Alkynyl sulfoxides as $\alpha$-sulfinyl carbene equivalents: Gold-catalysed oxidative cyclopropanation

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Contents
General Experimental ........................................................................................................................................ 2
Experimental Procedures and Spectroscopic Data ...................................................................................... 3
Preparation of Starting Materials .................................................................................................................. 3
Preparation of Alkynyl Sulfoxides .............................................................................................................. 5
Catalysis Reactions .................................................................................................................................... 21
Crystal Structure Determination of 10g: ................................................................................................... 31
References .................................................................................................................................................. 32
$^1$H NMR and $^{13}$C NMR Spectra of New Compounds .............................................................................. 33
Alkynyl Thioethers .................................................................................................................................... 35
Alkynyl Sulfoxides .................................................................................................................................... 56
Products of Catalysis ................................................................................................................................ 78
Reaction of an Alkynyl Sulfone .................................................................................................................. 106
General Experimental

Commercially available chemicals/reagents were purchased from major suppliers (Sigma-Aldrich, Fisher, Acros, Alfa Aesar, Strem, Fluorochem or VWR) and used without further purification unless otherwise stated. All catalysis reactions were carried out under argon in heat gun-dried glassware unless otherwise stated. Solvents were purified using a Pure Solv-MD solvent purification system except for CHCl₃ and 1,4-dioxane which were dried over activated 3 Å molecular sieves and were transferred under argon. For reactions above room temperature pre-heated Asynt DrySyn heating blocks on stirrer hotplates were employed and the temperature was controlled using an external probe. The following cooling baths were used: 0 °C (ice/water), -10 °C (NaCl/ice) and -78 °C (dry ice/acetone). Reactions were monitored by thin layer chromatography using Merck silica gel 60 F254 (aluminium support) TLC plates which were developed using standard visualizing agents: UV fluorescence (254 nm), potassium permanganate/Δ or vanillin/Δ. Flash column chromatography: Flash column chromatography was performed using Fluorochem silica gel 60 (0.043-0.063 mm) as the stationary phase. Infrared spectra were recorded neat on a Perkin-Elmer Spectrum 100 FTIR spectrometer. Wavelengths (ν) of selected absorbencies are reported in cm⁻¹. Mass spectra were obtained using Waters GCT Premier (El), Waters LCT (ES) or Waters Synapt (ES) spectrometers. High resolution spectra used a lock-mass to adjust the calibrated mass scale. MS data are reported as m/z (relative intensity). ¹H NMR and ¹³C NMR experiments were recorded using Bruker AVIII400 (¹H = 400 MHz, ¹³C = 101 MHz) or AVIII300 (¹H = 300 MHz, ¹³C = 75 MHz) spectrometers at 300 K. ¹³C NMR spectra were recorded using either the UDEFT or the PENDANT pulse sequences from the Bruker standard pulse program library. 2D HSQC and HMBC NMR spectra were recorded using the Bruker standard pulse program library. Spectra were processed using MestReNova 10.0. Chemical shifts (δ) are given in ppm relative to TMS and are calibrated using residual solvent peaks (CDCl₃: δC ≡ 77.16 ppm; residual CHCl₃ in CDCl₃: δH ≡ 7.26 ppm; DMSO-d₆: δC ≡ 39.52 ppm; residual DMSO in DMSO-d₆: δH ≡ 2.50 ppm).¹ Spectral data for ¹H NMR spectroscopy is reported as follows: Chemical shift (multiplicity, coupling constant, number of protons); and for ¹³C NMR spectroscopy: Chemical shift. The following abbreviations were used for multiplicity in ¹H NMR: s (singlet), d (doublet), t (triplet), q (quadruplet), quin (quintuplet), br. (broad), m (multiplet), app. (apparent). Coupling constants (J) are quoted in Hz to one decimal place. Melting points were measured in open capillaries using Stuart Scientific melting point apparatus and are uncorrected.

mCPBA was purified by washing with a pH 7 phosphate buffer unless otherwise stated: A buffer solution was prepared from 0.1 M NaOH (154 mL) and 0.2 M KH₂PO₄ (94 mL) and made up to 376 mL with distilled water. mCPBA (77% w/w, 10 g) was dissolved in diethyl ether (100 mL) and washed four times with the buffer solution. The organic extract was dried over MgSO₄ and carefully evaporated (CAUTION - potential explosive) under reduced pressure to yield pure mCPBA (7.3 g).²
Experimental Procedures and Spectroscopic Data

