Cycloaddition of Chiral *Tert*-butanesulfinimines with Trimethylenemethane

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Experimental

Unless otherwise stated, reagents were purchased from commercial sources and used without further purification. Tetrakis triphenylphosphine palladium (0) was purchased from Sigma-Aldrich® and recrystallised from boiling abs. EtOH immediately prior to use. All reactions were carried out in flame-dried glassware under an inert Ar or N₂ atmosphere. THF was distilled from Na/benzophenone immediately prior to use. Column chromatography was carried out either manually on silica gel Fluka 60 or on a Biotage® SP4 using either Biotage® SNAP KP-Sil or GraceResolv® Silica cartridges and petroleum ether (40-60 °C)/ethyl acetate as eluent, whilst monitoring by UV (254 nm) and thin layer chromatography (KMnO₄ stain). All NMR spectra were obtained in CDCl₃ at room temperature using Bruker® DPX300, Bruker® DPX400, Bruker® AV400, Bruker® AVIII400, Bruker® AVIII500 and Jeol 270 spectrometers for which chemical shifts are expressed in ppm relative to the solvent and coupling constants are expressed in Hz. Infrared spectroscopic data were recorded using a Bruker® Tensor27 FTIR spectrometer. Mass spectral data (and HRMS) were obtained using a Bruker® MicroTOF spectrometer. Optical rotations were measured on an ADP440 Polarimeter. Melting points were measured on a Gallenkamp® apparatus and are uncorrected. Elemental microanalyses for carbon, hydrogen and nitrogen were recorded on an Exeter® analytical CE-440 elemental analyser.

General procedure for the preparation of sulfinimines

To a dry round-bottom two-necked flask fitted with septa and stirrer bar, a 0.5 M solution of ketone or aldehyde (1.2 equivs.) in THF was charged with Ti(OEt)₄ (2 equivs.) under an inert atmosphere of Ar or N₂. The resulting solution was stirred at ambient conditions, to which (R₁)-tert-butanesulfinamide (1 equiv.) was added and stirred at room temperature overnight and monitored by TLC. The reaction mixture was then poured into an equal volume of saturated aqueous NaHCO₃.
Supplemental Material

solution, with rapid stirring and immediately filtered through celite. The filter cake was subsequently washed with EtOAc and the aqueous layer separated and extracted thrice with EtOAc. The resulting organic extracts were then combined, washed with brine, dried over MgSO$_4$ and concentrated in vacuo. The product was then purified by silica gel chromatography (either manually or on a Biotage® SP4; using petroleum ether/EtOAc as eluent) and the purified imines were stored at –20 °C under nitrogen or argon.

(R$_S$E)-2-Methyl-N-(thiophen-2-ylmethylene)propane-2-sulfinamide (1m)

The general procedure was followed using 2-thiophenecarboxaldehyde (0.25 mL, 2.67 mmol), (R$_S$)-tert-butanensulfinamide (270 mg, 2.23 mmol), Ti(OEt)$_4$ (0.93 mL) and THF (4.5 mL). Chromatography was performed on a Biotage® SP4 using a Biotage® KP-Sil 25 g Silica SNAP cartridge and eluting with 0-30% petroleum ether/EtOAc over 13 column volumes at a flow rate of 25 mL/min giving the product (362 mg, 75%) as a yellow solid.

mp = 87-89 °C

$\nu_{\text{max}}$ (CHCl$_3$)/cm$^{-1}$ 3011, 1589, 1193

Anal. Calcd for C$_9$H$_{13}$NOS$_2$: C 50.20%, H 6.09%, N 6.50%; Found: C 50.08%, H 6.03%, N 6.31%

[$\alpha$]$_D^{31}$ = +44.38 (c = 0.25 in CHCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.71 (1H, s), 7.62 (1H, m), 7.56 (1H, m), 7.19 (1H, m), 1.28 (9H, s)

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 155.5, 140.5, 133.8, 132.3, 128.2, 57.97, 22.56

HRMS (ESI) m/z, calculated for [C$_9$H$_{13}$NNaOS$_2$]+: 238.0331, found 238.0333.
(R$_5^E$)-2-Methyl-N-(naphthalen-2-ylmethylene)propane-2-sulfinamide (1n)

The general procedure was followed using 2-naphthaldehyde (300 mg, 1.92 mmol), (R$_5^E$)-tert-butanesulfinamide (194 mg, 1.60 mmol), Ti(OEt)$_4$ (0.67 mL) and THF (3.2 mL). Chromatography was performed on a Biotage® SP4 using a Biotage® KP-Sil 25 g Silica SNAP cartridge and eluting with 0-30% petroleum ether/EtOAc over 13 column volumes at a flow rate of 25 mL/min giving the product (390 mg, 94%) as a yellow solid.

mp = 90-92 °C

$\nu_{\text{max}}$ (CHCl$_3$)/cm$^{-1}$ 3011, 1606, 1069

Anal. Calcd for C$_{15}$H$_{17}$NOS: C 69.46%, H 6.61%, N 5.40%; Found: C 69.21%, H 6.60%, N 5.39%

$[\alpha]_{D}^{31} = -190.4$ (c = 0.18 in CHCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.78 (1H, s), 8.24 (1H, m), 8.08-7.89 (3H, m), 7.64-7.56 (3H, m), 1.33 (9H, s)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.8, 135.4, 132.5, 131.8, 128.9, 128.2, 128.0, 126.9, 123.8, 57.88, 22.67

HRMS (ESI) m/z, calculated for [C$_{15}$H$_{17}$NNaOS]$^+$: 282.0923, found 282.0916.

(R$_3^E$)-N-Cyclobutylidene-2-methylpropane-2-sulfinamide (3d)

The general procedure was followed using cyclobutanone (0.32 mL, 4.28 mmol), (R$_3^E$)-tert-butanesulfinamide (432 mg, 3.56 mmol), Ti(OEt)$_4$ (1.5 mL) and THF (7 mL). No chromatography was
required as residual cyclobutanone was removed \textit{in vacuo}, giving the product (470 mg, 76\%) as a yellow oil.

$\nu_{\text{max}}$ (CHCl$_3$/cm$^{-1}$) 3691, 3002, 1661, 1602, 1065

$[\alpha]_{D}^{31} = -275.0$ (c = 0.14 in CHCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.58-3.48 (1H, m), 3.34-3.25 (1H, m), 3.21-3.06 (2H, m), 2.17-2.06 (2H, m), 1.26 (9H, s)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 186.9, 56.75, 40.60, 39.93, 22.24, 15.11

HRMS (ESI) m/z, calculated for [C$_8$H$_{15}$NNaOS]$^+$: 196.0767, found 196.0769.
**General procedure for the asymmetric Pd-catalysed [3+2] cycloaddition of sulfinimines**

A 0.5 M solution of sulfinimine (1 equiv.) in THF was charged to freshly recrystallised Pd(PPh₃)₄ (0.1 equivs.), to which 2-(trimethylsilylmethyl)allyl acetate (1.5 to 2.0 equivs.) was added and stirred, either at room temperature or at 60 °C, overnight under an inert atmosphere of either Ar or N₂. The reaction was monitored by TLC and HRMS and when complete, the solvent was removed *in vacuo* and the crude material was then purified by silica gel chromatography (either manually or on a Biotage® SP4; using petroleum ether/EtOAc as eluent). The diastereomeric ratio of products was determined by comparison of peaks in the ¹H NMR of the unpurified reaction mixture.

