168.0; IR (neat): 2237, 1677; HRMS (ESI-TOF): \(m/z [M+H]^+\) calcd for \(\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}\) 257.1648, found 257.1647.

Note: Resonances for C(1), C(2)H and C(7) not detected due to signal broadening.

9-Aza-9-tert-butyl-1(S)-cyano-2,4,6-trimethylbicyclo[5.3.0]deca-2,4,6-trien-10-one\(^{[21]}\) (52)

This title compound was prepared according to Procedure C from \(N\)-(tert-butyl)-2-cyano-2-diazoo-\(N\)-(2',4',6'-trimethylbenzyl) acetamide (0.10 g, 0.37 mmol) and \(\text{Rh}_2(2\text{S}-\text{FOMePA})_4\) 9e (5.0 mg, 1.0 mol%) in dichloromethane (50 mL). Spectroscopic characteristics were consistent with previously reported data.\(^{[21]}\) Colourless crystals (0.070 g, 76%); m.p. 184–185 °C; Spec. Rot.: \([\alpha]_D^{20} +256.50\) (c 0.100, CHCl\(_3\)); HPLC: 63% ee (determined by chiral phase HPLC, see Table SI.6 for HPLC conditions); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta=\) 1.50 (9H, s), 1.84 (3H, s), 2.00 (3H, s), 2.10 (3H, s), 4.09 (1H, d, J 14.9), 4.28 (1H, d, J 14.8), 5.97 (1H, s), 6.41 (1H, s); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)): \(\delta=\) 17.8, 19.5, 24.3, 27.5, 48.3, 50.0, 55.4, 114.8, 116.1, 124.9, 127.8, 128.9, 130.0, 138.8, 166.8; IR (neat): 2236, 1699; HRMS (ESI-TOF): \(m/z [M+H]^+\) calcd for \(\text{C}_{17}\text{H}_{23}\text{N}_2\text{O}\) 271.1805, found 271.1799.

9-Aza-9-tert-butyl-1(S)-cyanobicyclo[5.3.0]deca-2,4,6-trien-10-one\(^{[21]}\) (53)

This title compound was prepared according to Procedure C from \(N\)-(tert-butyl)-2-cyano-2-diazoo-\(N\)-benzyl-acetamide (0.10 g, 0.44 mmol) and \(\text{Rh}_2(2\text{S}-\text{FOMePA})_4\) 9e (5.0 mg, 1.0 mol%) in dichloromethane (50 mL). Spectroscopic characteristics were consistent with previously reported data.\(^{[21]}\) Colourless crystals (0.080 g, 89%); m.p. 147–149 °C (Lit.\(^{[21]}\) 147–148 °C); Spec. Rot.: \([\alpha]_D^{20} +159.00\) (c 0.200, CHCl\(_3\)); HPLC: 72% ee (determined by chiral phase HPLC, see Table SI.6 for HPLC conditions); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta=\) 1.47 (9H, s), 4.17 (H, dd, J 14.9, 1.1), 4.38 (H, dd, J 14.9, 1.9), 5.08 (1H, d, J 8.8), 6.34–6.44 (2H, m), 6.69–6.74 (2H, m); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)): \(\delta=\) 27.4, 43.3, 48.9, 55.4, 107.9 br, 113.7 br, 114.5, 122.2, 128.2, 129.4, 130.2, 167.1; IR (neat): 2236, 1700.

9-Aza-9-tert-butyl-1(R)-cyano-4-nitro bicyclo[5.3.0]deca-2,4,6-trien-10-one (54)

This title compound was prepared according to Procedure C from \(N\)-(tert-butyl)-2-cyano-2-diazoo-\(N\) (4’-nitrobenzyl) acetamide (0.10 g, 0.37 mmol) and \(\text{Rh}_2(2\text{S}-\text{FOMePA})_4\) 9e (5.0 mg, 1.0 mol%) in dichloromethane (50 mL). Colourless crystals (0.063 g, 50%); m.p. 124–126 °C (Lit.\(^{[21]}\) 125–127 °C); Spec. Rot.: \([\alpha]_D^{20} -79.17\)
9-Aza-9-tert-butyl-1(S)-cyano-4-methoxycarbonylbicyclo[5.3.0]deca-2,4,6-trien-10-one[21] (55)

This title compound was prepared according to Procedure C from \(N\)-(tert-butyl)-2-cyano-2-diazo-\(N\)\(\prime\)-carbomethoxybenzyl) acetamide (0.10 g, 0.35 mmol) and \(\text{Rh}(2\text{S}-\text{FOMePA})_4\) \(9\text{e}\) (5.0 mg, 1.0 mol%) in dichloromethane (50 mL). Spectroscopic characteristics were consistent with previously reported data.[21] Colourless crystals (0.084 g, 82%); m.p. 170–172 °C (Lit.,[21] 173–174 °C); Spec. Rot.: \([\alpha]_D^{20} +35.83\) (c 0.120, CHCl\(_3\)); HPLC: 43% ee (determined by chiral phase HPLC, see Table Sl.6 for HPLC conditions); \(^1\text{H NMR (400 MHz, CDCl}\_3\)}: \(\delta= 1.50\) (9H, s), 3.87 (CH\(_3\), s) 4.19 (1H, d, J 15.5), 4.42 (1H, dd, J 15.7, 1.5), 5.11 (1H, d, J 9.0), 6.50 (1H, d, J 7.2), 7.07 (1H, d J 9.0), 7.68 (1H, d, J 7.2); \(^{13}\text{C NMR (100.6 MHz, CDCl}\_3\)}: \(\delta= 27.4, 41.9, 49.1, 52.6, 55.6, 105.3\) br, 113.7, 115.5 br, 121.6, 128.2, 131.9, 133.7, 166.3, 166.4; IR (neat): 2240, 1704.

9-Aza-9-tert-butyl-1(R)-cyano-4-trifluoromethylbicyclo[5.3.0]deca-2,4,6-trien-10-one[21] (56)

This title compound was prepared according to Procedure C from \(N\)-(tert-butyl)-2-cyano-2-diazo-\(N\)\(\prime\)-trifluoromethylbenzyl) acetamide (0.10 g, 0.34 mmol) and \(\text{Rh}(2\text{S}-\text{FOMePA})_4\) \(9\text{e}\) (5.0 mg, 1.0 mol%) in dichloromethane (50 mL). Spectroscopic characteristics were consistent with previously reported data.[21] Colourless crystals (0.074 g, 76%); m.p. 153–155 °C (Lit.,[21] 154–156 °C); Spec. Rot.: \([\alpha]_D^{20} –24.29\) (c 0.140, CHCl\(_3\)); HPLC: 27% ee (determined by chiral phase HPLC, see Table Sl.6 for HPLC conditions); \(^1\text{H NMR (400 MHz, CDCl}\_3\)}: \(\delta= 1.48\) (9H, s), 4.15 (1H, d, J 15.1), 4.39 (1H, d, J 15.2), 5.08 (1H, d, J 8.8), 6.47 (1H, d, J 7.1), 6.63 (1H, d J 8.9), 7.11 (1H, d, J 7.2); \(^{13}\text{C NMR (100.6 MHz, CDCl}\_3\)}: \(\delta= 27.4, 40.3\) br, 49.1, 55.7, 103.9 br, 113.1, 121.4, 123.1 (q, \(\text{J}\_\text{CF} 273.5\)), 124.2 (q, \(\text{J}\_\text{CF} 3.0\)), 127.6 (q, \(\text{J}\_\text{CF} 5.0\)), 131.7 (q, \(\text{J}\_\text{CF} 30.7\)), 166.1; \(^{19}\text{F NMR (376.5 MHz, CDCl}\_3\)}: \(\delta= –65.8\); IR (neat): 2245 (CN), 1703 (CO).

9-Aza-9-tert-butyl-1(S),4-dicyanobicyclo[5.3.0]deca-2,4,6-trien-10-one (57)

This title compound was prepared according to Procedure C from \(N\)-(tert-butyl)-2-cyano-2-diazo-\(N\)\(\prime\)-cyanobenzyl) acetamide (0.10 g, 0.40 mmol) and \(\text{Rh}(2\text{S}-\text{FOMePA})_4\) \(9\text{e}\) (5.0 mg, 1.0 mol%) in dichloromethane (50 mL). Colourless crystals (0.073 g, 80%); m.p. 153–155 °C; Spec. Rot.: \([\alpha]_D^{20} +27.09\) (c 0.120, CHCl\(_3\)); HPLC: 26% ee (determined by chiral phase HPLC, see Table Sl.6 for HPLC conditions); \(^1\text{H NMR (400 MHz, CDCl}\_3\)}: \(\delta= 1.48\) (9H, s), 4.23 (1H, d, J 16.1), 4.46 (1H, dd, J 16.2, 1.6), 5.23 (1H, d, J 9.0), 6.53 (1H, d, J 7.0), 6.61 (1H, d J 8.9), 7.26 (1H, d, J 6.5); \(^{13}\text{C NMR (100.6 MHz, CDCl}\_3\)}: \(\delta= 27.4, 43.0, 49.1, 55.9, 111.0\) br, 113.1, 115.1, 118.1, 120.7 br, 121.7, 128.4, 137.9 165.5; IR (neat): 2227, 1701; HRMS (ESI-TOF): \(m/z [\text{M}+\text{H}]^+\) calcd for \(\text{CsH}_{16}\text{NaO}_{254.1288}\), found 254.1289.
9-Aza-9-tert-butyl-1(S)-cyano-4-methoxybicyclo[5.3.0]deca-2,4,6-trien-10-one\textsuperscript{[21]} (58)

This title compound was prepared according to Procedure C from N-(tert-butyl)-2-cyano-2-diazo-N-(4'-methoxybenzyl)acetamide (0.10 g, 0.39 mmol) and Rho(2S-FOMePA)_4 9e (5.0 mg, 1.0 mol%) in dichloromethane (50 mL). Spectroscopic characteristics were consistent with previously reported data.\textsuperscript{[21]} Colourless crystals (0.080 g, 88%); m.p. 118–120 °C (Lit.\textsuperscript{[21]} 119–120 °C); Spec. Rot.: [\alpha]_D\textsuperscript{20} +36.50 (c 0.200, CHCl_3); HPLC: 20% ee (determined by chiral phase HPLC, see Table S16 for HPLC conditions); \textsuperscript{1}H NMR (400 MHz, CDCl_3): \(\delta\) = 1.45 (9H, s), 3.69 (3H, s), 4.03 (1H, d, J 13.7), 4.25 (1H, d, J 13.8), 4.83 (1H, br s), 5.95–6.03 (2H, m), 6.25 (1H, d J 8.1); \textsuperscript{13}C NMR (100.6 MHz, CDCl_3): \(\delta\) = 27.4, 49.0, 55.1, 55.3, 109.1 br, 114.5, 117.7 br, 122.0, 158.6, 167.2; IR (neat): 2235, 1703.