Preparation of Starting Materials

Sodium benzenesulfonothioate
Prepared in 83% yield according to a literature procedure. Data is in agreement with literature values.³

1,1-Dibromo-8-methylNona-1,7-diene
Prepared in 74% yield according to a literature procedure. Data matches that reported in the literature.⁴

(2,2-Dibromovinyl)cyclohexane
Prepared in 47% yield according to a literature procedure. Data matches that reported in the literature.⁵

1-Ethynyl-4-methylbenzene
Prepared in 43% yield according to a literature procedure. Data matches that reported in the literature.⁶

1-Ethynyl-4-methoxybenzene
Prepared in 90% yield according to a literature procedure. Data matches that reported in the literature.⁷

1-Ethynyl-2-isopropylbenzene
Prepared in 91% yield according to a literature procedure. Data is in agreement with literature values.⁸

2-(2,2-Dibromovinyl)naphthalene
Prepared in 84% yield according to a literature procedure. Data matches that reported in the literature.⁹

2-(2,2-Dibromovinyl)furan
Prepared in 64% yield according to a literature procedure. Data is in agreement with literature values.¹⁰

3-Bromo-2-ethynlthiophene
Prepared in 24% yield over three steps from 3-bromothiophene according to a literature procedure. Data is in agreement with literature values.¹¹

3-(Prop-2-yn-1-yloxy)prop-1-ene
Prepared in 36% yield according to the literature procedure. Data matches that reported in the literature.¹²

(E)-(3-(Prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene
Prepared in 49% yield according to a literature procedure. Data matches that reported in the literature.¹³
\[ N-(4\text{-Ethynylphenyl})\text{acetamide} \]
Prepared in 3 steps in a 44% yield according to a literature procedure.\textsuperscript{15b} Data matches that reported in the literature.

\[ 1-(2,2\text{-Dibromovinyl})\text{-}4\text{-}(\text{trifluoromethyl})\text{benzene} \]
Prepared in 74% yield according to a literature procedure.\textsuperscript{4} Data matches that reported in the literature.

\[ 1-(2,2\text{-Dibromovinyl})\text{-}4\text{-fluorobenzene} \]
Prepared in 79% yield according to a literature procedure.\textsuperscript{4} Data matches that reported in the literature.

\[ 3,5\text{-Dichloropyridine 1-oxide} \]
Prepared in 84% yield according to a literature procedure.\textsuperscript{2} Data is in agreement with literature values.\textsuperscript{16}

\[ \text{Chloro}[2\text{-dicyclohexyl}(2',6'\text{-dimethoxybiphenyl})\text{phosphine}]\text{ gold(I)} \]
Prepared in 80% yield according to a literature procedure.\textsuperscript{17} Data is in agreement with literature values.\textsuperscript{17}

\[ 2\text{-Dicyclohexyl}(2',6'\text{-dimethoxybiphenyl})\text{phosphine gold(I)} \text{bis(trifluoromethanesulfonyl)imide} \]
Prepared in 85% yield according to a literature procedure.\textsuperscript{18} Data is in agreement with literature values.\textsuperscript{18}

\[ S\text{-Methyl benzenesulfonothioate} \]
Prepared in 85% yield according to a literature procedure.\textsuperscript{19} Data is in agreement with literature values.\textsuperscript{19}

\[ (E)-(4\text{-Bromo-but-1-enyl})\text{benzene} ((E)-(4\text{-Chloro-but-1-enyl})\text{benzene (3:1 mixture)} \]
Prepared in 39% yield according to a literature procedure.\textsuperscript{20} Data is in agreement with literature values.\textsuperscript{20}

\[ \text{Methyl benzenesulfininate} \]
Prepared in 83% yield according to a literature procedure.\textsuperscript{21} Data is in agreement with literature values.\textsuperscript{21}