**1-((R₃)-tert-Butylsulfinyl)-4-methylene-2-phenylpyrrolidine**

The general procedure was followed using (R₃,E)-N-benzylidene-2-methylpropane-2-sulfinamide (1.00 g, 4.78 mmol), Pd(PPh₃)₄ (552 mg, 0.478 mmol), 2-(trimethylsilylmethyl)allyl acetate (1.5 mL, 7.17 mmol) and THF (10 mL) at room temperature. Chromatography was performed on a Biotage® SP4 using a Biotage® KP-Sil 100 g Silica SNAP cartridge and eluting with 6-50% petroleum ether/EtOAc over 12 column volumes at a flow rate of 40 mL/min giving the product (1.20 g, 95%) as needle crystals. The diastereomers were successfully separated by chromatography.
(R)-1-((R)-tert-Butylsulfinyl)-4-methylene-2-phenylpyrrolidine (2a) (major diastereomer)

m.p. = 69-70 °C

\( \nu_{\text{max}} \) (CHCl\(_3\))/cm\(^{-1}\) 2995, 1051

Anal. Calcd for C\(_{15}\)H\(_{21}\)NOS: C 68.40%, H 8.04%, N 5.32%; Found: C 68.26%, H 7.93%, N 5.07%

\([\alpha]_D^{25} = -177.3 \) (c 0.044 in CHCl\(_3\))

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.33-7.23 (5H, m), 5.18 (1H, d, \( J=9 \) Hz), 5.03 (1H, br), 4.95 (1H, br), 4.26-4.16 (2H, m), 2.99-2.93 (1H, m), 2.44-2.40 (1H, d, \( J=15 \) Hz), 1.11 (9H, s)

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 145.6, 143.5, 128.4, 126.9, 126.5, 107.2, 58.19, 57.83, 57.61, 43.29, 23.00

HRMS (ESI) m/z, calculated for [C\(_{15}\)H\(_{21}\)NNaOS]\(^+\): 286.1236, found 286.1233.

(S)-1-((R)-tert-Butylsulfinyl)-4-methylene-2-phenylpyrrolidine (minor diastereomer)

\([\alpha]_D^{25} = -350.9 \) (c 0.010 in CHCl\(_3\))

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.35-7.28 (5H, m), 5.02 (2H, br), 4.70 (1H, t, \( J=7 \) Hz), 4.42-4.37 (1H, d, \( J=14 \) Hz), 3.64-3.59 (1H, d, \( J=14 \) Hz), 2.96-2.89 (1H, m), 2.60-2.52 (1H, m), 1.14 (9H, s)

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 142.5, 128.4, 127.5, 126.5, 106.9, 68.49, 57.44, 45.75, 41.92, 23.86

HRMS (ESI) m/z, calculated for [C\(_{15}\)H\(_{21}\)NNaOS]\(^+\): 286.1236, found 286.1234.
1-((R,S)-Mesitylsulfinyl)-4-methylene-2-phenylpyrrolidine

The general procedure was followed using (R,S,E)-N-benzylidene-2,4,6-trimethylbenzenesulfinamide (50 mg, 0.184 mmol), Pd(PPh₃)₄ (21 mg, 0.018 mmol), 2-(trimethylsilylmethyl)allyl acetate (78 µL, 0.368 mmol) and THF (0.4 mL) at room temperature. Chromatography was performed on a Biotage SP4 using a GraceResolv® 24 g Silica cartridge and eluting with 4-32% petroleum ether/EtOAc over 12 column volumes at a flow rate of 25 mL/min giving the product (32 mg, 53%) as a yellow oil. The product was isolated as a 6:1 mixture of diastereomers; only data for the major diastereomer is shown.

(R)-1-((R,S)-Mesitylsulfinyl)-4-methylene-2-phenylpyrrolidine (2b)

ν max (CHCl₃)/cm⁻¹ 3010, 1602, 1079

¹H NMR (400 MHz, CDCl₃) δ 7.19-7.08 (5H, m), 6.69 (2H, s), 5.05-4.97 (3H, m), 4.29-4.24 (1H, dq, J=14, 2 Hz), 4.02-3.97 (1H, m), 3.12-3.04 (1H, m), 2.63-2.57 (1H, m), 2.51 (6H, s), 2.21 (3H, s)

¹³C NMR (100 MHz, CDCl₃) δ 145.4, 142.5, 140.1, 137.6, 134.6, 130.9, 128.1, 126.9, 126.2, 107.3, 62.61, 52.33, 42.71, 20.81, 19.71

HRMS calculated for [C₂₀H₂₃NNaOS]⁺: 348.1393, found 348.1397.
Supplemental Material

1-((R,S)-tert-Butylsulfinyl)-2-(4-methoxyphenyl)-4-methylenepyrrolidine

The general procedure was followed using (R,S)-N-(4-methoxybenzylidene)-2-methylpropane-2-sulfinamide (50 mg, 0.209 mmol), Pd(PPh₃)₄ (24 mg, 0.021 mmol), 2-(trimethylsilylmethyl)allyl acetate (89 µL, 0.418 mmol) and THF (0.4 mL) at room temperature. Chromatography was performed on a Biotage® SP4 using a GraceResolv® 24 g Silica cartridge and eluting with 10-65% petroleum ether/EtOAc over 12 column volumes at a flow rate of 25 mL/min giving the product (58 mg, 95%) as a yellow oil. The diastereomers were separated by chromatography; only data for the major diastereomer is shown.

(R)-1-((R,S)-tert-Butylsulfinyl)-2-(4-methoxyphenyl)-4-methylenepyrrolidine (2c)

ν_max (CHCl₃)/cm⁻¹ 3693, 3001, 1512, 1248, 1081

[α]_D³¹ = +30.59 (c 0.06 in CHCl₃)

¹H NMR (400 MHz, CDCl₃) δ 7.17-7.15 (2H, m), 6.87-6.85 (2H, m), 5.10-5.08 (1H, d, J=10 Hz), 5.02 (1H, br), 4.96 (1H, br), 4.26-4.20 (1H, dq, J=15, 2 Hz), 3.80 (3H, s), 2.97-2.88 (1H, m), 2.42-2.38 (1H, dt, J=15, 2 Hz), 1.11 (9H, s)

¹³C NMR (100 MHz, CDCl₃) δ 158.5, 145.8, 135.6, 127.7, 113.8, 107.1, 58.28, 57.59, 57.01, 55.20, 43.26, 23.08

HRMS calculated for [C₁₆H₂₃NNaO₂S⁺]: 316.1342, found 316.1334.
1-((R<sub>3</sub>)-tert-Butylsulfinyl)-4-methylene-2-(4-nitrophenyl)pyrrolidine

The general procedure was followed using (R<sub>3</sub>,E)-2-methyl-N-(4-nitrobenzylidene)propane-2-sulfinamide (50 mg, 0.197 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (23 mg, 0.020 mmol), 2-(trimethylsilylmethyl)allyl acetate (84 µL, 0.393 mmol) and THF (0.4 mL) at room temperature. Chromatography was performed on a Biotage® SP4 using a GraceResolv® 24 g Silica cartridge and eluting with 4-32% petroleum ether/EtOAc over 17 column volumes at a flow rate of 25 mL/min giving the product (61 mg, 100%) as an orange solid. The diastereomers were separated by chromatography; only data for the major diastereomer is shown.