2-Benzyl-3,6,8-trioxo-7-phenyl-2,3b,4,7,8-hexahydro-6H,10H-4,10-ethenopyrrole-[3',4':1,3]cyclopropa[1,2-d][1,2,4]triazolo[1,2-a]pyridazine-3a(1H)-carbonitride (59)

A 100 mL round bottom flask was charged with 32 (0.16 g, 0.62 mmol) and CH_2Cl_2 (20 mL). The flask was cooled to 0 °C after which 4-phenyl-1,2,4-triazolin-3,5-dione (0.08 g, 0.62 mmol) was added in one portion. The reaction solution was warmed to room temperature. The reaction solution was concentrated under reduced pressure and the residue was washed with chloroform to afford the pure cycloadduct xx. Colourless powder (0.136 g, 50%); m.p. 200–203 °C; \textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6): \(\delta\) = 2.48–2.53 (2H, m), 3.45 (1H, s, J 10.4), 3.86 (1H, s, J 10.4), 4.39 (2H, ABq, J 24.7, Hα \(\delta\) = 4.46, Hβ \(\delta\) = 4.32), 5.49 (1H, dd, J 6.0, 1.4), 5.59–5.66 (1H, m), 6.43–6.51 (1H, m), 6.56–6.64 (1H, m), 7.24–7.55 (10H, m); \textsuperscript{13}C NMR (100.6 MHz, DMSO-\textit{d}_6): \(\delta\) = 25.7, 28.2, 31.1, 46.2, 47.6, 51.7, 53.4, 114.9, 126.1, 127.7, 128.0, 128.1, 128.7, 129.1, 129.2, 130.7, 135.8, 155.7, 156.0, 164.5; IR (neat): 2238, 1706, 1402; HRMS (ESI-TOF): m/z [M+H]^+ calcd for C_{26}H_{31}N_{2}O_{3} 438.1561, found 438.1562.

9-Aza-9-tert-butyl-1-cyano-4-(methylphenyl)bicyclo[5.3.0]deca-2,4,6-trien-10-one (60)

Prepared according to literature procedure\textsuperscript{[22]}

A Schlenk tube was charged with 9-aza-9-tert-butyl-1-cyano-4-bromobicyclo(5.3.0)deca-2,4,6-trien-10-one 47 (0.37 g, 1.21 mmol), palladium(II) acetate (0.014 g, 5 mol%), 4-tolylboronic acid (0.33 g, 2.44 mmol), SPhos (0.050 g, 10 mol%) and dioxane (12 mL). The reaction mixture was sparged with N_2 gas for 20 minutes after which aqueous K_2PO_4 (2.0 mL, 3.0 M) was added. The reaction mixture was stirred for 16 hours in a 25 °C oil bath. The solution was concentrated under reduced pressure and the residue purified by silica gel chromatography using hexane:ethyl acetate (80:20) as eluent; White crystals (0.246 g, 65%); m.p. 200–201 °C; \textsuperscript{1}H NMR (400 MHz, CDCl_3): \(\delta\) = 1.47 (9H, s), 2.36 (3H, s), 4.10 (1H, d, J 14.3), 4.31 (1H, d, J 14.9), 4.88 (1H, d, J 8.5), 6.40 (1H, d, J 7.4), 6.50 (1H, d, J 8.5), 6.92 (1H, d, J 7.4), 7.19 (2H, d, J 8.0), 7.34 (2H, d, J 8.1); \textsuperscript{13}C NMR (100.6 MHz, CDCl_3): \(\delta\) = 21.2, 27.5, 39.2 br, 49.1, 55.4, 98.1 br, 102.2 br, 114.3, 122.5, 126.8, 127.0, 127.2, 129.4, 137.8, 138.0, 142.3, 167.2; IR (neat): 2977, 2238, 1700; HRMS (ESI-TOF): m/z [M+Na]^+ calcd for C_{24}H_{22}N_{2}O_{3}Na 341.1624, found 314.1627.
Methyl 9-aza-9-tert-butyl-4-methylbicyclo(5.3.0)deca-2,4,6-trien-10-one-1(R)-carboxylate (61)

Prepared according to literature procedure[21]

A 50 mL round bottom flask was charged with 9-aza-9-tert-butyl-1-cyano-4-methylbicyclo(5.3.0)deca-2,4,6-trien-10-one 50 (0.37 g, 1.5 mmol, 85% ee) and methanolic potassium hydroxide (10 mL, 2.2 M). The reaction solution was stirred at room temperature for 12 hours after which the solution was diluted with water (20 mL) and extracted with CH$_2$Cl$_2$ (2 × 20 mL). The organic solution was dried, concentrated under reduced pressure and the residue purified by silica gel chromatography using hexane:ethyl acetate (75:25) as eluent; White crystals (0.163 g, 40%); m.p. 143–145 °C; Spec. Rot.: [α]$_{D}^{20}$ +320.72 (c 0.070, CHCl$_3$); HPLC: 77% ee (determined by chiral phase HPLC, see Table SI.6 for HPLC conditions); $^1$H NMR (400 MHz, CDCl$_3$): δ= 1.45 (9H, s), 2.01 (3H, s), 3.62 (3H, s), 4.18 (1H, d, J 14.6), 4.38 (1H, d, J 14.6), 5.50 (1H, d, J 10.2), 6.11 (1H, d, J 6.5), 6.22 (1H, d, J 6.5), 6.36 (1H, d, J 10.2); $^{13}$C NMR (100.6 MHz, CDCl$_3$): δ= 24.4, 27.4, 49.6, 53.9, 54.6, 60.5, 119.4, 122.5, 126.0, 130.3, 132.3, 137.5, 166.8, 172.1; IR (neat): 2975, 1696, 1654; HRMS (ESI-TOF): m/z [M+Na]$^+$ calcd for C$_{16}$H$_{21}$NO$_3$Na 298.1414, found 298.1411.
7. Synthesis of 2-allyl-2-methoxycarbonyl-2,3-dihydrobenzofuran-3-one

7.1 Synthesis of α-diazo-β-keto ester

Methyl 2-diazo-3-(2-allyloxyphenyl)-3-oxopropionate\textsuperscript{[23]} (62)

Methyl 3-(2-allyloxyphenyl)-3-oxopropanoate (0.64 g, 2.7 mmol), \textit{p}-ABSA (0.70 g, 2.7 mmol), potassium carbonate (0.49 g, 3.6 mmol) and acetonitrile (30 mL) were used following the procedure described for 16 to give, following column chromatography on silica gel employing hexane/ethyl acetate (90:10) as the eluent, the α-diazo-β-keto ester 62 (0.59 g, 83%) as a yellow oil. Spectroscopic characteristics were consistent with previously reported data.\textsuperscript{[23]} \textit{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ = 3.74 (3H, s), 4.51–4.57 (2H, finely split dt, \textit{J} 5.0, 1.5), 5.27 (1H, dd, \textit{J} 10.7, 1.3), 5.37 (1H, dd, \textit{J} 17.3, 1.5), 5.92–6.04 (1H, m), 6.90 (1H, d, \textit{J} 8.4), 6.98–7.04 (1H, m), 7.35 (1H, dd, \textit{J} 7.6, 1.5), 7.37–7.45 (1H, m); IR (neat): 2124 (CN\textsubscript{2}), 1727, 1697 (CO), 1622, 1311, 752.

7.2 Dihydrobenzofuranone synthesis

General procedure for rhodium catalysed oxonium ylide formation-[2,3]-sigmatropic rearrangements to afford dihydrobenzofuranones

A solution of α-diazocarbonyl (100 mg, 1 equiv.) in solvent (5 mL) was added dropwise over ~15 min to a stirring solution of Rh(II) catalyst (1 mol%) in solvent (5 mL). The mixture was stirred at the temperature indicated until reaction completion was indicated by IR spectroscopy. The reaction mixture was then cooled to room temperature, concentrated under reduced pressure to give the crude product and a \textit{1}H NMR spectrum obtained. Purification by column chromatography employing ethyl acetate in hexane as eluent gave the pure cyclisation product.

2-Allyl-2-methoxycarbonyl-2,3-dihydrobenzofuran-3-one\textsuperscript{[24]} (63)

A solution of methyl 2-diazo-3-(2-allyloxyphenyl)-3-oxopropionate 62 (100 mg, 0.38 mmol) in toluene (5 mL) was added dropwise over ~15 min to a solution of 9b (6 mg, 1 mol%) in toluene (5 mL). The mixture was heated under reflux while stirring for 2 h then cooled to room temperature and concentrated under reduced pressure. Column chromatography on silica gel employing hexane/ethyl acetate (95:5) as the eluent gave the pure dihydrobenzofuranone 63 (64.3 mg, 72%) as a white solid. Spectroscopic characteristics were consistent with previously reported data.\textsuperscript{[24]} m.p. 58–60 °C; HPLC: 74% ee (determined by chiral phase HPLC, see Table SI.6 for HPLC conditions); \textit{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ = 2.84 (1H, dd, \textit{J} 14.5, 7.1), 3.07 (1H, dd, \textit{J} 14.5, 7.1), 3.77 (3H, s), 5.12 (1H, d, \textit{J} 10.1), 5.23 (1H, dd, \textit{J} 17.0, 0.8), 5.61–5.74 (1H, m), 7.13 (1H, t, \textit{J} 7.4), 7.23 (1H, d, \textit{J} 8.7), 7.62–7.70 (2H, m); IR (neat): 1748, 1709 (CO), 1607, 1250, 929, 752.
8. NMR Spectra

2-Phenylacetic acid (S1)

\[^1\text{H} \text{NMR (300 MHz, CDCl}_3\)]

\[
\begin{array}{c}
\text{Ph} \\
\text{S1}
\end{array}
\]

\[
\begin{array}{c}
\text{H} \\
\text{NMR}
\end{array}
\]

\[
\begin{array}{c}
\text{11.5} \\
\text{11.0} \\
\text{10.5} \\
\text{10.0} \\
\text{9.5} \\
\text{9.0} \\
\text{8.5} \\
\text{8.0} \\
\text{7.5} \\
\text{7.0} \\
\text{6.5} \\
\text{6.0} \\
\text{5.5} \\
\text{5.0} \\
\text{4.5} \\
\text{4.0} \\
\text{3.5} \\
\text{3.0} \\
\text{2.5} \\
\text{2.0} \\
\text{1.5} \\
\text{1.0} \\
\text{0.5} \\
\text{0.0} \\
\text{ppm}
\end{array}
\]

\[\text{S1}\]

\[
\text{tert-Butyl 2-phenylacetate (S2)}
\]

\[^1\text{H} \text{NMR (300 MHz, CDCl}_3\)]

\[
\begin{array}{c}
\text{Ph} \\
\text{CO}_2\text{Bu} \\
\text{S2}
\end{array}
\]

\[
\begin{array}{c}
\text{H} \\
\text{NMR}
\end{array}
\]

\[
\begin{array}{c}
\text{9.5} \\
\text{9.0} \\
\text{8.5} \\
\text{8.0} \\
\text{7.5} \\
\text{7.0} \\
\text{6.5} \\
\text{6.0} \\
\text{5.5} \\
\text{5.0} \\
\text{4.5} \\
\text{4.0} \\
\text{3.5} \\
\text{3.0} \\
\text{2.5} \\
\text{2.0} \\
\text{1.5} \\
\text{1.0} \\
\text{0.5} \\
\text{0.0} \\
\text{ppm}
\end{array}
\]
**SUPPORTING INFORMATION**

*tet-Butyl 2-(naphthalen-2-yl)acetate (S3)*

**$^1$H NMR (400 MHz, CDCl$_3$)**

![NMR Spectrum of S3](image)