\[ S\text{-}(\text{But-3-en-1-yl})\text{benzenesulfonothioate (S1)} \]
\[ S1 \text{ was prepared following a literature procedure.} \textsuperscript{24} \]
Sodium benzenesulfonothioate (7.60 g, 38.7 mmol, 1.0 eq) was added to a RBF and the flask was evacuated and refilled with argon (× 3). Anhydrous DMF (60 mL) was added and the mixture was stirred at rt. 4-bromo-1-butene (4.0 mL, 40 mmol, 1.03 eq.) was added over 5 minutes by syringe and the mixture was stirred for 4 days. The mixture was poured into ice/water (200 mL) and was extracted Et\textsubscript{2}O (6 × 50 mL). The combined organic phases were washed with NaHCO\textsubscript{3} (sat) solution (50 mL), brine (3 × 50 mL), dried over Na\textsubscript{2}SO\textsubscript{4} filtered, concentrated under reduced pressure and purified by column chromatography (9:1 hexane:EtoAc) to afford 1 (8.90 g, 86%) as a pale orange oil; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): δ = 8.01 – 7.87 (m, 2H), 7.75 – 7.49 (m, 3H), 5.67 (ddt, J = 17.0, 10.4, 6.7 Hz,
The flask was cooled to 0 °C, the organics were allowed to warm to rt overnight. The reaction was quenched with NH₄Cl (sat) solution (15 mL), brine (3 × 15 mL), dried over Na₂SO₄, filtered, concentrated under reduced pressure and purified by column chromatography (95:5 hexane:EtOAc to 9:1 hexane:EtOAc) to afford the sulfonothioate (930 mg, 76%) as a viscous orange oil; ¹H NMR (300 MHz, CDCl₃): δ = 8.01 – 7.91 (m, 2H), 7.71 – 7.51 (m, 3H), 7.33 – 7.28 (m, 4H), 7.25 – 7.19 (m, 1H), 6.34 (dt, J = 15.8, 1.3 Hz, 1H), 6.04 (dt, J = 15.8, 7.2 Hz, 1H), 3.15 (t, J = 7.2 Hz, 2H), 2.53 (app qd, J = 7.2, 1.3 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃): δ = 145.0 (C), 136.9 (C), 133.8 (CH), 132.9 (CH), 129.5 (2CH), 128.7 (2CH), 127.7 (2CH), 127.1 (2CH), 126.3 (2CH), 35.8 (CH₂), 32.3 (CH₃); IR (neat): v = 3060, 3026, 2933, 1597, 1581, 1446, 1307, 1320, 1138, 1076, 966, 744, 714, 684, 594; HR-MS (ES-TOF): m/z: calcd for C₁₆H₁₂O₂NaS₂: 327.0489, found 327.0484 [M + Na]⁺.

(E)-S-(4-Phenylbut-3-en-1-yl) benzenesulfonothioate

(E)-S-(4-Phenylbut-3-en-1-yl) benzenesulfonothioate was prepared following a literature procedure.²⁴ Sodium benzenesulfonothioate (981 mg, 5.0 mmol, 1.2 eq.) was added to a RBF and the flask was evacuated and refilled with argon (× 3). Anhydrous DMF (7 mL) was added and the mixture was stirred at rt for 10 minutes. (E)-(4-Bromo-but-1-enyl)benzene (1.00 g, 4.0 mmol from a 3:1 mixture with its chloro-analogue, 1.0 eq.) was added over 5 minutes by syringe and the mixture was stirred at rt for 2.5 days. The mixture was poured into ice/water (20 mL) and was extracted with Et₂O (6 × 15 mL). The combined organics were washed with NaHCO₃ (sat) solution (15 mL), brine (3 × 15 mL), dried over Na₂SO₄, filtered, concentrated under reduced pressure and purified by column chromatography (95:5 hexane:EtOAc to 9:1 hexane:EtOAc) to afford the sulfonothioate (930 mg, 76%) as a viscous orange oil; ¹H NMR (300 MHz, CDCl₃): δ = 8.01 – 7.91 (m, 2H), 7.71 – 7.51 (m, 3H), 7.33 – 7.28 (m, 4H), 7.25 – 7.19 (m, 1H), 6.34 (dt, J = 15.8, 1.3 Hz, 1H), 6.04 (dt, J = 15.8, 7.2 Hz, 1H), 3.15 (t, J = 7.2 Hz, 2H), 2.53 (app qd, J = 7.2, 1.3 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃): δ = 145.0 (C), 136.9 (C), 133.8 (CH), 132.9 (CH), 129.5 (2CH), 128.7 (2CH), 127.7 (2CH), 127.1 (2CH), 126.3 (2CH), 35.8 (CH₂), 32.3 (CH₃); IR (neat): v = 3060, 3026, 2933, 1597, 1581, 1446, 1307, 1320, 1138, 1076, 966, 744, 714, 684, 594; HR-MS (ES-TOF): m/z: calcd for C₁₆H₁₂O₂NaS₂: 327.0489, found 327.0484 [M + Na]⁺.