(R)-1-((R<sub>3</sub>)-tert-Butylsulfinyl)-4-methylene-2-(4-nitrophenyl)pyrrolidine (2d)

m.p. = 97-98 °C

ν<sub>max</sub> (CHCl<sub>3</sub>) /cm<sup>-1</sup> 3607, 3010, 1602, 1523, 1350, 1057

[α]<sup>21</sup> = +82.08 (c 0.135 in CHCl<sub>3</sub>)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.21-8.17 (2H, m), 7.42-7.39 (2H, m), 5.29-5.26 (1H, d, J=9 Hz), 5.06 (1H, br), 4.97 (1H, br), 4.22 (2H, br), 3.05-2.96 (1H, m), 2.40-2.34 (1H, d, J=15 Hz), 1.08 (9H, s)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 151.2, 147.0, 144.2, 127.3, 123.8, 108.2, 57.92, 57.74, 57.46, 42.95, 22.88

HRMS calculated for [C<sub>15</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>S]<sup>+</sup>: 331.1087, found 331.1078.
2-(1-((R,S)-tert-Butylsulfinyl)-4-methylenepyrrolidin-2-yl)phenol

The general procedure was followed using (R,S,E)-N-(2-hydroxybenzylidene)-2-methylpropane-2-sulfinamide (50 mg, 0.222 mmol), Pd(PPh3)4 (26 mg, 0.004 mmol), 2-(trimethylsilylmethyl)allyl acetate (94 µL, 0.444 mmol) and THF (0.4 mL) at room temperature. Chromatography was performed on a Biotage® SP4 using a GraceResolv® 24 g Silica cartridge and eluting with 12-100% petroleum ether/EtOAc over 12 column volumes at a flow rate of 25 mL/min giving the product (21 mg, 34%) as a colourless oil. The diastereomers were separated by chromatography; only data for the major diastereomer is shown.

\[ \text{2-((R)-1-((R)-tert-Butylsulfinyl)-4-methylene} \text{pyrrolidin-2-yl)phenol (2e)} \]

\[ \nu_{\text{max}} (\text{CHCl}_3)/\text{cm}^{-1} \ 3691, 3011, 1596, 1484, 1453, 1245, 1070 \]

\[ \alpha_{\text{D}}^{31} = -102.1 \ (c \ 0.005 \text{ in CHCl}_3) \]

\[ ^1H \text{ NMR (400 MHz, CDCl}_3) \delta \ 9.14 \ (1H, \text{ br}), \ 8.03-8.00 \ (1H, \text{ m}), \ 7.48-7.43 \ (1H, \text{ m}), \ 7.06-6.96 \ (2H, \text{ m}), \ 5.13-5.11 \ (1H, \text{ br}), \ 5.04-5.02 \ (1H, \text{ br}), \ 4.57-4.55 \ (2H, \text{ br}), \ 1.87-1.85 \ (3H, \text{ m}), \ 1.29 \ (9H, \text{ s}) \]

\[ ^{13}C \text{ NMR (100 MHz, CDCl}_3) \delta \ 158.8, \ 140.2, \ 133.8, \ 128.4, \ 123.2, \ 120.8, \ 113.2, \ 112.8, \ 72.16, \ 57.62, \ 22.67, \ 19.44 \]

HRMS calculated for [C_{15}H_{21}NNaO_2S]^+: 302.1185, found 302.1209.
1-[(R,S)-tert-Butylsulfinyl]-2-(2-chlorophenyl)-4-methyleneypyrrolidine

The general procedure was followed using (R,S)-N-(2-chlorobenzylidene)-2-methylpropane-2-sulfinamid (50 mg, 0.205 mmol), Pd(PPh3)4 (24 mg, 0.021 mmol), 2-(trimethylsilylmethyl)allyl acetate (87 µL, 0.410 mmol) and THF (0.4 mL) at room temperature. Chromatography was performed on a Biotage® SP4 using a GraceResolv® 24 g Silica cartridge and eluting with 4-32% petroleum ether/EtOAc over 12 column volumes at a flow rate of 25 mL/min giving the product (54 mg, 89%) as an orange oil. The diastereomers were separated by chromatography.

(R)-1-[(R,S)-tert-Butylsulfinyl]-2-(2-chlorophenyl)-4-methyleneypyrrolidine (2f)

ν<sub>max</sub> (CHCl₃)/cm⁻¹ 3693, 3003, 1602, 1058

[α]<sub>D</sub> <sup>31</sup> = +53.32 (c 0.10 in CHCl₃)

<sup>1</sup>H NMR (400 MHz, CDCl₃) δ 7.39-7.18 (4H, m), 5.59-5.54 (1H, d, J=8 Hz), 5.02 (1H, br), 4.93 (1H, br), 4.27 (2H, br), 3.05-2.95 (1H, m), 2.45-2.37 (1H, d, J=15 Hz), 1.10 (9H, s)

<sup>13</sup>C NMR (100 MHz, CDCl₃) δ 144.9, 141.0, 132.3, 130.0, 128.2, 127.9, 126.7, 107.6, 58.83, 57.64, 55.37, 41.92, 22.92

HRMS calculated for [C₁₅H₂₀ClNaOS]⁺: 320.0846, found 320.0842.

(S)-1-[(R,S)-tert-Butylsulfinyl]-2-(2-chlorophenyl)-4-methyleneypyrrolidine
$\nu_{\text{max}} (\text{CHCl}_3)/\text{cm}^{-1}$ 3693, 3011, 1602, 1242, 1058

$[\alpha]_{D}^{31} = -51.94$ (c 0.01 in CHCl$_3$

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40-7.36 (2H, m), 7.26-7.19 (2H, m), 5.31-5.28 (1H, q, $J=4$ Hz), 5.04 (1H, m), 4.98 (1H, m), 4.54-4.50 (1H, m), 3.62-3.58 (1H, dq, $J=15$, 2 Hz), 3.08-3.00 (1H, m), 2.48-2.35 (1H, m), 1.19 (9H, s)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.4, 140.6, 132.5, 129.6, 128.4, 128.0, 126.7, 107.5, 66.24, 57.75, 45.88, 40.49, 23.77

HRMS calculated for [C$_{15}$H$_{20}$ClNNaOS]$^+$: 320.0846, found 320.0842.

2-(2-Bromophenyl)-1-((R$_{S}$)-tert-butylsulfanyl)-4-methyleneprrolidine

The general procedure was followed using (R$_{S}$,E)-N-(2-bromobenzylidene)-2-methylpropane-2-sulfinamide (35 mg, 0.153 mmol), Pd(PPh$_3$)$_4$ (20 mg, 0.017 mmol), 2-(trimethylsilylmethyl)allyl acetate (74 $\mu$L, 0.347 mmol) and THF (0.3 mL) at room temperature. Chromatography was performed on a Biotage® SP4 using a GraceResolv® 24 g Silica cartridge and eluting with 8-66% petroleum ether/EtOAc over 12 column volumes at a flow rate of 25 mL/min giving the product (37 mg, 71%) as a yellow solid. The diastereomers were separated by chromatography; only data for the major diastereomer is shown.

(R)-2-(2-Bromophenyl)-1-((R$_{S}$)-tert-butylsulfanyl)-4-methyleneprrolidine (2g)

m.p. = 54-56 °C

$\nu_{\text{max}} (\text{CHCl}_3)/\text{cm}^{-1}$ 3693, 3011, 1602, 1242, 1058
[α]D$_{31}$ = −7.46 (c 0.065 in CHCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.57-7.54 (1H, m), 7.32-7.26 (2H, m), 7.15-7.11 (1H, m), 5.52-5.49 (1H, m), 5.03 (1H, br), 4.93 (1H, br), 4.28 (2H, m), 3.04-2.96 (1H, m), 2.43-2.39 (1H, d, J=15 Hz), 1.09 (9H, s)

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 144.7, 142.6, 132.9, 128.5, 128.1, 127.3, 122.4, 107.7, 58.97, 57.63, 57.56, 42.04, 22.93

HRMS calculated for [C$_{15}$H$_{20}$BrNaOS]$^+$: 364.0341, found 364.0333.

1-((R$_S$)-tert-Butylsulfinyl)-2-methyl-4-methylene.pyrrolidine

The general procedure was followed using (R$_S$)-N-ethylidene-2-methylpropane-2-sulfinamide (50 mg, 0.340 mmol), Pd(PPh$_3$)$_4$ (39 mg, 0.034 mmol), 2-(trimethylsilylmethyl)allyl acetate (144 µL, 0.679 mmol) and THF (0.7 mL) at room temperature. Chromatography was performed on a Biotage® SP4 using a GraceResolv® 24 g Silica cartridge and eluting with 4-32% petroleum ether/EtOAc over 12 column volumes at a flow rate of 25 mL/min giving the product (62 mg, 91%) as an orange oil. The product was isolated as a 4:1 mixture of diastereomers; only data for the major diastereomer is shown.