*tet-Butyl 2-(naphthalen-1-yl)acetate (S4)*

**$^1$H NMR (400 MHz, CDCl$_3$)**

![NMR Spectrum of S4](image)
**SUPPORTING INFORMATION**

**tert-Butyl 2-(4-bromophenyl)acetate (S5)**

\[^1\text{H} \text{NMR (400 MHz, CDCl}_3\text{)}\]

![Chemical structure of tert-Butyl 2-(4-bromophenyl)acetate (S5)](image)

**tert-Butyl 2-(4-methoxyphenyl)acetate (S6)**

\[^1\text{H} \text{NMR (300 MHz, CDCl}_3\text{)}\]

![Chemical structure of tert-Butyl 2-(4-methoxyphenyl)acetate (S6)](image)
SUPPORTING INFORMATION

**tert-Butyl 2-diazo-2-phenylacetate (6a)**

\[ \text{N}_2 \quad \text{CO}_2 \text{Bu} \]

\(^1H\) NMR (300 MHz, CDCl₃)

**tert-Butyl 2-diazo-2-(naphthalen-2-yl)acetate (6b)**

\[ \text{N}_2 \quad \text{CO}_2 \text{Bu} \]

\(^1H\) NMR (400 MHz, CDCl₃)
**SUPPORTING INFORMATION**

**tert-Butyl 2-diazo-2-(naphthalen-1-yl)acetate (6c)**

**1H NMR (400 MHz, CDCl3)**

**13C NMR (75.5 MHz, CDCl3)**
SUPPORTING INFORMATION

**tert-Butyl 2-(4-bromophenyl)-2-diazoacetate (6d)**

$^1$H NMR (400 MHz, CDCl$_3$)
tert-Butyl 2-(4-methoxyphenyl)-2-diazoacetate (6e)

^{1}H NMR (400 MHz, CDCl\textsubscript{3})

\begin{center}
\begin{tikzpicture}
  \node at (0,0) {\textbf{N}};
  \node at (-1.5,0) {\textbf{C}};
  \node at (-2.5,0) {\textbf{MeO}};
  \node at (0.5,0) {\textbf{CO}_2^t\textbf{Bu}};
\end{tikzpicture}
\end{center}

^{13}C NMR (75.5 MHz, CDCl\textsubscript{3})

\begin{center}
\begin{tikzpicture}
  \node at (0,0) {\textbf{N}};
  \node at (-1.5,0) {\textbf{C}};
  \node at (-2.5,0) {\textbf{MeO}};
  \node at (0.5,0) {\textbf{CO}_2^t\textbf{Bu}};
\end{tikzpicture}
\end{center}
**tert-Butyl (2S)-2-(1''R,2''R,4''S)-fenchylhydroxy-2-phenylacetate (7a)**

\[ \text{H NMR (300 MHz, CDCl}_3\text{)} \]

\[ \text{C NMR (75.5 MHz, CDCl}_3\text{)} \]
SUPPORTING INFORMATION

**tert-Butyl (2S)-2-(1''R,2''R,4''S)-fenchyloxy-2-(naphthalen-1'-yl)acetate (7c)**

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
tert-Butyl (2S)-2-(4′-bromophenyl)-2-(1″R,2″R,4″S)-fenchyloxyacetate (7d)

**1H NMR (400 MHz, CDCl₃)**

**13C NMR (100.6 MHz, CDCl₃)**
tert-Butyl (2S)-2-(1″R,2″R,4″S)-fenchyloxy-2-(4′-methoxyphenyl)acetate (7e)

\[ \text{SI-73} \]

\[ 1H \text{ NMR (400 MHz, CDCl}_3) \]

\[ \text{13C NMR (100.6 MHz, CDCl}_3) \]
tert-Butyl (2S)-2-(1″R,2″S,5″R)-menthyl-2-phenylacetate (7f)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
**SUPPORTING INFORMATION**

**tert-Butyl 2-(1″R,2″R,5″S)-menthloxy-2-(naphthalen-2-yl)acetate (7g)**

\[ \text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3) \]

\[ \text{\textsuperscript{13}C NMR (100.6 MHz, CDCl}_3) \]
**SUPPORTING INFORMATION**

*tert-Butyl (2S)-2-(4′-bromophenyl)-2-(1″R,2″R,5″S)-menthylxyacetate (7h)*

**1H NMR (400 MHz, CDCl₃)**

**13C NMR (100.6 MHz, CDCl₃)**
(2S)-2-(1″R,2″R,4″S)-Fenchyloxy-2-phenylacetic acid (8a)

^1H NMR (400 MHz, CDCl3)
(2S)-2-(1''R,2''R,4''S)-Fenchyloxy-2-(naphthalen-2'-yl)acetic acid (8b)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
(2S)-2-(4′-Bromophenyl)-2-(1″R,2″R,4″S)-fenchyloxyacetic acid (8d)

$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
(2S)-2-(1"R,2"R,4"S)-Fenhydrate-2-(4'-methoxy)phenylacetic acid (8e)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
(2S)-2-(1''R,2''S,5''S)-Menthylloxy-2-phenylacetic acid (8f)

$^1$H NMR (300 MHz, CDCl₃)

$^{13}$C NMR (75.5 MHz, CDCl₃)
(2S)-2-(1″R,2″S,5″R)-Menthylxy-2-(naphthalen-2′-yl)acetic acid (8g)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
(2S)- 2-(4′-Bromophenyl)-2-(1′R,2′S,5′R)-menthyloxyacetic acid (8h)

$^{1}$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
Dirhodium tetrakis [(2S)-2-(1″R,2″R,4″S)-fenchyloxy-2-phenylacetate] (2S-FPA) (9a)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
Dirhodium tetrakis [(2S)-2-(1''R,2''R,4''S)-fenchyloxy-2-(naphthalen-2'-yl)acetate] (2S-F-2'-NA) (9b)

$^{1}\text{H NMR (400 MHz, CDCl}_3\text{)}$

$^{13}\text{C NMR (100.6 MHz, CDCl}_3\text{)}$
Dirhodium tetrakis [(2S)-2-(1"R,2"R,4"S)-fenchyloxy-2-(naphthalen-1'-yl)acetate] (2S-F-1'-NA) (9c)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
Dirhodium tetrakis [(2S)-2-(4′-bromophenyl)-2-(1″R,2″R,4″S)-fenchyloxyacetate] (2S-FBrPA) (9d)

$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100.6 MHz, CDCl$_3$)
Dirhodium tetrakis [(2\(S\)-2-(1"R,2"R,4"S)-fenchyloxy-2-(4'-methoxyphenyl)acetate)] (2\(S\)-FMeOPA) (9e)

\(^1\)H NMR (400 MHz, CDCl\(_3\))

\(^{13}\)C NMR (100.6 MHz, CDCl\(_3\))
Dirhodium tetrakis [(2S)-2-(1″R,2″S,5″R)-menthylxyo-2-phenylacetate] (2S-MPA) (9f)

$^{1}H$ NMR (300 MHz, CDCl$_3$)

$^{13}C$ NMR (75.5 MHz, CDCl$_3$)
Dirhodium tetrakis [(2S)-2-(1″R,2″S,5″R)-menthylxyo-2-(naphthalen-2'-yl)acetate] (2S-M-2″-NA) (9g)

$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100.6 MHz, CDCl$_3$)
Dirhodium tetrakis [(2S)-2-(4′-bromophenyl)-2-(1″R,2″S,5″R)-menthloxyacetate] (2S-MBrPA) (9h)

$\text{H NMR (400 MHz, CDCl}_3\text{)}$

$\text{C NMR (100.6 MHz, CDCl}_3\text{)}$
**Methyl 2-(2-(benzyloxy)phenyl)acetate (S17)**

\[ \text{\textsuperscript{1}H NMR (300 MHz, CDCl\(_3\))} \]

\[ \begin{array}{c}
\text{CO}_2\text{Me} \\
\text{OBn}
\end{array} \]

**Benzyl 2-(2-(benzyloxy)phenyl)acetate (S18)**

\[ \text{\textsuperscript{1}H NMR (400 MHz, CDCl\(_3\))} \]

\[ \begin{array}{c}
\text{CO}_2\text{Bn} \\
\text{OBn}
\end{array} \]
Methyl 2-(2-(benzyloxy)phenyl)-2-diazoacetate (10)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
**Supporting Information**

**Benzyl 2-(2-(benzyloxy)phenyl)-2-diazoacetate (12)**

^1H NMR (400 MHz, CDCl₃)

![^1H NMR spectrum of Benzyl 2-(2-(benzyloxy)phenyl)-2-diazoacetate (12)]

^13C NMR (100.6 MHz, CDCl₃)

![^13C NMR spectrum of Benzyl 2-(2-(benzyloxy)phenyl)-2-diazoacetate (12)]
Isopropyl 2-(2-(benzyloxy)phenyl)-2-diazoacetate (13)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
(2R,3R)-trans-3-Methoxycarbonyl-2-phenyl-2,3-dihydrobenzofuran[17] (11a)

\[
\text{H NMR (400 MHz, CDCl}_3\text{)}
\]

(2S,3R)-cis-3-Methoxycarbonyl-2-phenyl-2,3-dihydrobenzofuran[17] (11b)

\[
\text{H NMR (400 MHz, CDCl}_3\text{)}
\]
(2R,3R)-trans-3-Benzyloxycarbonyl-2-phenyl-2,3-dihydrobenzofuran (14a)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
(2S,3R)-cis-3-Benzylcarboxyl-2-phenyl-2,3-dihydrobenzofuran (14b)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
(2R,3R)-trans-3-Isopropoxy carbonyl-2-phenyl-2,3-dihydrobenzofuran (15a)

**$^1$H NMR (400 MHz, CDCl$_3$)**

**$^{13}$C NMR (100.6 MHz, CDCl$_3$)**
(2S,3R)-cis-3-Isopropylxoy carbonyl-2-phenyl-2,3-dihydro benzofuran (15b)

$^1$H NMR (400 MHz, CDCl$_3$)

$^13$C NMR (100.6 MHz, CDCl$_3$)
Methyl 2-(2-(benzyloxy)phenyl)-2-oxoacetate (S19)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
Methyl 2-(2-(benzyloxy)phenyl)-2-oxoacetate (S20)

$^1$H NMR (400 MHz, CDCl$_3$)
Benzyl 2-(2-(benzyloxy)phenyl)-2-hydroxyacetate (S21)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
The $^1$H NMR and $^{13}$C NMR spectra of the C–H insertion products isolated in this work are reported below. For the compounds we have previously reported, namely the cis thiopyran dioxides and the α-diazocarbonyl compounds (16, 19–24) the spectroscopic details are in agreement with previously reported data.[19-20]

Methyl 2-diazo-2-((4′-phenylbutyl)sulfonyl)acetate (16)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
Methyl 2-diazo-2-((4’-(p-toly)butyl)sulfonyl)acetate (19)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
SUPPORTING INFORMATION

Methyl 2-diazo-2-((4’-(4”-methoxyphenyl)butyl)sulfonyl)acetate (20)

\[ \text{H NMR (300 MHz, CDCl}_3\text{)} \]

\[ \text{C NMR (75.5 MHz, CDCl}_3\text{)} \]
Methyl 2-diazo-2-((4’-((4”-fluorophenyl)butyl)sulfonyl)acetate (21)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
2-Diazo-1-phenyl-2-((4′-phenylbutyl)sulfonyl)ethan-1-one (22)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
Benzyl 2-diazo-2-(dodecylsulfonyl)acetate (23)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
Methyl 2-((2'-cyclohexylethyl)sulfonyl)-2-diazoacetate (24)

\[ \text{Methyl 2-((2'-cyclohexylethyl)sulfonyl)-2-diazoacetate (24)} \]

**\(^1\)H NMR (300 MHz, CDCl}_3\)**

**\(^{13}\)C NMR (75.5 MHz, CDCl}_3\)**
Methyl (2R,3S)-3-phenyltetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide (17a)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
Methyl (2S,3S)-3-phenyltetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide (17b)

$^1$H NMR (300 MHz, CDCl$_3$)

$^1$C NMR (75.5 MHz, CDCl$_3$)
For the sulfolanes in some instances signals for the minor diastereoisomer can be seen in the spectra; these are reported in the experimental section.