Preparation of Alkynyl Sulfoxides

Alkynyl Thioethers

General Procedure 1: Preparation of alkynyl thioethers (GP1)
Dibromoolefin (1.1 eq.) and anhydrous THF (0.2 M) were added to a flame dried two-neck RBF under argon. The flask was cooled to -78 °C. n-ButLi (2.5 M in hexane) (2.3 eq.) was added dropwise and on complete addition the mixture was stirred at 78 °C for an hour before S-(but-3-en-1-yl) benzenesulfonothioate (S1) (1.0 eq.) was added dropwise. The reaction was allowed to warm to rt overnight. The reaction was quenched with NH₄Cl (sat) (0.2 M with respect to the alkyne) and the mixture was extracted Et₂O (3 × reaction volume), the organics were washed with brine, dried over Na₂SO₄, filtered, concentrated under reduced pressure and the residue was purified by column chromatography.

General Procedure 2: Preparation of alkynyl thioethers (GP2)
Alkyne (1.1 eq.) and anhydrous THF (0.2 M) were added to a flame dried two-neck RBF under argon. The flask was cooled to -78 °C. LiHMDS (1 M in ethylbenzene) (1.1 eq.) was added dropwise and on complete addition the mixture was stirred at -78 °C for an hour before S-(but-3-en-1-yl) benzenesulfonothioate (S1) (1.0 eq.) was added dropwise. The reaction was allowed to warm to rt overnight. The reaction was quenched with NH₄Cl (sat) (0.2 M with respect to alkyne added) and the mixture was extracted Et₂O (3 × reaction volume), the organics were
washed with brine, dried over Na$_2$SO$_4$, filtered, concentrated under reduced pressure and the residue was purified by column chromatography.

**But-3-en-1-yl(hex-1-yn-1-yl)sulfane (S2a)**

S2a was prepared according to a literature procedure.$^{25}$ 1-Hexyne (822 mg, 10.0 mmol) and THF (50 mL) were added to a 50 mL three-neck RBF. The mixture was cooled to -78 °C and n-BuLi (6.7 mL, 11.0 mmol, 1.1 eq.) was added dropwise. After complete addition the mixture was stirred for 1 h at -78 °C before addition of sulfur (321 mg, 10.0 mmol, 1.0 eq.) the resulting red solution was stirred for a further 1 h at -78 °C before warming to 0 °C slowly. 4-bromo-1-butene (1.35 g, 10.0 mmol, 1.0 eq.) was added and the mixture was stirred for 2 h at 0 °C and left to warm to rt for 13 h. The mixture was quenched with NH$_4$Cl (50 mL of a saturated solution), extracted with Et$_2$O (3 x 30 mL), washed with brine (50 mL), dried over Na$_2$SO$_4$, concentrated under reduced pressure and purified by column chromatography (hexane) to afford S2a (1.03 g, 61%) as a pale yellow oil; $^1$H NMR (300 MHz CDCl$_3$): $\delta$ = 5.84 (ddt, $J = 17.3, 10.4, 6.6$ Hz, 1H), 5.12 (dd, $J = 17.3, 1.3$ Hz, 1H), 5.07 (dd, $J = 10.4, 1.3$ Hz, 1H), 2.71 (t, $J = 7.4$ Hz, 2H), 2.48 (td, $J = 7.4, 6.6$ Hz, 2H) 2.30 (t, $J = 6.8, 2H$), 1.55 – 1.34 (m, 4H), 0.91 (t, $J = 7.1, 3H$); $^{13}$C NMR (101 MHz CDCl$_3$): $\delta$ = 136.0 (CH), 116.6 (CH$_2$), 94.8 (C), 67.8 (C), 34.6 (CH$_3$), 33.4 (CH$_2$), 30.9 (CH$_3$), 22.0 (CH$_3$), 19.9 (CH$_3$), 13.6 (CH$_3$); IR (neat): $\nu$ = 3079, 2960, 2929, 2167, 1641, 1571, 1442, 1417, 752, 689. HR-MS (ES-TOF): m/z calcd. for C$_{12}$H$_{16}$S 168.0973, found 168.0979 [M + H]$^+$.  