(S)-1-((R$_S$)-tert-Butylsulfinyl)-2-methyl-4-methylene.pyrrolidine (2h)

ν$_{max}$ (CHCl$_3$)/cm$^{-1}$ 2991, 1050

$^1$H NMR (400 MHz, CDCl$_3$) δ 5.03 (1H, br), 4.99 (1H, br), 4.12-4.06 (1H, m), 4.01-3.94 (1H, dq, J=5, 2 Hz), 3.77-3.71 (1H, m), 2.68-2.61 (1H, m), 2.18-2.11 (1H, d, J=15 Hz), 1.23-1.19 (12H, m)
Supplemental Material

$^1\text{C}$ NMR (100 MHz, CDCl$_3$) δ 146.5, 106.6, 60.64, 57.33, 45.12, 41.14, 23.42, 19.67

HRMS calculated for [C$_{10}$H$_{19}$NNaOS]$^+$: 224.1080, found 224.1086.

1-((R$_S$)-tert-Butylsulfinyl)-4-methylene-2-propylpyrrolidine

The general procedure was followed using (R$_S$,E)-N-butylidene-2-methylpropane-2-sulfinamide (50 mg, 0.285 mmol), Pd(PPh$_3$)$_4$ (33 mg, 0.029 mmol), 2-(trimethylsilylmethyl)allyl acetate (121 µL, 0.570 mmol) and THF (0.6 mL) at room temperature. Chromatography was performed on a Biotage® SP4 using a GraceResolv® 24 g Silica cartridge and eluting with 6-50% petroleum ether/EtOAc over 12 column volumes at a flow rate of 25 mL/min giving the product (37 mg, 57%) as an orange oil. The diastereomers were separated by chromatography; only data for the major diastereomer is shown.

(S)-1-((R$_S$)-tert-Butylsulfinyl)-4-methylene-2-propylpyrrolidine (2i)

$\nu_{\text{max}}$ (CHCl$_3$)/cm$^{-1}$ 3691, 2991, 1602, 1050

$[\alpha]_D^{31} = -80.97$ (c 0.13 in CHCl$_3$)

$^1\text{H}$ NMR (400 MHz, CDCl$_3$) δ 5.04-5.01 (1H, m), 4.99-4.94 (1H, m), 4.08-4.02 (1H, dq, J=15, 2 Hz), 3.83-3.75 (2H, m), 2.60-2.51 (1H, m), 2.30-2.23 (1H, m), 1.68-1.59 (2H, m), 1.53-1.43 (1H, m), 1.41-1.26 (1H, m), 1.23-1.21 (12H, m)

$^1\text{C}$ NMR (100 MHz, CDCl$_3$) δ 146.8, 106.3, 57.44, 48.42, 38.48, 35.76, 23.90, 23.44, 19.94, 14.07

HRMS calculated for [C$_{12}$H$_{23}$NNaOS]$^+$: 252.1393, found 252.1387.
1-((R,s)-tert-Butylsulfinyl)-2-cyclohexyl-4-methylenepyrrolidine

The general procedure was followed using (R,s,E)-N-(cyclohexylmethylene)-2-methylpropane-2-sulfinamide (50 mg, 0.232 mmol), Pd(PPh₃)₄ (27 mg, 0.023 mmol), 2-(trimethylsilylmethyl)allyl acetate (99 µL, 0.464 mmol) and THF (0.5 mL) at room temperature. Chromatography was performed on a Biotage® SP4 using a Biotage® KP-Sil 25 g Silica SNAP cartridge and eluting with 0-10% petroleum ether/EtOAc over 15 column volumes at a flow rate of 25 mL/min giving the product (61 mg, 98%) as a yellow solid. The diastereomers were separated by chromatography.

(R)-1-((R,s)-tert-Butylsulfinyl)-2-cyclohexyl-4-methylenepyrrolidine (2)

νₓₓₙₓ (CHCl₃)/cm⁻¹ 2929, 2338, 1711, 1047

[α]₀²⁵ = −53.50 (c 0.055 in CHCl₃)

¹H NMR (400 MHz, CDCl₃) δ 5.00-4.97 (1H, m), 4.93-4.90 (1H, m), 4.06-3.99 (1H, m), 3.86-3.80 (1H, m), 3.68-3.63 (1H, m), 2.55-2.47 (1H, m), 2.42-2.35 (1H, m), 1.82-1.62 (6H, m), 1.23 (9H, s), 1.21-0.89 (5H, m)

¹³C NMR (100 MHz, CDCl₃) δ 147.8, 105.3, 63.64, 57.62, 54.19, 42.15, 35.84, 30.70, 28.19, 26.41, 23.51

HRMS calculated for [C₁₅H₂₇NNaOS]⁺: 292.1706, found 292.1701.
**Supplemental Material**

\begin{equation*}
\text{(S)-1-}([R_s]-\text{tert-Butylsulfinyl})-2\text{-cyclohexyl-4-methylenepyrrolidine}
\end{equation*}

\text{m.p. = 45-47 °C}

\text{\(\nu_{\text{max}}\) (CHCl\textsubscript{3})/cm\textsuperscript{-1} 3692, 2993, 1602, 1050}

\[\alpha\]\textsubscript{D}\textsuperscript{25} = +6.93 (c 0.035 in CHCl\textsubscript{3})

\(1^H \text{ NMR (400 MHz, CDCl}_3\) \(\delta 4.96\) (1H, m), 4.94-4.92 (1H, m), 4.34-4.29 (1H, m), 3.36-3.31 (1H, m), 2.58-2.49 (1H, m), 2.38-2.32 (1H, m), 1.79-1.64 (6H, m), 1.24 (9H, s), 1.18-0.87 (5H, m)

\(13^C \text{ NMR (100 MHz, CDCl}_3\) \(\delta 147.9, 105.8, 71.39, 57.91, 45.55, 42.90, 34.56, 29.97, 27.93, 26.56, 24.12\)

HRMS calculated for [C\textsubscript{15}H\textsubscript{27}NNaOS\textsuperscript{+}]\textsuperscript{+}: 292.1706, found 292.1698.

\text{2-}([\text{tert-Butyl}])-1-([R_s]-\text{tert-butylsulfinyl})-4\text{-methylenepyrrolidine}

The general procedure was followed using \((R_s,E)-N-\text{(2,2-dimethylpropylidene)}-2\text{-methylpropane-2-sulfinamide (50 mg, 0.264 mmol), Pd(PPh}_3\textsubscript{4} (31 mg, 0.026 mmol), 2-\text{(trimethylsilylmethyl)allyl acetate (112 µL, 0.528 mmol) and THF (0.5 mL) at room temperature. Chromatography was performed on a Biotage® SP4 using a Biotage® KP-Sil 25 g Silica SNAP cartridge and eluting with 0-10% petroleum ether/EtOAc over 15 column volumes at a flow rate of 25 mL/min giving the product (52 mg, 81%) as a yellow oil. The product was isolated as a 5:1 mixture of diastereomers; only data for the major diastereomer is shown.}
\( (R)-2-(\text{tert-Butyl})-1-((R,S)-\text{tert-butylsulfinyl})-4\)-methyleneppyrrolidine (2k) \)

\( \nu_{\text{max}} \text{(CHCl}_3)/\text{cm}^{-1} \) 3650, 2964, 1602, 1055

\( ^1H \text{ NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 5.01-4.99 (1H, m), 4.92-4.89 (1H, m), 4.00-3.84 (2H, m), 3.61-3.57 (2H, m), 2.63-2.52 (1H, m), 1.24 (9H, s), 0.96 (9H, s)

\( ^{13}C \text{ NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 148.0, 105.3, 68.90, 58.83, 52.47, 36.59, 34.61, 27.27, 23.89

HRMS calculated for \([C_{13}H_{25}NNaOS]^+\): 266.1549, found 266.1551.