**Methyl (2R,3R*)-3-benzyltetrahydrothiophene-2-carboxylate 1,1-dioxide (18a)**

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
Methyl 2-((4'-phenylbut-3'-en-1'-yl)sulfonyl)acetate (S22)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (150.9 MHz, CDCl$_3$)
Methyl (2R,3S)-3-(p-tolyl)tetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide (25a)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
Methyl (2R,3R)-3-(p-tolyl)tetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide (25b)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
Methyl (2\textit{R*},3\textit{R*})-3-(4'-methylbenzyl)tetrahydrothiophene-2-carboxylate 1,1-dioxide (S23a)

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3})

\textsuperscript{13}C NMR (75.5 MHz, CDCl\textsubscript{3})
Methyl 2-((4ʹ-(p-tolyl)but-3ʹ-en-1ʹ-yl)sulfonyl)acetate (S24)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
Methyl (2R,3S)-3-(4′-methoxyphenyl)tetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide (26a)

$\text{H NMR (300 MHz, CDCl}_3\)$

$\text{C NMR (75.5 MHz, CDCl}_3\)$
Methyl (2S,3S)-3-(4'-methoxyphenyl)tetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide (26b)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
Methyl \((2R^*,3R^*)\)-3-(4'-methoxybenzyl)tetrahydrothiophene-2-carboxylate 1,1-dioxide (S25a)

\(^1\)H NMR (300 MHz, CDCl\(_3\))

\(^{13}\)C NMR (75.5 MHz, CDCl\(_3\))
Methyl 2-((4''-(4''-methoxyphenyl)but-3''-en-1''-yl)sulfonyl)acetate (S26)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
Methyl (2R,3S)-3-(4′-fluorophenyl)tetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide (27a)

$^1$H NMR (300 MHz, CDCl₃)

$^{13}$C NMR (75.5 MHz, CDCl₃)
$^{19}$F NMR (282.4 MHz, CDCl$_3$)
Methyl (2S,3S)-3-(4'-fluorophenyl)tetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide (27b)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
$^{19}$F NMR (282.4 MHz, CDCl$_3$)
Methyl (2$R^*,3R^*$)-3-(4'-fluorobenzyl)tetrahydrothiophene-2-carboxylate 1,1-dioxide (S27a)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
$^{19}$F NMR (282.4 MHz, CDCl$_3$)

![Chemical Structure](image)
Methyl 2-\((4'\text{-}(4''\text{-fluorophenyl})\text{but-3'-en-1'-yl})\text{sulfonyl})\text{acetate (S28)}\)

\[^1\text{H NMR (300 MHz, CDCl}_3\text{)}\]

\[^{13}\text{C NMR (75.5 MHz, CDCl}_3\text{)}\]
$^{19}\text{F NMR} \ (282.4 \text{ MHz, CDCl}_3)$

![Chemical Structure](image)
((2R*,3S*)-1,1-Dioxido-3-phenyltetrahydro-2H-thiopyran-2-yl)(phenyl)methanone (28a)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
Benzyl (2R,3R)-3-octyltetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide (29a)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
Benzyl (2\textit{R},3\textit{S})-3-octyltetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide (29b)

$^1\text{H}$ NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
Benzyl (2\textit{R}*,3\textit{R}*)-3-nonyltetrahydrothiophene-2-carboxylate 1,1-dioxide (S30a)

\(^1\)H NMR (300 MHz, CDCl\textsubscript{3})

\(^{13}\)C NMR (75.5 MHz, CDCl\textsubscript{3})

SI-135
Methyl (1R,4aS,8aR)-octahydro-1H-isothiochromene-1-carboxylate 2,2-dioxide (30a)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
Methyl (1$R^*,4aR^*,8aS^*$)-octahydro-1H-isothiochromene-1-carboxylate 2,2-dioxide (30b)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
**Supporting Information**

*N,N*-Dibenzy1-2-cyano-2-diazoacetamide (31)

**1H NMR (400 MHz, CDCl₃)**

![HNMR spectrum of 31](image_1)

**13C NMR (100.6 MHz, CDCl₃)**

![CNR spectrum of 31](image_2)
N-(tert-Butyl)-2-cyano-2-diazo-N-(4'-fluorobenzyl)acetamide (33)

$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100.6 MHz, CDCl$_3$)
$\text{SI-140}$

$^{19}$F NMR (376.5 MHz, CDCl$_3$)

![NMR spectrum diagram](image)
N-(tert-Butyl)-2-cyano-2-diazo-N-(4'-bromobenzyl)acetamide (34)

\[ \text{1}^\text{H} \text{ NMR (400 MHz, CDCl}_3\text{)} \]

\[ \text{1}^\text{3} \text{C NMR (100.6 MHz, CDCl}_3\text{)} \]
$N$-(tert-Butyl)-2-cyano-2-diazo-$N$-(4'-chlorobenzyl)acetamide (35)

$^1$H NMR (400 MHz, CDCl$_3$)

$^1$C NMR (100.6 MHz, CDCl$_3$)
N-(tert-Butyl)-2-cyano-2-diazo-N-(2',6'-dichlorobenzyl)acetamide (36)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
$N$-(tert-Butyl)-2-cyano-2-diazo-$N$-(4'-methylbenzyl)acetamide (37)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
$N$-(tert-Butyl)-2-cyano-2-diazo-$N$-(3',5'-dimethylbenzyl)acetamide (38)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
N-(tert-Butyl)-2-cyano-2-diazo-N-(2',4',6'-trimethylbenzyl)acetamide (39)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
Supporting Information

N-Benzyl-N-(tert-butyl)-2-cyano-2-diazoacetamide (40)

\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \]

\[ \text{^{13}C NMR (100.6 MHz, CDCl}_3\text{)} \]
N-(tert-Butyl)-2-cyano-2-diazo-N-(4'-nitrobenzyl)acetamide (41)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
**SUPPORTING INFORMATION**

*N-(tert-Butyl)-2-cyano-2-diazo-N-(4’-methoxycarbonylbenzyl)acetamide (42)*

**$^1$H NMR (400 MHz, CDCl₃)**

![NMR spectrum](image)

**$^{13}$C NMR (100.6 MHz, CDCl₃)**

![NMR spectrum](image)
$N$-(tert-Butyl)-2-cyano-2-diazo-$N$-(4'-trifluoromethylbenzyl)acetamide (43)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
$^{19}$F NMR (376.5 MHz, CDCl$_3$)
$N$-(tert-Butyl)-2-cyano-2-diazo-$N$-(4'-cyanobenzyl)acetamide (44)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
**SUPPORTING INFORMATION**

*N-(tert-Butyl)-2-cyano-2-diazo-N-(4′-methoxybenzyl)acetamide (45)*

**1H NMR (400 MHz, CDCl3)**

![1H NMR spectrum](image)

**13C NMR (100.6 MHz, CDCl3)**

![13C NMR spectrum](image)
9-Aza-9-benzyl-1(S)-cyano-4-bicyclo[5.3.0]deca-2,4,6-trien-10-one (32)

$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100.6 MHz, CDCl$_3$)
9-Aza-9-tert-buty1-1(S)-cyano-4-fluorobicyclo[5.3.0]deca-2,4,6-trien-10-one (46)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
$^{19}$F NMR (376.5 MHz, CDCl$_3$)
9-Aza-9-tert-butyl-1(S)-cyano-4-bromobicyclo[5.3.0]deca-2,4,6-trien-10-one (47)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
9-Aza-9-tert-butyl-1(S)-cyano-4-chlorobicyclo[5.3.0]deca-2,4,6-trien-10-one (48)

$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100.6 MHz, CDCl$_3$)
9-Aza-9-tert-butyl-1(R)-cyano-2,6-dichlorobicyclo[5.3.0]deca-2,4,6-trien-10-one (49)

$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100.6 MHz, CDCl$_3$)
9-Aza-9-tert-butyl-1(S)-cyano-4-methylbicyclo[5.3.0]deca-2,4,6-trien-10-one (50)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
9-Aza-9-tert-butyl-1\(S\)-cyano-3,5-dimethylbicyclo[5.3.0]deca-2,4,6-trien-10-one (51)

\(^1\)H NMR (400 MHz, CDCl\(_3\))

\(^{13}\)C NMR (100.6 MHz, CDCl\(_3\))
9-Aza-9-tert-butyl-1(S)-cyano-2,4,6-trimethylbicyclo[5.3.0]deca-2,4,6-trien-10-one (52)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
9-Aza-9-tert-butyl-1(S)-cyanobicyclo[5.3.0]deca-2,4,6-trien-10-one (53)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
9-Aza-9-tert-butyl-1(R)-cyano-4-nitrobicyclo[5.3.0]deca-2,4,6-trien-10-one (54)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
9-Aza-9-tert-butyl-1(S)-cyano-4-methoxycarbonylbicyclo[5.3.0]deca-2,4,6-trien-10-one (55)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
9-Aza-9-tert-butyl-1(R)-cyano-4-fluorobicyclo[5.3.0]deca-2,4,6-trien-10-one (56)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
$^{19}$F NMR (376.5 MHz, CDCl$_3$)
9-Aza-9-tert-butyl-1(S),4-dicyanobicyclo[5.3.0]deca-2,4,6-trien-10-one (57)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
9-Aza-9-tert-butyl-1(S)-cyano-4-methoxybicyclo[5.3.0]deca-2,4,6-trien-10-one (58)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
2-Benzyl-3,6,8-trioxo-7-phenyl-2,3,3b,4,7,8-hexahydro-6H,10H-4,10-ethenopyrrolo[3′,4′:1,3]cyclopropa[1,2-d][1,2,4]triazolo[1,2-a]pyridazine-3a(1H)-carbonitrile (59)

$^1$H NMR (400 MHz, DMSO-$d_6$)

![NMR Spectrum of Compound 59](image-url)
9-Aza-9-tert-buty1-1-cyano-4-(4-methylphenyl)bicyclo[5.3.0]deca-2,4,6-trien-10-one (60)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
Methyl-9-aza-9-tert-butyl-4-methylbicyclo[5.3.0]deca-2,4,6-trien-10-one-1(\textit{R})-carboxylate (61)

$^1\text{H}$ NMR (400 MHz, CDCl$_3$)

$^{13}\text{C}$ NMR (100.6 MHz, CDCl$_3$)
Methyl 2-diazo-3-(2-allyloxyphenyl)-3-oxopropionate[23] (62)

\[ \text{H NMR (400 MHz, CDCl}_3 \text{)} \]