**But-3-en-1-yl(4-phenylbut-1-yn-1-yl)sulfane (S2b)**

S2b was prepared according to a literature procedure.$^{25}$ 4-Phenyl-1-butene (391 mg, 3.0 mmol, 1.0 eq.) and THF (15 mL) were added to a 50 mL three-neck RBF. The mixture was cooled to -78 °C and n-BuLi (2.0 mL, 3.3 mmol, 1.1 eq.) was added dropwise. After complete addition the mixture was stirred for 1 h at -78 °C before addition of sulfur (96.3 mg, 3.0 mmol, 1.0 eq.) the resulting red solution was stirred for a further 1 h at -78 °C before warming to 0 °C slowly. 4-bromo-1-butene (405 mg, 0.30 mL, 3.0 mmol, 1.0 eq.) was added and the mixture was stirred for 2 h at 0 °C and left to warm to rt for 2 h. The mixture was quenched with NH$_4$Cl (20 mL of a saturated solution), extracted with Et$_2$O (3 x 10 mL), washed with brine (20 mL), dried over Na$_2$SO$_4$, concentrated under reduced pressure and purified by column chromatography (hexane) to afford S2b (214 mg, 33%) as a pale yellow oil; $^1$H NMR (300 MHz CDCl$_3$): $\delta$ = 7.36 – 7.21 (m, 5H), 5.84 (ddt, $J = 17.1, 10.2, 6.6$ Hz, 1H), 5.17-5.05 (m, 2H), 2.87 (t, $J = 7.5$ Hz, 2H), 2.71 (t, $J = 7.4$ Hz, 2H), 2.64 (t, $J = 7.4$ Hz, 2H), 2.44 (td, $J = 7.5, 6.6$ Hz, 2H); $^{13}$C NMR (101 MHz CDCl$_3$): $\delta$ = 140.6 (C), 135.9 (CH), 128.5 (2CH), 128.4 (2CH), 126.3 (CH), 116.6 (CH$_2$), 93.8 (C), 69.0 (C), 35.2 (CH$_3$), 34.5 (CH$_2$), 33.4 (CH$_2$), 22.3 (CH$_3$); IR (neat): $\nu$ = 3063, 3027, 2923, 1640, 1537, 1453, 1337, 1276, 1030, 993, 915, 747, 697; HR-MS (ES-TOF): m/z calcd. for C$_{14}$H$_{15}$S 217.1048, found 217.1051 [M + H]$^+$.  

(R)-But-3-en-1-yl(4,8-dimethylnon-7-yn-1-yl)sulfane (S2c)

S2c was prepared according to GP2 using 1,1-dibromo-8-methylnona-1,7-diene (828 mg, 2.67 mmol), n-BuLi (2.4 M in hexanes) (2.2 mL, 5.5 mmol), S1 (547 mg, 2.40 mmol) and THF (20 mL). The reaction time was 16 hours. Aqueous workup and purification by column chromatography (hexane) provided S2c (346 mg, 62%) as a colourless oil; $[\alpha]_D^{21}$ 11.60 (c 0.010 in CHCl$_3$); $^1$H NMR (300 MHz, CDCl$_3$):
δ = 5.84 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.17 – 5.03 (m, 3H), 2.76 – 2.68 (m, 2H), 2.53 – 2.43 (m, 2H), 2.24 (qd, J = 16.8, 6.2 Hz, 2H), 1.98 (dd, J = 15.1, 7.5 Hz, 2H), 1.75 – 1.58 (m, 7H), 1.52 – 1.37 (m, 1H), 1.32 – 1.16 (m, 1H), 0.98 (d, J = 6.7 Hz, 3H); 13C NMR (101 MHz, CDCl3): δ = 136.1 (CH), 131.6 (C), 124.6 (CH), 116.7 (CH2), 93.7 (C), 68.8 (C), 36.2 (CH2), 34.8 (CH2), 33.6 (CH2), 32.5 (CH), 27.5 (CH3), 25.7 (CH3), 19.6 (CH3), 17.8 (CH3); IR (neat): v = 2964, 2914, 1641, 1445, 1377, 1277, 1222, 993, 916, 825; HR-MS (El-TOF): m/z: calcd for C15H32S: 236.1599, found 236.1604 [M + H]+.

But-3-en-1-yl(cyclohexylethynyl)sulfane (S2d)

S2d was prepared according to GP1 using (2,3-dibromovinyl)cyclohexane (630 mg, 2.35 mmol), n-BuLi (2.5 M in hexanes) (2.0 mL, 4.9 mmol), S1 (448 mg, 2.14 mmol) and THF (10 mL).