\( 1-((R,S)-\text{tert-Butylsulfinyl})-2-(\text{furan-2-y1})-4\)-methyleneppyrrolidine \)

The general procedure was followed using \((R,S,E)-N-(\text{furan-2-ylmethylene})-2\)-methylpropane-2-sulfinamide (40 mg, 0.335 mmol), Pd(PPh\(_3\))\(_4\) (39 mg, 0.034 mmol), 2-(trimethylsilylmethyl)allyl acetate (107 \( \mu \)L, 0.503 mmol) and THF (0.7 mL) at 65 °C. Chromatography was performed on a Biotage® SP4 using a GraceResolv® 24 g Silica cartridge and eluting with 8-66% petroleum ether/EtOAc over 12 column volumes at a flow rate of 25 mL/min giving the product (41 mg, 48%) as a yellow oil. The diastereomers were separated by chromatography; only data for the major diastereomer is shown.
(R)-1-((R₃)-tert-Butylsulfinyl)-2-(furan-2-yl)-4-methylenepyrrolidine (2l)

νₘₐₚ(CHCl₃)/cm⁻¹ 3000, 1602, 1056

[α]₀D₃₁ = −6.62 (c 0.115 in CHCl₃)

¹H NMR (400 MHz, CDCl₃) δ 7.36 (1H, m), 6.31 (1H, m), 6.19-6.17 (1H, m), 5.08-5.00 (3H, m), 4.18-4.12 (1H, m), 4.00-3.94 (1H, m), 2.85-2.76 (1H, m), 2.66-2.60 (1H, m), 1.18 (9H, s)

¹³C NMR (100 MHz, CDCl₃) δ 155.1, 146.1, 142.0, 110.1, 106.7, 106.4, 57.74, 55.66, 53.84, 39.59, 22.90

HRMS calculated for [C₁₃H₁₉NNaO₂S]⁺: 276.1029, found 276.1020.

The general procedure was followed using (R₃,E)-2-methyl-N-(thiophen-2-ylmethylene)propane-2-sulfinamide (50 mg, 0.232 mmol), Pd(PPh₃)₄ (27 mg, 0.023 mmol), 2-(trimethylsilylmethyl)allyl acetate (99 µL, 0.464 mmol) and THF (0.5 mL) at room temperature. Chromatography was performed on a Biotage® SP4 using a GraceResolv® 24 g Silica cartridge and eluting with 8-66% petroleum ether/EtOAc over 12 column volumes at a flow rate of 25 mL/min giving the product (54 mg, 86%) as a yellow oil. The diastereomers were separated by chromatography.
(R)-1-((R3)-tert-Butylsulfinyl)-4-methylene-2(thiophen-2-yl)pyrrolidine (2m)

ν\textsubscript{max} (CHCl\textsubscript{3})/cm\textsuperscript{-1} 3003, 1054

[α]\textsubscript{D}\textsuperscript{31} = +19.93 (c 0.41 in CHCl\textsubscript{3})

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.18-7.16 (1H, m), 6.95-6.93 (1H, m), 6.90-6.88 (1H, m), 5.35-5.33 (1H, d, J=8 Hz), 5.05-5.03 (2H, br), 4.22-4.16 (1H, dd, J=15, 2 Hz), 4.09-4.04 (1H, dt, J=15, 2 Hz), 2.96-2.88 (1H, m), 2.57-2.52 (1H, dt, J=15, 2 Hz), 1.17 (9H, s)

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 147.1, 145.6, 126.8, 124.1, 107.4, 57.79, 56.78, 55.08, 43.51, 22.85

HRMS calculated for [C\textsubscript{13}H\textsubscript{19}NNaOS\textsubscript{2}]\textsuperscript{+}: 292.0800, found 292.0800.

(S)-1-((R3)-tert-Butylsulfinyl)-4-methylene-2(thiophen-2-yl)pyrrolidine

ν\textsubscript{max} (CHCl\textsubscript{3})/cm\textsuperscript{-1} 3692, 3007, 1602, 1242, 1053

[α]\textsubscript{D}\textsuperscript{31} = −110.8 (c 0.005 in CHCl\textsubscript{3})

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.25-7.23 (1H, m), 6.98-6.94 (2H, m), 5.06-4.99 (3H, m), 4.40-4.33 (1H, dq, J=15, 2 Hz), 3.59-3.54 (1H, d, J=13 Hz), 3.00-2.93 (1H, m), 2.72-2.65 (1H, m), 1.19 (9H, s)

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 150.9, 145.2, 126.7, 124.9, 107.2, 64.62, 57.79, 45.25, 42.27, 23.78

HRMS calculated for [C\textsubscript{13}H\textsubscript{19}NNaOS\textsubscript{2}]\textsuperscript{+}: 292.0800, found 292.0800.
1-((R₃)-tert-Butylsulfinyl)-4-methylene-2-(naphthalen-2-yl)pyrrolidine

The general procedure was followed using (R₃,E)-2-methyl-N-(naphthalen-2-ylmethylene)propane-2-sulfinamide (10 mg, 0.039 mmol), Pd(PPh₃)₄ (4 mg, 0.004 mmol), 2-(trimethylsilylmethyl)allyl acetate (16 µL, 0.077 mmol) and THF (0.1 mL) at 65 °C. Chromatography was performed on a Biotage® SP4 using a Biotage® KP-Sil 10 g Silica SNAP cartridge and eluting with 6-50% petroleum ether/EtOAc over 12 column volumes at a flow rate of 15 mL/min giving the product (5 mg, 42%) as a yellow oil. The product was isolated as a 3:1 mixture of diastereomers; only data for the major diastereomer is shown.

(R)-1-((R₃)-tert-Butylsulfinyl)-4-methylene-2-(naphthalen-2-yl)pyrrolidine (2n)

νₑₑ =(CHCl₃)/cm⁻¹ 3692, 3045, 1602, 1053

¹H NMR (400 MHz, CDCl₃) δ 7.86-7.36 (7H, m), 5.38-5.34 (1H, d, J=8 Hz), 5.08-5.04 (1H, m), 4.97-4.94 (1H, br), 4.48-4.24 (1H, m), 3.08-2.94 (1H, m), 2.54-2.49 (1H, dt, J=15, 2 Hz), 1.13 (9H, s)

¹³C NMR (100 MHz, CDCl₃) δ 145.5, 141.0, 132.5, 128.4, 127.9, 127.7, 126.2, 125.7, 125.0, 124.9, 107.3, 57.70, 43.25, 23.05

HRMS calculated for [C₁₉H₂₃NNaOS]⁺: 336.1393, found 336.1395.
The general procedure was followed using (R,S)-2-methyl-N-(propan-2-ylidene)propane-2-sulfinamide (50 mg, 0.310 mmol), Pd(PPh$_3$)$_4$ (36 mg, 0.031 mmol), 2-(trimethylsilylmethyl)allyl acetate (132 µL, 0.620 mmol) and THF (0.6 mL) at room temperature. Chromatography was performed on a Biotage® SP4 using a Biotage® KP-Sil 10 g Silica SNAP cartridge and eluting with 6-50% petroleum ether/EtOAc over 12 column volumes at a flow rate of 15 mL/min giving the product (36 mg, 54%) as a yellow oil.

$\nu_{\text{max}}$(CHCl$_3$)/cm$^{-1}$: 2980, 1050

$[\alpha]_D^{31}$ = –128.5 (c 0.145 in CHCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$) δ 5.00-4.95 (2H, br), 4.26-4.20 (1H, d, $J$=15 Hz), 3.56-3.50 (1H, d, $J$=15 Hz), 2.46-2.39 (1H, d, $J$=15 Hz), 2.35-2.29 (1H, d, $J$=15 Hz), 1.34-1.29 (6H, m), 1.22 (9H, s)

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 145.0, 106.7, 64.69, 56.91, 47.82, 44.92, 28.86, 25.17, 24.19

HRMS calculated for [C$_{11}$H$_{21}$NNaOS]$^+$: 238.1236, found 238.1240.