2-Allyl-2-methoxycarbonyl-2,3-dihydrobenzofuran-3-one[24] (63)

\[ \text{H NMR (400 MHz, CDCl}_3 \text{)} \]
# 9. HPLC Chromatograms

**Table SI.7 HPLC Chromatograms**

| Compound | Compound Number | Column | λ max (cm⁻¹) | Mobile Phase (Hexane: IPA) | Temp (°C) | Flow Rate (mL/min) | Retention Time |
|----------|----------------|--------|--------------|---------------------------|-----------|--------------------|----------------|
| ![ Benzene](image1.png) | 11a | Phenomenex Lux® 3μm Amylose-1 | 210 | 99 : 1 | 25 | 1.0 | Enantiomer | Min |
| ![ Benzene](image2.png) | 11b | Phenomenex Lux® 3μm Amylose-1 | 210 | 99 : 1 | 25 | 1.0 | (+)-(2S,3S) | 11 |
| ![ Benzene](image3.png) | 12 | (-)-(2R,3R) | 12 |
| ![ Benzene](image4.png) | 13 | Phenomenex Lux® 3μm Amylose-1 | 210 | 99 : 1 | 25 | 1.0 | (+)-(2R,3S) | 15 |
| ![ Benzene](image5.png) | 14a | Phenomenex Lux® 3μm Amylose-1 | 210 | 99 : 1 | 25 | 1.0 | (+)-(2S,3S) | 17 |
| ![ Benzene](image6.png) | 14b | Phenomenex Lux® 3μm Amylose-1 | 210 | 95 : 5 | 25 | 1.0 | (+)-(2R,3S) | 17 |
| ![ Benzene](image7.png) | 15a | Daicel Chiralcel® OJ-H | 210 | 99 : 1 | 25 | 1.0 | (+)-(2S,3S) | 17 |
| ![ Benzene](image8.png) | 15b | Phenomenex Lux® 3μm Amylose-1 | 210 | 95 : 5 | 25 | 1.0 | (+)-(2R,3S) | 19 |
| ![ Benzene](image9.png) | 16 | (-)-(2R,3R) | 19 |
| ![ Benzene](image10.png) | 17a | Phenomenex Lux® 3μm Amylose-1 | 209.8 | 90 : 10 | 25 | 1.0 | (-)-(2R,3S) | 35 |
| ![ Benzene](image11.png) | 17b | Phenomenex Lux® 3μm Amylose-1 | 209.8 | 90 : 10 | 25 | 1.0 | (+)-(2S,3R) | 38 |
| Compound | Compound Number | Column | λ max (cm⁻¹) | Mobile Phase (Hexane: IPA) | Temp (°C) | Flow Rate (mL/min) | Retention Time | Enantiomer |
|----------|----------------|--------|---------------|---------------------------|-----------|-------------------|----------------|------------|
| O=S=O    | 25a            | Phenomenex Lux® 3μm Amylose-1 | 212 | 80 : 20 | 25 | 1.0 | (-) | (2R,3S) | 14 |
| O=S=O    | 27a            | Phenomenex Lux® 3μm Amylose-1 | 209.8 | 80 : 20 | 25 | 1.0 | (-) | (2R,3S) | 17 |
| O=S=O    | 26a            | Phenomenex Lux® 3μm Amylose-1 | 226.2 | 80 : 20 | 25 | 1.0 | (+) | (2S,3R) | 20 |
| O=S=O    | 28a            | Phenomenex Lux® 3μm Amylose-1 | 209.8 | 90 : 10 | 25 | 1.0 | (-) | 28 |
| O=S=O    | 29a            | Phenomenex Lux® 3μm Amylose-1 | 209.8 | 90 : 10 | 25 | 1.0 | (+) | 13 |
| O=S=O    | 30a            | Phenomenex Lux® 3μm Amylose-1 | 216 | 90 : 10 | 25 | 1.0 | (+) | (1S,4aR,8aS) | 19 |
| O=S=O    |                |        |               |                           |           |                  | (-) | (1R,4aS,8aR) | 25 |
| Compound | Compound Number | Column | λ max (cm⁻¹) | Mobile Phase (Hexane: IPA) | Temp (°C) | Flow Rate (mL/min) | Retention Time | Enantiomer |
|----------|-----------------|--------|--------------|----------------------------|-----------|-------------------|----------------|------------|
| ![Compound Image](Phenomenex Lux® 3µm Amylose-1) | 32 | Phenomenex Lux® 3µm Amylose-1 | 209.8 | 85 : 25 | 25 | 1.0 | 16 | (−)-(1R) |
| ![Compound Image](Phenomenex Lux® 3µm Amylose-1) | 46 | Phenomenex Lux® 3µm Amylose-1 | 209.8 | 85 : 25 | 25 | 1.0 | 8 | (−)-(1R) |
| ![Compound Image](Phenomenex Lux® 3µm Amylose-1) | 47 | Phenomenex Lux® 3µm Amylose-1 | 209.8 | 85 : 25 | 25 | 1.0 | 8 | (−)-(1R) |
| ![Compound Image](Phenomenex Lux® 3µm Amylose-1) | 48 | Phenomenex Lux® 3µm Amylose-1 | 209.8 | 85 : 25 | 25 | 1.0 | 8 | (−)-(1R) |
| ![Compound Image](Phenomenex Lux® 3µm Amylose-1) | 49 | Phenomenex Lux® 3µm Amylose-1 | 214.5 | 95 : 05 | 25 | 0.5 | 19 | (−)-(1S) |
| ![Compound Image](Phenomenex Lux® 3µm Amylose-1) | 50 | Phenomenex Lux® 3µm Amylose-1 | 209.8 | 85 : 25 | 25 | 1.0 | 6 | (−)-(1R) |
| Compound | Compound Number | Column | λ max (cm⁻¹) | Mobile Phase (Hexane: IPA) | Temp (°C) | Flow Rate (mL/min) | Retention Time | Enantiomer | Min |
|----------|----------------|--------|--------------|----------------------------|-----------|-------------------|-----------------|------------|-----|
| ![Chemical Structure](image1.png) | 51 | Phenomenex Lux® 3µm Amylose-1 | 209.8 | 85 : 25 | 25 | 1.0 | (-)-(1R) 6 |
| ![Chemical Structure](image2.png) | 52 | Phenomenex Lux® 3µm Amylose-1 | 211.0 | 90 : 10 | 25 | 0.5 | (-)-(1R) 11 |
| ![Chemical Structure](image3.png) | 53 | Phenomenex Lux® 3µm Amylose-1 | 209.8 | 85 : 25 | 25 | 1.0 | (+)-(1S) 9 |
| ![Chemical Structure](image4.png) | 54 | Phenomenex Lux® 3µm Amylose-1 | 209.8 | 85 : 25 | 25 | 1.0 | (+)-(1S) 23 |
| ![Chemical Structure](image5.png) | 55 | Phenomenex Lux® 3µm Amylose-1 | 209.8 | 85 : 25 | 25 | 1.0 | (+)-(1S) 15 |
| ![Chemical Structure](image6.png) | 56 | Phenomenex Lux® 3µm Amylose-1 | 209.8 | 85 : 25 | 25 | 1.0 | (+)-(1S) 10 |
| ![Chemical Structure](image7.png) | 57 | Phenomenex Lux® 3µm Amylose-1 | 209.8 | 90 : 10 | 25 | 0.5 | (+)-(1S) 44 |
| Compound | Compound Number | Column | λ max (cm⁻¹) | Mobile Phase (Hexane: IPA) | Temp (°C) | Flow Rate (mL/min) | Retention Time |
|----------|----------------|--------|-------------|-----------------|----------|------------------|----------------|
| ![Compound Image](image) | 58 | Phenomenex Lux® 3μm Amylose-1 | 209.8 | 85 : 25 | 25 | 1.0 | (-)-(1R) 8  
| | | | | | | | (+)-(1S) 11 |
| ![Compound Image](image) | 61 | Phenomenex Lux® 3μm Amylose-1 | 209.8 | 85 : 25 | 25 | 1.0 | (+)-(1R) 30  
| | | | | | | | (-)-(1S) 32 |
| ![Compound Image](image) | 63 | Phenomenex Lux® 3μm Amylose-1 | 210 | 99 : 1 | 25 | 0.5 | 2S 29  
| | | | | | | | 2R 31 |
(2R\(^*\),3R\(^*\))-trans-3-Methoxycarbonyl-2-phenyl-2,3-dihydrobenzofuran (11a)

*Isolated from the reaction of 10 in the presence of Rh\(_2\)(OAc)\(_4\).

(2R,3R)-2,3-trans-3-Methoxycarbonyl-2-phenyl-2,3-dihydrobenzofuran (11a)

*Isolated from the reaction of 10 in the presence of Rh\(_2\)(2S-M-2'\(\cdot\)NA)\(_4\)\(9g\) (Table 1, entry 9).

| Compound | Column                | \(\lambda_{\text{max}}\) (nm) | Mobile Phase (Hex:IPA) | Temp (°C) | Flow (mL/min) | Retention Time |
|----------|-----------------------|-------------------------------|------------------------|-----------|---------------|----------------|
| 11a      | Phenomenex Lux\(^*\) 3\(\mu\)m Amylose-1 | 210                           | 99:1                   | 25        | 1.0           | 11 (2S,3S)     |
|          |                       |                               |                        |           |               | 12 (2R,3R)     |
(2S*,3R*)-cis-3-Methoxycarbonyl-2-phenyl-2,3-dihydrobenzofuran (11b)

*Isolated from the reaction of 10 in the presence of Rh₂(OAc)₄.

(2S,3R)-2,3-cis-3-Methoxycarbonyl-2-phenyl-2,3-dihydrobenzofuran (11b)

*Isolated from the reaction of 10 in the presence of Rh₂(2S-M-2'-NA)₄ 9g (Table 1, entry 9).

| Compound | Column          | λ max (nm) | Mobile Phase (Hex:IPA) | Temp (°C) | Flow (mL/min) | Enantiomer | Retention Time |
|----------|----------------|------------|------------------------|-----------|---------------|-------------|---------------|
| 11b      | Phenomenex Lux® 3 μm Amylose-1 | 210        | 99:1                   | 25        | 1.0           | (−) (2S,3R) | 15            |
|          |                |            |                        |           |               | (+) (2R,3S) | 17            |
**SUPPORTING INFORMATION**

(2R\(^*\),3R\(^*\))-trans-3-Benzylloxycarbonyl-2-phenyl-2,3-dihydrobenzofuran (14a)

*Isolated from the reaction of 12 in the presence of Rh\(_2\)(OAc)\(_4\).*

(2R,3R)-2,3-trans-3-Benzylloxycarbonyl-2-phenyl-2,3-dihydrobenzofuran (14a)

*Isolated from the reaction of 12 in the presence of Rh\(_2\)(25-MPA)\(_4\) 9f (*Table 2*, entry 14).

| Compound | Column                        | λ \text{ max} (nm) | Mobile Phase (Hex:IPA) | Temp (°C) | Flow (mL/min) | Retention Time |
|----------|-------------------------------|--------------------|------------------------|-----------|---------------|----------------|
| 14a      | Phenomenex Lux\(^*\) 3μm Amylose-1 | 210                | 99:1                   | 25        | 1.0           |                |

Enantiomer | min  |

(+) (2S,3S) | 17    |
(−) (2R,3R) | 19    |
**(2S*,3R*)-cis-3-Benzoyloxy carbonyl-2-phenyl-2,3-dihydrobenzofuran (14b)**

*Isolated from the reaction of 12 in the presence of Rh₂(OAc)₄.