The reaction time was 17 hours. Aqueous work-up and purification by column chromatography (hexane) provided S2d (260 mg, 63%) as a colourless oil; 1H NMR (300 MHz, CDCl3): δ = 5.85 (ddt, J = 17.0, 10.2, 6.6 Hz, 1H), 5.12 (dd, J = 17.0, 1.6 Hz, 1H), 5.07 (dd, J = 10.2, 1.6 Hz, 1H), 2.71 (t, J = 7.2 Hz, 2H), 2.55 – 2.41 (m, 3H), 1.73 (ddt, J = 14.7, 12.0, 6.0 Hz, 4H), 1.55 – 1.37 (m, 3H), 1.37 – 1.20 (m, 3H); 13C NMR (101 MHz, CDCl3): δ = 136.1 (CH), 116.7 (CH2), 99.0 (C), 67.9 (C), 34.8 (CH), 33.5 (2CH2), 32.8 (CH2), 30.5 (CH), 26.0 (2CH2), 25.0 (CH); IR (neat): v = 2928, 2853, 1641, 1496, 1447, 993, 910, 730; HR-MS (ES-TOF): m/z: calcd for C12H18S: 194.1129, found 194.1134 [M + H]+.

But-3-en-1-yl(3,3-dimethylbut-1-yn-1-yl)sulfane (S2e)

S2e was prepared according to GP3 using 3,3-dimethyl-1-butylene (400 µL, 3.30 mmol), LiHMDS (1 M, 3.30 mL, 3.30 mmol), S1 (678 mg, 3.00 mmol) and THF (10 mL). The reaction time was 20 hours. Aqueous workup and purification by column chromatography (hexane) provided S2e (336 mg, 67%) as a colourless oil; 1H NMR (300 MHz CDCl3): δ = 5.85 (ddt, J = 17.2, 10.2, 6.6, 1H), 5.12 (dd, J = 17.2, 1.7, 1H), 5.07 (dd, J = 10.2, 1.7, 1H), 2.71 (t, J = 7.2, 2H), 2.48 (td, J = 7.2, 6.6, 2H), 1.23 (s, 9H); 13C NMR (101 MHz CDCl3): δ = 136.2 (CH), 116.7 (CH2), 103.0 (C), 66.7 (C), 34.8 (CH2), 33.5 (CH2), 31.2 (3CH3), 29.0 (C); IR (neat): v = 2963, 2865, 1706, 1640, 1467, 1393, 1362, 1218, 991, 914, 744. HR-MS (ES-TOF): m/z: calcd. for C16H16S 244.0957, found 244.0971 [M + H]+.

But-3-en-1-yl(cyclopropylethynyl)sulfane (S2f)

S2f was prepared according to a literature procedure. Cyclopropylacetylene (198.3 mg, 3.00 mmol, 1.0 eq.) and THF (15 mL) were added to a 50 mL three-neck RBF. The mixture was cooled to -78 °C and n-BuLi (2.0 mL, 3.3 mmol, 1.1 eq.) was added dropwise. After complete addition the mixture was stirred for 1 h at -78 °C before addition of sulfur (66.3 mg, 3.0 mmol, 1.0 eq.) the resulting red solution was stirred for a further 1 h at -78 °C before warming to 0 °C slowly. 4-bromo-1-butene (400 µL, 0.3 mL, 3.0 mmol, 1.0 eq.) was added and the mixture was stirred for 2 h at 0 °C and left to warm to rt for 15 h. The mixture was quenched with NH4Cl (20 mL of a saturated solution), extracted with Et2O (3 × 10 mL), washed with brine (20 mL), dried over Na2SO4, concentrated under reduced pressure and purified by column chromatography (hexane) to afford S2f (139 mg, 30%) as a pale yellow oil; 1H NMR (300 MHz CDCl3): δ = 5.86 (ddt, J = 17.2, 10.3, 6.6 Hz, 1H), 5.12 (dd, J = 17.2, 1.7 Hz, 1H), 5.06 (dd, J = 10.3, 1.7 Hz, 1H), 2.72 (t, J = 7.4 Hz, 2H), 2.48 (td, J = 7.4, 6.6 Hz, 2H) 1.34 (tt, J = 7.5, 6.0 Hz, 1H), 0.84-0.78 (m, 13H); δ = 5.86 (ddt, J = 17.2, 10.3, 6.6 Hz, 1H), 5.12 (dd, J = 17.2, 1.7 Hz, 1H), 5.06 (dd, J = 10.3, 1.7 Hz, 1H), 2.72 (t, J = 7.4 Hz, 2H), 2.48 (td, J = 7.4, 6.6 Hz, 2H) 1.34 (tt, J = 7.5, 6.0 Hz, 1H), 0.84-0.78 (m,
But-3-en-1-yl(phenylethynyl)sulfane (S2g)