1-((R$_S$)-tert-Butylsulfinyl)-2-methyl-4-methylene-2-phenylpyrroolidine

The general procedure was followed using (R$_S$,E)-2-methyl-N-(1-phenylethylidene)propane-2-sulfinamide (10 mg, 0.045 mmol), Pd(PPh$_3$)$_4$ (5 mg, 0.004 mmol), 2-(trimethylsilylmethyl)allyl acetate (19 µL, 0.090 mmol) and THF (0.1 mL) at 65 °C. Chromatography was performed on a Biotage® SP4 using a Biotage® KP-Sil 10 g Silica SNAP cartridge and eluting with 6-50% petroleum ether/EtOAc over 12 column volumes at a flow rate of 15 mL/min giving the product (4.5 mg, 38%) as a yellow oil.
The product was isolated as a 2:1 mixture of diastereomers; only data for the major diastereomer is shown.

\[(R)-1-\{(R)_{3}\text{-}\text{tert-Butylsulfinyl}\}-2\text{-methyl-4-methylene-2-phenylpyrrolidine (4b)}\]

\[\nu_{\text{max}}\text{(CHCl}_3\text{)/cm}^{-1} 3011, 1241, 1052\]

\[^{1}\text{H}\text{ NMR (400 MHz, CDCl}_3\text{)} \ delta 7.90-7.83 (2H, m), 7.54-7.42 (3H, m), 4.81-4.79 (1H, br), 4.78-4.76 (1H, br), 3.52-3.40 (1H, br), 3.37-3.26 (1H, br), 2.46-2.29 (2H, m), 1.82 (3H, s), 1.35 (9H, s)\]

\[^{13}\text{C}\text{ NMR (125 MHz, CDCl}_3\text{)} \ delta 144.2, 143.5, 131.6, 128.6, 127.5, 110.9, 66.84, 57.56, 36.23, 33.97, 31.08, 22.70\]

HRMS calculated for \([C_{16}H_{23}NNaOS]^+: 300.1393\), found 300.1393.

1-\{(R)_{3}\text{-}\text{tert-Butylsulfinyl}\}-2\text{-methyl-4-methylene-2-(naphthalen-2-yl)pyrrolidine}

The general procedure was followed using \((R,S,E)-2\text{-methyl-}N\text{-}(1\text{-}(naphthalen-2-yl)ethylidene)propane-2-sulfinamide (2.5 mg, 0.037 mmol), Pd(PPh}_3\text{)}_4 (4 mg, 0.004 mmol), 2-(trimethylsilylmethyl)allyl acetate (16 \mu L, 0.077 mmol) and THF (0.1 mL) at 65 °C. Chromatography was performed on a Biotage® SP4 using a Biotage® KP-Sil 10 g Silica SNAP cartridge and eluting with 8-66% petroleum ether/EtOAc over 12 column volumes at a flow rate of 15 mL/min giving the product (2 mg, 67%) as a yellow oil. The product was isolated as a 2:1 mixture of diastereomers; only data for the major diastereomer is shown.

S-23
(R)-1-((R,S)-2-methyl-4-methylene-2-(naphthalen-2-yl)pyrrolidine (4c)

$\nu_{\text{max}} (\text{CHCl}_3)/\text{cm}^{-1}$ 2929, 1734, 1590, 1457, 1242, 1071

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.08-7.51 (7H, m), 4.84-4.80 (2H, m), 3.64-3.53 (1H, m), 3.49-3.36 (1H, m), 2.59-2.33 (2H, m), 2.12 (3H, s), 1.58 (9H, s)

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 144.3, 134.8, 132.8, 129.3, 128.4, 127.7, 124.3, 110.9, 66.84, 64.53, 57.66, 36.43, 31.08, 22.75

HRMS calculated for [C$_{20}$H$_{25}$NNaOS]$^+$: 350.1549, found 350.1565.

(RS)-5-((tert-Butylsulfinyl)-7-methylene-5-azaspiro[3.4]octane (4d)

The general procedure was followed using (R,S)-N-cyclobutylidene-2-methylpropane-2-sulfinamide (50 mg, 0.289 mmol), Pd(PPh$_3$)$_4$ (33 mg, 0.029 mmol), 2-(trimethylsilylmethyl)allyl acetate (122 $\mu$L, 0.577 mmol) and THF (0.6 mL) at room temperature. Chromatography was performed on a Biotage® SP4 using a GraceResolv® 24 g Silica cartridge and eluting with 8-66% petroleum ether/EtOAc over 12 column volumes at a flow rate of 25 mL/min giving the product (19 mg, 29%) as an orange oil.

$\nu_{\text{max}} (\text{CHCl}_3)/\text{cm}^{-1}$ 3693, 2989, 1602, 1053

$[\alpha]_D^{31} = -103.9$ (c 0.11 in CHCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.04-5.01 (1H, m), 4.98-4.95 (1H, m), 4.22-4.16 (1H, dq, $J$=15, 2 Hz), 3.49-3.43 (1H, m), 2.66-2.48 (2H, m), 2.34-2.05 (2H, m), 2.00-1.89 (2H, m), 1.83-1.62 (2H, m), 1.22 (9H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.7, 106.9, 68.35, 56.97, 45.29, 34.89, 33.15, 23.93, 22.47, 14.05
HRMS calculated for [C_{12}H_{21}N NaOS]^+: 250.1236, found 250.1237.

1'-[(R,R)-tert-Butylsulfinyl]-4'-methylene-2,3-dihydrospiro[indene-1,2'-pyrrolidine]

The general procedure was followed using (R_s,E)-N-(2,3-dihydro-1H-inden-1-ylidene)-2-methylpropane-2-sulfinamide (10 mg, 0.042 mmol), Pd(PPh_3)_4 (5 mg, 0.004 mmol), 2-(trimethylsilylmethyl)allyl acetate (18 µL, 0.085 mmol) and THF (0.1 mL) at 65 °C. Chromatography was performed on a Biotage® SP4 using a Biotage® KP-Sil 10 g Silica SNAP cartridge and eluting with 8-66% petroleum ether/EtOAc over 12 column volumes at a flow rate of 15 mL/min giving the product (6 mg, 50%) as an orange oil. The product was isolated as a 2:1 mixture of diastereomers; only data for the major diastereomer is shown.

(R)-1'-[(R,R)-tert-Butylsulfinyl]-4'-methylene-2,3-dihydrospiro[indene-1,2'-pyrrolidine] (4e)

\n
HRMS calculated for [C_{17}H_{23}N NaOS]^+: 312.1393, found 312.1390.
General procedure for the deprotection of sulfinylpyrrolidines

(R)-4-Methylene-2-phenylpyrrolidine (5)

A solution of (R)-1-((R,S)-tert-butylsulfinyl)-4-methylene-2-phenylpyrrolidine (2a) (50 mg, 0.190 mmol) in dry diethyl ether (0.4 mL) was charged with 2 M HCl in diethyl ether (0.47 mL, 0.950 mmol) dropwise with stirring under an inert atmosphere of argon. A white suspension was immediately formed. The resulting solid was subsequently filtered and washed with diethyl ether before being taken up into EtOAc and charging saturated NaHCO₃ (aq.) solution until the effervescence subsided. The aqueous layer was then separated and extracted thrice with EtOAc and the resulting organic extracts combined, dried over MgSO₄ (s), filtered and concentrated in vacuo giving the product (30 mg, 100%) as an orange oil.