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**(2S,3R)-2,3-cis-3-Benzoyloxy carbonyl-2-phenyl-2,3-dihydrobenzofuran (14b)**

*Isolated from the reaction of 12 in the presence of Rh₂(2S-MPA)₄ 9f (Table 2, entry 14).

### Chromatographic Data

| Compound | Column | λ max (nm) | Mobile Phase (Hex:IPA) | Temp (°C) | Flow (mL/min) | Retention Time (min) |
|----------|--------|------------|-------------------------|-----------|---------------|----------------------|
| 14b      | Phenomenex Lux® 3μm Amylose-1 | 210 | 95:5 | 25 | 1.0 | (-) (2S,3R) 12
|          |        |            |                         |           |               | (+) (2R,3S) 16      |

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(2R*,3R*)-trans-3-Isoproplyoxycarbonyl-2-phenyl-2,3-dihydrobenzofuran (15a)

*Isolated from the reaction of 13 in the presence of Rh$_2$(OAc)$_4$.

(2R,3R)-2,3-trans-3-Isopropylcarboxy-phenyl-2,3-dihydrobenzofuran (15a)

*Isolated from the reaction of 13 in the presence of Rh$_2$(2S-MPA)$_4$ 9f (Table 2, entry 22).

| Compound | Column        | $\lambda_{\text{max}}$ (nm) | Mobile Phase (Hex:IPA) | Temp ($^\circ$C) | Flow (mL/min) | Retention Time |
|----------|---------------|-----------------------------|------------------------|------------------|--------------|----------------|
| 15a      | Daicel Chiracel® OJ-H | 210                         | 99:1                   | 25               | 1.0          | (-) (2R,3R) 10 |
|          |               |                             |                        |                  |              | (+) (2S,3S) 14 |
(2S*,3R*)-cis-3-Isopropyl oxycarbonyl-2-phenyl-2,3-dihydrobenzofuran (15b)

*Isolated from the reaction of 13 in the presence of Rh₂(OAc)₄.

(2S,3R)-2,3-cis-3-Isopropyl oxycarbonyl-2-phenyl-2,3-dihydrobenzofuran (15b)

*Isolated from the reaction of 13 in the presence of Rh₂(2S-MPA)_4 9f (Table 2, entry 22).

| Compound | Column | λ max (nm) | Mobile Phase (Hex:IPA) | Temp (°C) | Flow (mL/min) | Retention Time |
|----------|--------|------------|------------------------|-----------|--------------|----------------|
| 15b      | Phenomenex Lux® 3μm Amylose-1 | 210 | 95:5 | 25 | 1.0 | (-) (2S,3R) 6.5  
|          |        |            |                        |           |              | (+) (2R,3S) 6.7 |
Methyl (2R*,3S*)-3-phenyltetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide (17a)

*Isolated from reaction of 16 in the presence of Rh$_2$(OAc)$_4$ at room temperature.

Methyl (2R,3S)-3-phenyltetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide (17a)

*Isolated from reaction of 16 in the presence of Rh$_2$(2S-F-2'-NA)$_4$ 9b (Table 4).

| Compound | Column | $\lambda$ max (nm) | Mobile Phase (Hex:IPA) | Temp (°C) | Flow (mL/min) | Retention Time |
|----------|--------|-------------------|------------------------|-----------|---------------|----------------|
| 17a      | Phenomenex Lux® 3μm Amylose-1 | 209.8 | 90:10 | 25 | 1.0 | Enantiomer | min |
|          |        |                   |                        |           |               | (-) (2R,3S)   | 35 |
|          |        |                   |                        |           |               | (+) (2S,3R)   | 38 |
Methyl (2R*,3S*)-3-(p-tolyl)tetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide (25a)

*Isolated from reaction of 19 in the presence of Rh2(OAc)4 at room temperature.

Methyl (2R,3S)-3-(p-tolyl)tetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide (25a)

*Isolated from reaction of 19 in the presence of Rh2(2S-F-2'-NA) 9b (Table 4).

| Compound | Column | \( \lambda \) max (nm) | Mobile Phase (Hex:IPA) | Temp (°C) | Flow (mL/min) | Retention Time |
|----------|--------|-------------------------|------------------------|-----------|--------------|----------------|
| 25a      | Phenomenex Lux® 3μm Amylose-1 | 212 | 80:20 | 25 | 1.0 | \((-) (2R,3S)\) 14 \((+) (2S,3R)\) 16 |
Methyl (2R,3S)-3-(4ʹ-methoxyphenyl)tetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide (26a)

*Isolated from reaction of 20 in the presence of Rh₂(OAc)₄ at room temperature.

Methyl (2R,3S)-3-(4ʹ-methoxyphenyl)tetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide (26a)

*Isolated from reaction of 20 in the presence of Rh₂(2S-F-2ʹ-N̄A)₄ 9b (Table 4).

| Compound | Column | λ max (nm) | Mobile Phase (Hex:IPA) | Temp (°C) | Flow (mL/min) | Retention Time |
|----------|--------|------------|------------------------|-----------|--------------|----------------|
| 26a      | Phenomenex Lux® 3μm Amylose-1 | 226.2 | 80:20 | 25 | 1.0 | (−) (2R,3S) 19
|          |        |            |                        |           |              | (+) (2S,3R) 23 |
Methyl (2\textit{R},3\textit{S})-3-(4'-fluorophenyl)tetrahydro-2\textit{H}-thiopyran-2-carboxylate 1,1-dioxide (27a)

*Isolated from reaction of 21 in the presence of Rh\textit{2}(OAc)\textsubscript{4} at room temperature.

Methyl (2\textit{R},3\textit{S})-3-(4'-fluorophenyl)tetrahydro-2\textit{H}-thiopyran-2-carboxylate 1,1-dioxide (27a)

*Isolated from reaction of 21 in the presence of Rh\textit{2}(2\textit{S}-F-2'-NA)\textsubscript{4} 9b (Table 4).

| Compound | Column | $\lambda$ max (nm) | Mobile Phase (Hex:IPA) | Temp ($^\circ$C) | Flow (mL/min) | Retention Time |
|----------|--------|--------------------|------------------------|-----------------|---------------|----------------|
| 27a      | Phenomenex Lux\textsuperscript{®} 3μm Amylose-1 | 209.8 | 80:20 | 25 | 1.0 | (-) (2\textit{R},3\textit{S}) 17 |
|          |        |                    |                        |                 |               | (+) (2\textit{S},3\textit{R}) 20 |
**Supporting Information**

**((2R*,3S*)-1,1-Dioxido-3-phenyltetrahydro-2H-thiopyran-2-yl)(phenyl)methanone (28a)**

*Isolated from reaction of 22 in the presence of Rh$_2$(OAc)$_4$ at room temperature.

**((2R*,3S*)-1,1-Dioxido-3-phenyltetrahydro-2H-thiopyran-2-yl)(phenyl)methanone (28a)**

*Isolated from reaction of 22 in the presence of Rh$_2$(2S-F-2'-NA)$_4$ 9b (Table 4).

| Compound | Column       | λ max (nm) | Mobile Phase (Hex:IPA) | Temp (°C) | Flow (mL/min) | Retention Time |
|----------|--------------|------------|------------------------|-----------|---------------|----------------|
| 28a      | Phenomenex Lux® 3μm Amylose-1 | 209.8      | 90:10                  | 25        | 1.0           | (−) 28         |

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Benzyl (2R*,3R*)-3-octyltetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide (29a)

*Isolated from reaction of 23 in the presence of Rh₂(OAc)₄ at room temperature.

Benzyl (2R,3R)-3-octyltetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide (29a)

*Isolated from reaction of 23 in the presence of Rh₂(O2F)₂·2F⋅2′-NA 9b (Table 4).

| Compound | Column                  | λ max (nm) | Mobile Phase (Hex:IPA) | Temp (°C) | Flow (mL/min) | Retention Time (min) | Enantiomer |
|----------|-------------------------|------------|------------------------|-----------|---------------|---------------------|------------|
| 29a      | Phenomenex Lux® 3μm Amylose-1 | 209.8      | 90:10                  | 25        | 1.0           | 13                  | (+) 2S,3S  |
|          |                         |            |                        |           |               |                     | (2R,3R)   | 18        |
Methyl (1R,4aS,8aR)-octahydro-1H-isothiochromene-1-carboxylate 2,2-dioxide (30a)

*Isolated from reaction of 24 in the presence of Rh$_2$(OAc)$_4$ at room temperature.

**Table 4**

| Compound | Column | $\lambda$ max (nm) | Mobile Phase (Hex:IPA) | Temp (°C) | Flow (mL/min) | Retention Time |
|----------|--------|------------------|------------------------|-----------|---------------|---------------|
| 30a      | Phenomenex Lux® 3μm Amylose-1 | 216               | 90:10                  | 25        | 1.0           | (+) (1S,4aR,8aS) 19 min
|          |        |                  |                        |           |               | (-) (1R,4aS,8aR) 25 min |
9-Aza-9-benzyl-1(\(R^*\))-cyanobicyclo[5.3.0]deca-2,4,6-trien-10-one (32)

*Isolated from reaction of 31 in the presence of Rh\(2(OAc)_4\) at room temperature.

| Compound     | Column               | \(\lambda\) max (nm) | Mobile Phase (Hex:IPA) | Temp (°C) | Flow (mL/min) | Retention Time Enantiomer |
|--------------|----------------------|-----------------------|-------------------------|-----------|---------------|---------------------------|
| 32           | Phenomenex Lux\(^\circ\) 3µm Amylose-1 | 209.8                 | 85 : 25                 | 25        | 1.0           | (−)(1\(R\)) 16            |
|              |                      |                       |                         |           |               | (+)(1\(S\)) 24            |
9-Aza-9-tert-butyl-1(\textit{R'})-cyano-4-fluorobicyclo[5.3.0]deca-2,4,6-trien-10-one (46)

*Isolated from reaction of 33 in the presence of Rh\(_2\)(OAc)_4 at room temperature.

9-Aza-9-tert-butyl-1(\textit{S})-cyano-4-fluorobicyclo[5.3.0]deca-2,4,6-trien-10-one (46)

| Compound | Column | \(\lambda_{\text{max}}\) (nm) | Mobile Phase (Hex:IPA) | Temp (°C) | Flow (mL/min) | Retention Time (min) |
|----------|--------|----------------------------|------------------------|-----------|--------------|----------------------|
| 46       | Phenomenex Lux\textsuperscript{®} 3μm Amylose-1 | 209.8 | 85 : 25 | 25 | 1.0 | Enantiomer
|          |        |                           |                        |           |              | (-) (1\textit{R'}) 8 |
|          |        |                           |                        |           |              | (+) (1\textit{S}) 11 |
**9-Aza-9-tert-butyl-1(R*)-cyano-4-bromobicyclo[5.3.0]deca-2,4,6-trien-10-one (47)**

*Isolated from reaction of 34 in the presence of Rh$_2$(OAc)$_4$ at room temperature.