ν max (CHCl₃)/cm⁻¹ 3694, 2930, 1602, 886.8

[α]D³¹ = +50.07 (c 0.065 in CHCl₃)

1H NMR (400 MHz, CDCl₃) δ 7.42-7.26 (5H, m), 5.03-4.97 (2H, dt, J=15, 2 Hz), 4.30-4.25 (1H, ABX, J=7, 3 Hz), 3.84-3.78 (1H, d, J=15 Hz), 3.70-3.64 (1H, m), 2.90-2.83 (1H, m), 2.75-2.67 (1H, br), 2.53-2.44 (1H, m)

13C NMR (100 MHz, CDCl₃) δ 149.3, 143.1, 128.5, 127.2, 126.6, 105.0, 62.80, 51.75, 41.24

General procedure for the hydrogenation of sulfinylpyrrolidines

\((2R)-1-(\text{ }(R,S)-\text{ tert-butylsulfinyl})-4\text{-methylene}-2\text{-phenylpyrrolidine (6)\)}

A solution of \((R)-1-(\text{ }(R,S)-\text{ tert-butylsulfinyl})-4\text{-methylene}-2\text{-phenylpyrrolidine (2a)\)} (50 mg, 0.190 mmol) in EtOAc (5 mL) was charged with PtO\(_2\) (4 mg, 0.019 mmol) and degassed under reduced pressure before being flushed with argon. The mixture was then hydrogenated at 1 atm overnight. The catalyst was subsequently removed by filtration through a pad of celite and the solvent removed \textit{in vacuo}. Chromatography was performed on a Biotage® SP4 using a GraceResolv® 24 g Silica cartridge and eluting with 8-66% petroleum ether/EtOAc over 12 column volumes at a flow rate of 25 mL/min, giving the product (36 mg, 72%) as a yellow solid. The product was isolated as a 1.33:1 mixture of diastereomers.

\(\nu_{\text{max}}\) (CHCl\(_3\))/cm\(^{-1}\) 2994, 1057

Anal. Calcd for C\(_{15}\)H\(_{23}\)NOS: C 67.88%, H 8.73%, N 5.28%; Found: C 67.72%, H 8.72%, N 5.24%

\(^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta\) 7.34-7.20 (8.75H, m), 5.10-5.06 (0.75H, m), 5.03-4.99 (1H, t, \(J=8\) Hz), 3.85-3.81 (0.75H, dd, \(J=7, 2\) Hz), 3.70-3.65 (1H, qd, \(J=6, 1\) Hz), 3.21-3.15 (1H, t, \(J=11\) Hz), 3.12-3.07 (0.75H, t, \(J=10\) Hz), 2.61-2.54 (1H, m), 2.39-2.17 (1.75H, m), 1.96-1.77 (1.75H, m), 1.38-1.21 (0.75H, m), 1.09-0.96 (21H, m)

\(^{13}\text{C NMR (100 MHz, CDCl}_3\) \(\delta\) 145.6, 144.8, 128.6, 128.3, 126.6, 126.5, 64.45, 57.48, 57.38, 46.02, 44.70, 35.63, 31.12, 23.16, 23.07, 17.12, 16.32

HRMS calculated for [C\(_{15}\)H\(_{23}\)NNaOS]\(^+\): 288.1393, found 288.1385.
General procedure for the hydroboration/oxidation of sulfinylpyrrolidines

\([(S)R]-1-(R_3)-\text{tert-Butylsulfinyl})-5\text{-phenylpyrrolidin-3-yl}]\text{methanol (7)}

A solution of \((R)-1-(\text{R}_3)-\text{tert-Butylsulfinyl})-4\text{-methylene-2-phenylpyrrolidine (2a)}\) (50 mg, 0.190 mmol) in anhydrous THF (1.5 mL) was charged with 9-borabicyclo[3.3.1]nonane (0.5 M in THF) (1.5 mL, 0.759 mmol) slowly at 0 °C and stirred under an inert atmosphere of argon overnight. Water (0.5 mL), NaOH (8 M in water) (0.3 mL) and \(\text{H}_2\text{O}_2\) (30% in water) (1 mL) were then charged and the resulting suspension stirred overnight. The resulting mixture was subsequently diluted with water, extracted thrice with \(\text{EtOAc}\) and the combined organics dried over \(\text{MgSO}_4\) (s), filtered and concentrated \textit{in vacuo}. Chromatography was performed on a Biotage® SP4 using a GraceResolv® 24 g Silica cartridge and eluting with 8-66% petroleum ether/EtOAc over 12 column volumes at a flow rate of 25 mL/min, followed by elution with \(\text{CH}_2\text{Cl}_2/\text{MeOH (85:15)}\) and \(\text{Et}_3\text{N (3%)}\) giving the product (49 mg, 92%) as a yellow solid. The product was isolated as a 3:1 mixture of diastereomers; only data for the major diastereomer is shown.

\(\nu_{\text{max}}\) (CHCl\(_3\))/cm\(^{-1}\) 3613, 3011, 2933, 2452, 1602, 1474, 1242, 1053

\(^1\text{H} \text{NMR (400 MHz, CDCl}_3\) \(\delta 7.33-7.18 \text{ (5H, m)}, 5.08-4.96 \text{ (1H, m), } 3.85-3.59 \text{ (2H, m), } 3.49-3.39 \text{ (1H, m), } 3.12-3.05 \text{ (1H, m), } 2.52-2.41 \text{ (1H, m), } 2.01-1.36 \text{ (3H, m), } 1.01 \text{ (9H, s)\)\)\)

\(^{13}\text{C} \text{ NMR (100 MHz, CDCl}_3\) \(\delta 144.3, 128.6, 128.5, 126.7, 71.69, 64.05, 62.56, 45.81, 43.19, 36.31, 23.08\)\)

HRMS calculated for \([\text{C}_{15}\text{H}_{23}\text{NNaO}_2\text{S}]^+\): 304.1342, found 304.1335.
General procedure for the oxidative cleavage of sulfinylpyrrolidines

(R)-1-((tert-Butylsulfonyl)-5-phenylpyrrolidin-3-one (8)

A solution of (R)-1-((R,R)-tert-butylsulfinyl)-4-methylene-2-phenylpyrrolidine (2a) (200 mg, 0.759 mmol) in CCl₄ (4 mL), MeCN (4 mL) and water (6 mL) was charged with NaIO₄ (649 mg, 3.04 mmol) and RuCl₃·xH₂O (4 mg, 0.023 mmol) and was rapidly stirred overnight at room temperature. The mixture was then diluted with CH₂Cl₂ and water and the aqueous layer separated and extracted thrice with CH₂Cl₂. The organic extracts were then combined and dried over MgSO₄ (s), filtered and concentrated *in vacuo*. Chromatography was performed on a Biotage® SP4 using a Biotage® KP-Si 100 g Silica SNAP cartridge and eluting with 10-70% petroleum ether/EtOAc over 12 column volumes at a flow rate of 40 mL/min giving the product (143 mg, 67%) as a white solid.

m.p. = 105-106 °C

νₘₐₓ (CHCl₃)/cm⁻¹ 1764, 1320, 1125

[α]D⁰₃¹ = −40.17 (c 0.15 in CHCl₃)

¹H NMR (400 MHz, CDCl₃) δ 7.39-7.23 (5H, m), 5.75-5.72 (1H, dd, J=10, 2 Hz), 4.44-4.39 (1H, d, J=18 Hz), 3.78-3.73 (1H, d, J=18 Hz), 3.20-3.13 (1H, ABX, J=10 Hz), 2.61-2.57 (1H, dt, J=18, 1 Hz), 1.26 (9H, s)

¹³C NMR (100 MHz, CDCl₃) δ 211.1, 141.7, 129.1, 128.1, 126.2, 61.25, 60.46, 55.24, 46.13, 24.21

HRMS calculated for [C₁₄H₁₉NNaO₃S⁺]: 304.0978, found 304.0971.
Supplemental Material

General procedure for the cross-metathesis of sulfinylpyrrolidines

*Methyl 2-\((R)-1-((R_3)(R_5)-\text{tert-butylsulfinyl})-5\)-phenylpyrrolidin-3-ylidene)acetate*

A solution of \((R)-1-((R_3)(R_5)-\text{tert-butylsulfinyl})-4\)-methylene-2-phenylpyrrolidine (30 mg, 0.114 mmol) and methyl acrylate (62 µL, 0.683 mmol) in CH₂Cl₂ (3 mL) was charged with Hoveyda-Grubbs second generation catalyst (4 mg, 0.006 mmol) and irradiated with microwaves at 110 °C for 2h. The catalyst was removed by filtration through a pad of celite and the solvent removed *in vacuo*. Chromatography was performed on a Biotage® SP4 using a GraceResolv® 12 g Silica cartridge and eluting with 6-50% petroleum ether/EtOAc over 12 column volumes at a flow rate of 15 mL/min, giving the product (24 mg, 65%) as an orange oil. The product was isolated as a 1.5:1 mixture of diastereomers.

ν<sub>max</sub> (CHCl<sub>3</sub>)/cm<sup>-1</sup> 3003, 1715, 1071

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36-7.23 (15H, m), 5.88-5.85 (1H, m), 5.83-5.80 (0.67H, m), 5.34-2.27 (1.67H, m), 4.80-4.66 (1.33H, m), 4.46-4.28 (2H, m), 3.72 (2H, s), 3.68 (3H, s), 3.39-3.12 (2.67H, m), 2.70-2.64 (0.67H, br), 1.16-1.12 (15H, m)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 166.5, 161.6, 160.6, 142.4, 142.1, 128.7, 127.1, 126.4, 126.3, 112.5, 112.0, 67.48, 65.94, 59.07, 58.03, 56.19, 54.28, 54.15, 51.20, 45.02, 42.33, 22.88, 22.82

HRMS calculated for [C<sub>17</sub>H<sub>23</sub>NNaO<sub>3</sub>S]<sup>+</sup>: 344.1291, found 344.1291.
Methyl 2-\{(5R)-1-\{(R,R)-tert-butylsulfanyl\}-5-phenylpyrrolidin-3-yl\}acetate (9)

A solution of methyl 2-\{(5R)-1-\{(R,S)-tert-butylsulfanyl\}-5-phenylpyrrolidin-3-ylidene\}acetate (24 mg, 0.075 mmol) and PtO₂ (2 mg, 0.0075 mmol) in EtOAc (5 mL) was hydrogenated at a pressure of 10 atm overnight at room temperature. The catalyst was removed by filtration through a pad of celite and the solvent removed \textit{in vacuo}. Chromatography was performed on a Biotage® SP4 using a GraceResolv® 12 g Silica cartridge and eluting with 8-66% petroleum ether/EtOAc over 12 column volumes at a flow rate of 15 mL/min, giving the product (17 mg, 71%) as a yellow oil. The product was isolated as a 7:1 mixture of diastereomers. Only data for the major diastereomer is shown.

\[ \nu_{\text{max}} \text{(CHCl}_3)/\text{cm}^{-1} \] 3011, 1733, 1240

\(^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta \)} 7.37-7.30 (3H, m), 7.28-7.22 (2H, m), 5.08-5.02 (1H, t, \(J=8\) Hz), 3.88-3.82 (1H, m), 3.68 (3H, s), 3.34-3.26 (1H, m), 2.71-2.53 (2H, m), 2.44-2.29 (2H, m), 1.48-1.42 (1H, m), 1.03 (9H, s)

\(^{13}\text{C NMR (100 MHz, CDCl}_3\) \(\delta \)} 172.5, 144.8, 128.7, 126.8, 126.5, 57.53, 51.68, 43.51, 37.29, 36.95, 33.45, 28.05, 23.05

HRMS calculated for [C\(_{17}\)H\(_{25}\)N\(_3\)NaO\(_3\)S]: 346.1447, found 346.1438.
(R<sub>3</sub>,E)-2-Methyl-N-(thiophen-2-ylmethylene)propane-2-sulfinamide (1m)
(R,S)-2-Methyl-N-(naphthalen-2-ylmethylene)propane-2-sulfinamide (1n)
(R)-1-((R)-tert-Butylsulfinyl)-4-methylene-2-phenylpyrrolidine (2a)
Supplemental Material

(S)-1-((R)s)-tert-Butylsulfinyl)-4-methylene-2-phenylpyrrolidine

![Chemical Shift Graph](G_PRO.GP-PYRR-C02.001.esp)

![Chemical Shift Graph](G_PRO.GP-PYRR-C02.002.esp)
Supplemental Material

(R)-1-((R$_3$)-Mesitylsulfinyl)-4-methylene-2-phenylpyrrolidine (2b)

![NMR Spectra](image1)

![NMR Spectra](image2)
(R)-1-((R3)-tert-Butylsulfanyl)-2-(4-methoxyphenyl)-4-methyleneypyrrolidine (2c)
(R)-1-((R\textsubscript{3})-tert-Butylsulfinyl)-4-methylene-2-(4-nitrophenyl)pyrrolidine (2d)
2-((R)-1-((R2)-tert-Butylsulfinyl)-4-methyleneptyrrolidin-2-yl)phenol (2e)
(R)-1-([(R\textsubscript{3})-tert-Butylsulfinyl]-2-(2-chlorophenyl)-4-methyleneprrolidine (2f)
(S)-1-[(R₃)-tert-Butylsulfinyl]-2-(2-chlorophenyl)-4-methylenepyrrolidine
(R)-2-(2-Bromophenyl)-1-((R₃)-tert-butylsulfinyl)-4-methylenepyrrolidine (2g)
(S)-1-((R₃)-tert-Butylsulfinyl)-2-methyl-4-methyleneypyrrolidine (2h)
(S)-1-((R_5)-tert-Butylsulfinyl)-4-methylene-2-propylpyrrolidine (2i)
(R)-1-(((R₃)-tert-Butylsulfinyl)-2-cyclohexyl-4-methylene.pyrrolidine (2j)
(S)-1-((R_3)-tert-Butylsulfinyl)-2-cyclohexyl-4-methylenepyrrolidine
(R)-2-(tert-Butyl)-1-((R,S)-tert-butylsulfinyl)-4-methylenepyrrolidine (2k)
Supplemental Material

(R)-1-((R$_3$)-tert-Butylsulfinyl)-2-(furan-2-yl)-4-methylenepyrrolidine (2l)
(R)-1-((R₃)-tert-Butylsulfinyl)-4-methylene-2-(thiophen-2-yl)pyrrolidine (2m)
Supplemental Material

(S)-1-((R₃)-tert-Butylsulfinyl)-4-methylene-2-(thiophen-2-yl)pyrrolidine

Chemical Shift (ppm)

Normalized Intensity

Chemical Shift (ppm)
(R)-1-((R_s)-tert-Butylsulfinyl)-4-methylene-2-(naphthalen-2-yl)pyrrolidine (2n)
(R)\textsubscript{3}-1-\textit{(tert-Butylsulfinyl)}-2,2-dimethyl-4-methyleneypyrrolidine (4a)
(R)-1-((R₃)-tert-Butylsulfinyl)-2-methyl-4-methylene-2-phenylpyrrolidine (4b)

![Chemical structures and spectra](G_Pro.GP4-147-01.001.esp)

![Chemical structures and spectra](G_Pro.GP4-147-01.002.esp)
(R)-1'-((R)-tert-Butylsulfinyl)-4'-methylene-2,3-dihydrospiro[indene-1,2'-pyrrolidine] (4e)
(R)-4-Methylene-2-phenylpyrrolidine (5)
(2R)-1-((R)₃-tert-Butylsulfinyl)-4-methyl-2-phenylpyrrolidine (6)

Supplemental Material
((SR)-1-((R_5)-tert-Butylsulfinyl)-5-phenylpyrrolidin-3-yl)methanol (7)
(R)-1-(tert-Butylsulfonyl)-5-phenylpyrrolidin-3-one (8)
Methyl 2-\{(R)-1-\{(R,S)-tert-butylsulfinyl\}-5-phenylpyrrolidin-3-ylidene\}acetate

Supplemental Material
Methyl 2-\{(5R)-1-\{(R,S)-\text{tert-butylsulfinyl})-5\text{-phenylpyrrolidin-3-yl}\}acetate (9)