**9-Aza-9-tert-butyl-1(S*)-cyano-4-bromobicyclo[5.3.0]deca-2,4,6-trien-10-one (47)**

*Isolated from reaction of 34 in the presence of Rh$_2$(2S-FOMePA)$_4$ 9e (Table 5).

| Compound | Column | λ max (nm) | Mobile Phase (Hex:IPA) | Temp (°C) | Flow (mL/min) | Retention Time |
|----------|--------|------------|------------------------|-----------|---------------|----------------|
| 47       | Phenomenex Lux® 3μm Amylose-1 | 209.8 | 85 : 25 | 25 | 1.0 | Enantiomer min |
|          |        |            |                        |           |               | (−) (1R) 8 |
|          |        |            |                        |           |               | (+) (1S) 12 |
*Isolated from reaction of 35 in the presence of Rh$_2$(OAc)$_4$ at room temperature.

*Isolated from reaction of 35 in the presence of Rh$_2$(2S-FOMePA)$_4$ 9e (Table 5).

| Compound | Column | $\lambda$ max (nm) | Mobile Phase (Hex:IPA) | Temp (°C) | Flow (mL/min) | Retention Time |
|----------|--------|-------------------|-----------------------|-----------|---------------|----------------|
| 48       | Phenomenex Lux$^\circledR$ 3μm Amylose-1 | 209.8 | 85 : 25 | 25 | 1.0 | Enantiomer min |
|          |        |                   |                       |           |               | (−) (1R) 8 |
|          |        |                   |                       |           |               | (+) (1S) 11 |
SUPPORTING INFORMATION

9-Aza-9-tert-butyl-1(\(R^*\))-cyano-2,6-dichlorobicyclo[5.3.0]deca-2,4,6-trien-10-one (49)

*Isolated from reaction of 36 in the presence of Rh\(\text{2}(\text{OAc})_4\) at room temperature.

9-Aza-9-tert-butyl-1(\(R\))-cyano-2,6-dichlorobicyclo[5.3.0]deca-2,4,6-trien-10-one (49)

*Isolated from reaction of 36 in the presence of Rh\(\text{2}(2S-\text{FOMePA})_4\) 9e (Table 5).

| Compound | Column | \(\lambda_{\text{max}}\) (nm) | Mobile Phase (Hex:IPA) | Temp (\(\degree\)C) | Flow (mL/min) | Retention Time |
|----------|--------|-----------------------------|------------------------|---------------------|---------------|----------------|
| 49       | Phenomenex Lux\(^{\circledR}\) 3\(\mu\)m Amylose-1 | 214.5 | 95 : 05 | 25 | 0.5 | Enantiomer | (\(-\)) | 19 |
|          |        |                             |                        |                     |               | (\(+\)) | 20 |

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9-Aza-9-tert-butyl-1(R*)-cyano-4-methylbicyclo[5.3.0]deca-2,4,6-trien-10-one (50)

*Isolated from reaction of 37 in the presence of Rh₂(OAc)₄ at room temperature.

9-Aza-9-tert-butyl-1(S)-cyano-4-methylbicyclo[5.3.0]deca-2,4,6-trien-10-one (50)

*Isolated from reaction of 37 in the presence of Rh₂(2S-FOMePA)₄ 9e (Table 5).

| Compound | Column | λ max (nm) | Mobile Phase (Hex:IPA) | Temp (°C) | Flow (mL/min) | Retention Time |
|----------|--------|------------|------------------------|-----------|---------------|----------------|
| 50       | Phenomenex Lux® 3μm Amylose-1 | 209.8 | 85:25 | 25 | 1.0 | (-) (1R) 6  
|          |        |            |                        |           |               | (+) (1S) 9   |
9-Aza-9-tert-butyl-1(R\textsuperscript{+})-cyano-3,5-dimethylbicyclo[5.3.0]deca-2,4,6-trien-10-one (51)

*Isolated from reaction of 38 in the presence of Rh\textsubscript{2}(OAc)\textsubscript{4} at room temperature.

9-Aza-9-tert-butyl-1(S)-cyano-3,5-dimethylbicyclo[5.3.0]deca-2,4,6-trien-10-one (51)

*Isolated from reaction of 38 in the presence of Rh\textsubscript{2}(2S-FOMePA)\textsubscript{4} 9e (Table 5).

| Compound | Column | λ\textsubscript{max} (nm) | Mobile Phase (Hex:IPA) | Temp (°C) | Flow (mL/min) | Retention Time |
|----------|--------|-------------------------|------------------------|-----------|---------------|----------------|
| 51       | Phenomenex Lux\textsuperscript{®} 3μm Amylose-1 | 209.8 | 85 : 25 | 25       | 1.0           | (−) 1R 6 min   |
|          |        |                         |                        |           |               | (+) 1S 7 min   |
9-Aza-9-tert-butyl-1(\textit{R})-cyano-2,4,6-trimethylbicyclo[5.3.0]deca-2,4,6-trien-10-one (52)

\*Isolated from reaction of 39 in the presence of Rh$_2$(OAc)$_4$ at room temperature.

| Compound | Column | $\lambda$ max (nm) | Mobile Phase (Hex:IPA) | Temp (°C) | Flow (mL/min) | Retention Time |
|----------|--------|---------------------|------------------------|-----------|---------------|----------------|
| 52       | Phenomenex Lux$^\text{®}$. 3μm Amylose-1 | 211.0 | 90 : 10 | 25 | 0.5 | Enantiomer \hspace{1cm} | min |
|          |        |                     |                        |           |               | (−) (1\textit{R}) | 11 |
|          |        |                     |                        |           |               | (+) (1\textit{S}) | 12 |
9-Aza-9-tert-butyl-1(\(R^*\))-cyanobicyclo[5.3.0]deca-2,4,6-trien-10-one (53)

*Isolated from reaction of 40 in the presence of \(\text{Rh}_2(\text{OAc})_4\) at room temperature.

9-Aza-9-tert-butyl-1(\(S^*\))-cyanobicyclo[5.3.0]deca-2,4,6-trien-10-one (53)

*Isolated from reaction of 40 in the presence of \(\text{Rh}_2(2\text{S-}\text{FOMePA})_4\) 9e (Table 5).

| Compound | Column | \(\lambda_{\text{max}}\) (nm) | Mobile Phase (Hex:IPA) | Temp (°C) | Flow (mL/min) | Retention Time |
|----------|--------|-----------------|-----------------------|----------|--------------|----------------|
| 53       | Phenomenex Lux® 3μm Amylose-1 | 209.8 | 85 : 25 | 25       | 1.0          | (-) 7 (+) 9    |
9-Aza-9-tert-butyl-1(\(R^*\))-cyano-4-nitro bicyclo[5.3.0]deca-2,4,6-trien-10-one (54)

*Isolated from reaction of 41 in the presence of \(\text{Rh}_2(\text{OAc})_4\) at room temperature.

9-Aza-9-tert-butyl-1(\(R\))-cyano-4-nitro bicyclo[5.3.0]deca-2,4,6-trien-10-one (54)

*Isolated from reaction of 41 in the presence of \(\text{Rh}_2(2\text{S}-\text{FOMePA})_4\) 9e (Table 5).

| Compound | Column                      | \(\lambda_{\text{max}}\) (nm) | Mobile Phase (Hex:IPA) | Temp (°C) | Flow (mL/min) | Retention Time Enantiomer | min |
|----------|-----------------------------|-------------------------------|------------------------|-----------|---------------|--------------------------|-----|
| 54       | Phenomenex Lux\(^*\) 3μm Amylose-1 | 209.8                         | 85 : 25                | 25        | 1.0           | (-) (1\(R^*\))            | 16  |
|          |                             |                               |                        |           |               | (+) (1\(S\))             | 23  |
9-Aza-9-tert-butyl-1(R\textsuperscript{*})-cyano-4-methoxycarbonylbicyclo[5.3.0]deca-2,4,6-trien-10-one (55)

*Isolated from reaction of 42 in the presence of Rh\textsubscript{2}(OAc)\textsubscript{4} at room temperature.

9-Aza-9-tert-butyl-1(S)-cyano-4-methoxycarbonylbicyclo[5.3.0]deca-2,4,6-trien-10-one (55)

*Isolated from reaction of 42 in the presence of Rh\textsubscript{2}(2S-FOMePA)\textsubscript{4} 9e (Table 5).

| Compound | Column | \(\lambda\) max (nm) | Mobile Phase (Hex:IPA) | Temp (°C) | Flow (mL/min) | Retention Time |
|----------|--------|---------------------|------------------------|-----------|---------------|----------------|
| 55       | Phenomenex Lux\textsuperscript{®} 3\mu m Amylose-1 | 209.8 | 85 : 25 | 25 | 1.0 | (-) (1R) 12 \n (+) (1S) 15 |
**Supporting Information**

*Isolated from reaction of 43 in the presence of Rh\textsubscript{2}(OAc)\textsubscript{4} at room temperature.*

9-Aza-9-tert-butyl-1\((R^*)\)-cyano-4-trifluoromethylbicyclo[5.3.0]deca-2,4,6-trien-10-one (56)

| Compound | Column | λ\textsubscript{max} (nm) | Mobile Phase (Hex:IPA) | Temp (°C) | Flow (mL/min) | Retention Time |
|----------|--------|---------------------------|------------------------|-----------|----------------|----------------|
| 56       | Phenomenex Lux\textsuperscript{®} 3μm Amylose-1 | 209.8                   | 85 : 25                | 25        | 1.0            | (-) (1R) 7  (+) (1S) 10 |

*Isolated from reaction of 43 in the presence of Rh\textsubscript{2}(2S-FOMePA)\textsubscript{4} 9e (Table 5).*
9-Aza-9-tert-butyl-1(\(R^*\)),4-dicyanobicyclo[5.3.0]deca-2,4,6-trien-10-one (57)

*Isolated from reaction of 44 in the presence of \(\text{Rh}_2(\text{OAc})_4\) at room temperature.

9-Aza-9-tert-butyl-1(\(S\)),4-dicyanobicyclo[5.3.0]deca-2,4,6-trien-10-one (57)

*Isolated from reaction of 44 in the presence of \(\text{Rh}_2(2\text{S}-\text{FOMePA})_4\) \(9\text{e}\) (Table 5).

| Compound | Column | \(\lambda\) max (nm) | Mobile Phase (Hex:IPA) | Temp (°C) | Flow (mL/min) | Retention Time |
|----------|--------|----------------------|------------------------|-----------|--------------|---------------|
| 57       | Phenomenex Lux\(^\text{®}\) 3μm Amylose-1 | 209.8 | 90 : 10 | 25 | 0.5 | Enantiomer min |
|          |        |                      |                        |           |              | (−) 26 |
|          |        |                      |                        |           |              | (1\(R\)) |
|          |        |                      |                        |           |              | (+) 44 |
|          |        |                      |                        |           |              | (1\(S\)) |
9-Aza-9-tert-butyl-1(R*)-cyano-4-methoxybicyclo[5.3.0]deca-2,4,6-trien-10-one (58)

*Isolated from reaction of 45 in the presence of Rh2(OAc)4 at room temperature.

9-Aza-9-tert-butyl-1(S)-cyano-4-methoxybicyclo[5.3.0]deca-2,4,6-trien-10-one (58)

*Isolated from reaction of 45 in the presence of Rh2(2S-FOMePA)4 9e (Table 5).

| Compound | Column | λ max (nm) | Mobile Phase (Hex:IPA) | Temp (°C) | Flow (mL/min) | Retention Time |
|----------|--------|------------|------------------------|-----------|---------------|----------------|
| 58       | Phenomenex Lux® 3μm Amylose-1 | 209.8       | 85 : 25                | 25        | 1.0           | (-) (1R) 8     |
|          |        |            |                        |           |               | (+) (1S) 11    |
Basic hydrolysis of enantioenriched 50 (Scheme 4).

| Compound | Column | λ max (nm) | Mobile Phase (Hex:IPA) | Temp (°C) | Flow (mL/min) | Retention Time |
|----------|--------|------------|------------------------|-----------|---------------|----------------|
| 61       | Phenomenex Lux® 3μm Amylose-1 | 209.8 | 85 : 25 | 25 | 1.0 | (+) (1R) 30 |
|          |        |            |                        |           |               | (−) (1S) 32  |

Methyl 9-aza-9-tert-butyl-4-methylbicyclo[5.3.0]deca-2,4,6-trien-10-one-1(R)-carboxylate (61)
*Isolated from the reaction of 62 in the presence of Rh₂(OAc)₄.

*Isolated from the reaction of 62 in the presence of Rh₂(2S-F-2′-NA)₉b (Scheme 5).
10. Crystal Structures and Data

(+)-<i>tert</i>-Butyl (2<i>S</i>)-2-(1′′<i>R</i>,2′′<i>R</i>,4′′<i>S</i>)-fenchyloxy-2-(naphthalen-2′-yl)acetate (7b)

The stereochemistry was determined by single crystal X-ray diffraction on a crystalline sample of (2<i>S</i>)-7b grown by slow evaporation over a number of days from a saturated solution of (2<i>S</i>)-7b in acetonitrile in a 20 mL vial.

An ORTEP view of (2<i>S</i>)-7b showing the structure and relative stereochemistry. Anisotropic parameters are drawn at the 30% probability level.

The X-ray crystallography data of (2<i>S</i>)-7b can be found in Table SI.7.
(−)-tert-Butyl (2S)-2-(1″R,2″R,4″S)-fenchyloxy-2-(naphthalen-1′-yl)acetate (7c)

The stereochemistry was determined by single crystal X-ray diffraction on a crystalline sample of (2S)-7c grown by slow evaporation over a number of days from a saturated solution of (2S)-7c in acetonitrile in a 20 mL vial.

An ORTEP view of (2S)-7c showing the structure and relative stereochemistry. Anisotropic parameters are drawn at the 30% probability level. Only one disordered component is shown for clarity.

The X-ray crystallography data of (2S)-7c can be found in Table SI.7.
(+)-tert-Butyl (2S)-2-(4′-bromophenyl)-2-(1″R,2″R,4″S)-fenchyloxyacetate (7d)

The stereochemistry was determined by single crystal X-ray diffraction on a crystalline sample of (2S)-7d grown by slow evaporation over a number of days from a saturated solution of (2S)-7d in acetonitrile in a 20 mL vial.

An ORTEP view of (2S)-7d showing the structure and relative stereochemistry. Anisotropic parameters are drawn at the 30% probability level.

The X-ray crystallography data of (2S)-7d can be found in Table SI.7.
(−)-tert-Butyl (2S)-2-(1″R,2″S,5″R)-menthylxy-2-phenylacetate (7f)

The stereochemistry was determined by single crystal X-ray diffraction on a crystalline sample of (2S)-7f grown by slow evaporation over a number of days from a saturated solution of (2S)-7f in acetonitrile in a 20 mL vial.

An ORTEP view of (2S)-7f showing the structure and relative stereochemistry. Anisotropic parameters are drawn at the 30% probability level.

The X-ray crystallography data of (2S)-7f can be found in Table SI.7.
(-)-tert-Butyl (2S)-2-(4'-bromophenyl)-2-(1''R,2''S,5''R)-menthylxoyacetate (7h)

The stereochemistry was determined by single crystal X-ray diffraction on a crystalline sample of (2S)-7h grown by slow evaporation over a number of days from a saturated solution of (2S)-7h in acetonitrile in a 20 mL vial.

An ORTEP view of (2S)-7h showing the structure and relative stereochemistry. Anisotropic parameters are drawn at the 30% probability level.

The X-ray crystallography data of (2S)-7h can be found in Table SI.7.
(−)-Methyl (2R,3S)-3-(4′-fluorophenyl)tetrahydro-2H-thiopyran-2-carboxylate 1,1-dioxide (27a)

The stereochemistry was determined by single crystal X-ray diffraction on a crystalline sample of 27a grown by slow evaporation over a number of days from a saturated solution of 27a in ethyl acetate in a 25 mL roundbottom flask.

An ORTEP view of (2R,3S)-27a showing the structure and relative stereochemistry. Anisotropic parameters are drawn at the 50% probability level.

The X-ray crystallography data of 27a can be found in Table SI.7.
(−)-Methyl (1R,4aS,8aR)-octahydro-1H-isothiochromene-1-carboxylate 2,2-dioxide (30a)

The stereochemistry was determined by single crystal X-ray diffraction on a crystalline sample of 30a grown by slow evaporation over a number of days from a saturated solution of 30a in ethyl acetate in a 25 mL roundbottom flask.

An ORTEP view of (1R,4aS,8aR)-30a showing the structure and relative stereochemistry. Anisotropic parameters are drawn at the 50% probability level.

The X-ray crystallography data of 30a can be found in Table SI.7.
(+)-9-Aza-9-tert-butyl-1(S)-cyano-4-bromobicyclo[5.3.0]deca-2,4,6-trien-10-one (47)

The stereochemistry was determined by single crystal X-ray diffraction on crystalline sample of 47 crystallised from chloroform.

An ORTEP view of 47 showing the structure and relative stereochemistry. Anisotropic displacement parameters are drawn at the 30% probability level. There is disorder in the tert-butyl group.

The X-ray crystallography data of 47 can be found in Table SI.7.
### Table SI.8: Crystallographic Data

| Compound No | 7b    | 7c    | 7d    | 7f    | 7h    |
|-------------|-------|-------|-------|-------|-------|
| **CCDC No.** | 2081765 | 2081766 | 2081767 | 2081768 | 2081769 |
| **Crystal System** | orthorhombic | orthorhombic | orthorhombic | orthorhombic | orthorhombic |
| **Space Group, Z** | P2₁2₁2₁, 4 | P2₁2₁2₁, 4 | P2₁2₁2₁, 4 | P2₁2₁2₁, 4 | P2₁2₁2₁, 4 |
| **Empirical Formula** | C₂₆H₃₄O₃ | C₂₆H₃₄O₃ | C₂₂H₃₃BrO₃ | C₂₂H₃₃O₃ | C₂₂H₃₃BrO₃ |
| **Formula Weight** | 394.53 | 394.53 | 423.38 | 346.49 | 425.39 |
| **Crystal size (mm)** | 0.33 x 0.26 x 0.12 | 0.60 x 0.55 x 0.12 | 0.43 x 0.36 x 0.30 | 0.33 x 0.29 x 0.25 | 0.30 x 0.27 x 0.24 |
| **Wavelength (Å)** | 1.54178 | 0.71073 | 1.54178 | 1.54178 | 1.54178 |
| **a (Å)** | 10.3931(2) | 11.0136(15) | 6.3385(2) | 8.8806(2) | 8.7929(2) |
| **b (Å)** | 14.9104(3) | 12.953(2) | 11.9385(3) | 10.9577(3) | 10.8463(3) |
| **c (Å)** | 15.0088(3) | 16.420(3) | 29.4096(7) | 22.7011(6) | 24.7189(6) |
| **α (°)** | 90 | 90 | 90 | 90 | 90 |
| **β (°)** | 90 | 90 | 90 | 90 | 90 |
| **γ (°)** | 90 | 90 | 90 | 90 | 90 |
| **Volume, V (Å³)** | 2325.84(8) | 2342.5(6) | 2225.49(10) | 2209.07(10) | 2357.45(10) |
| **Temperature (K)** | 296(2) | 300(2) | 296(2) | 296(2) | 296(2) |
| **Calculated Density, (g·cm⁻³)** | 1.127 | 1.119 | 1.264 | 1.042 | 1.199 |
| **μ (mm⁻¹)** | 0.563 | 0.071 | 2.644 | 0.527 | 2.496 |
| **F(000)** | 856 | 856 | 888 | 760 | 896 |
| **θ range** | 4.18 – 67.31 | 3.10 – 26.82 | 4.00 – 67.28 | 5.61 – 67.36 | 6.18 – 66.93 |
| **No. unique reflections** | 3940 | 4961 | 3822 | 3789 | 3922 |
| **No. observed reflections** | 3896 | 3472 | 3791 | 3684 | 3809 |
| **R₁ (I>2σ(I))** | 0.0356 | 0.0461 | 0.0313 | 0.0395 | 0.0371 |
| **wR²** | 0.1020 | 0.1226 | 0.0830 | 0.1142 | 0.1021 |
| **S (Goof)** | 1.067 | 1.062 | 1.105 | 1.057 | 1.092 |
| **Flack** | -0.01(3) | 0.0(5) | 0.050(6) | 0.09(4) | 0.024(6) |
| Compound No | 27a  | 30a  | 47    |
|-------------|------|------|------|
| CCDC No.    | 2081770 | 2081771 | 2081772 |
| Crystal System | monoclinic | monoclinic | orthorhombic |
| Space Group, Z | P2₁, 2 | P2₁, 2 | P2₁;2;2; |
| Empirical Formula | C₁₃H₁₈FO₄S | C₁₁H₁₈O₃S | C₄H₁₈BrN₂O |
| Formula Weight | 286.31 | 246.31 | 307.19 |
| Crystal size (mm) | 0.39 x 0.31 x 0.16 | 0.30 x 0.10 x 0.02 | 0.35 x 0.29 x 0.25 |
| Wavelength, (Å) | 0.71073 | 1.54178 | 0.71073 |
| a (Å) | 5.0934(9) | 5.0811(2) | 9.8104(9) |
| b (Å) | 10.1689(19) | 10.4886(4) | 35.977(3) |
| c (Å) | 13.539(2) | 11.6887(4) | 8.0365(7) |
| α (°) | 90 | 90 | 90 |
| β (°) | 96.887(3) | 94.910(2) | 90 |
| γ (°) | 90 | 90 | 90 |
| Volume, V(Å³) | 696.2(2) | 620.65(4) | 2836.5(4) |
| Temperature (K) | 296 | 293 | 293 |
| Calculated Density, (g·cm⁻³) | 1.366 | 1.318 | 1.439 |
| μ (mm⁻¹) | 0.251 | 2.316 | 2.889 |
| F(000) | 300 | 264 | 1248 |
| θ range | 1.51 – 27.18 | 7.60 – 66.56 | 1.13 – 26.00 |
| No. unique reflections | 2730 | 1144 | 5474 |
| No. observed reflections | 1762 | 1082 | 3332 |
| R₁ [I>2σ(I)] | 0.0441 | 0.0544 | 0.0480 |
| wR² | 0.1048 | 0.1566 | 0.1200 |
| S (Goof) | 1.031 | 1.116 | 1.019 |
| Flack | 0.03(6) | 0.03(4) | 0.009(9) |
10. Author Contributions

The synthetic work described in the paper was undertaken by Aoife M. Buckley, Daniel C. Crowley, Thomas A. Brouder and Alan Ford (equal contribution); the crystallography was undertaken by U. B. Rao Khandavilli and Simon E. Lawrence, while Anita R. Maguire had overall responsibility for the project.

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