S2g was prepared according to GP3 using phenylacetylene (563 mg, 5.5 mmol), LiHMDS (1 M, 5.5 mL, 5.5 mmol), 1 (1.14 g, 5.0 mmol) and THF (25 mL). The reaction time was 19 hours. Aqueous workup and purification by column chromatography (hexane) provided S2g (804 mg, 94%) as a colourless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.46 – 7.37 (m, 2H), 7.34 – 7.27 (m, 3H), 5.88 (ddt, \(J = 17.0, 10.2, 6.6\) Hz, 1H), 5.16 (dd, \(J = 17.0, 1.6\) Hz, 1H), 5.10 (dd, \(J = 10.2, 1.6\) Hz, 1H), 2.85 (t, \(J = 7.5\) Hz, 2H), 2.56 (dt, \(J = 7.5, 6.4\) Hz, 2H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta = 135.8 (CH), 131.7 (2CH), 128.5 (2CH), 128.3 (C), 117.1 (CH\(_2\)), 93.5 (C), 35.1 (CH\(_2\)), 33.7 (CH\(_2\)); IR (neat): \(\nu = 3079, 2979, 2921, 2166, 1641, 1506, 1434, 1417, 916, 813\); HR-MS (ES-TOF): \(m/z: \text{calcd for C}_{12}H_{15}S: 203.0894, \text{found 203.0893 [M + H]}^+\).

But-3-en-1-yl((4-methoxyphenyl)ethynyl)sulfane (S2i)

S2i was prepared according to a literature procedure.\(^{25}\) 1-Ethynyl-4-methoxybenzene (170 mg, 1.29 mmol, 1.0 eq.) and THF (7 mL) were added to a 50 mL three-neck RBF. The mixture was cooled to -78 °C and n-BuLi (2.5 M in hexanes) (0.72 mL, 1.8 mmol, 1.0 eq.) was added dropwise. On complete addition the mixture was stirred for 1 hour at -78 °C before addition of sulfur (52.6 mg, 1.64 mmol, 1.0 eq.). The resulting red solution was stirred for a further hour at -78 °C before warming to 0 °C over 1 hour. 4 Bromo-1-butene (131 µL, 1.29 mmol, 1.0 eq.) was added and the mixture was stirred for 2 hours at 0 °C and left to warm to rt for 16 hours. The mixture was quenched with NH\(_4\)Cl (10 mL of a saturated solution), extracted with Et\(_2\)O (3 x 10 mL), washed with brine (10 mL), dried over Na\(_2\)SO\(_4\), concentrated under reduced pressure and purified by column chromatography (hexane) to afford S2i (222 mg, 67%) as a colourless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.32 (d, \(J = 8.0\) Hz, 2H), 7.11 (d, \(J = 8.0\) Hz, 2H), 5.88 (ddt, \(J = 17.0, 10.2, 6.4\) Hz, 1H), 5.15 (dd, \(J = 17.0, 1.6\) Hz, 1H), 5.20 – 5.07 (dd, 10.2, 1.6 Hz, 2H), 2.85 (t, \(J = 7.5\) Hz, 2H), 2.56 (dt, \(J = 7.5, 6.4\) Hz, 2H), 2.34 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta = 138.4 (C), 135.8 (CH), 131.7 (2CH), 129.2 (2CH), 120.5 (C), 116.9 (CH\(_3\)), 93.5 (C), 78.2 (C), 35.1 (CH\(_3\)), 33.6 (CH\(_2\)), 21.6 (CH\(_3\)); IR (neat): \(\nu = 3079, 3028, 2979, 2921, 2166, 1641, 1506, 1434, 1417, 916, 813\); HR-MS (ES-TOF): \(m/z: \text{calcd for C}_{13}H_{15}S: 203.0894, \text{found 203.0893 [M + H]}^+\).
16 h. The mixture was quenched with NH₄Cl (10 mL of a saturated solution), extracted with 
Et₂O (3 × 10 mL), washed with brine (10 mL), dried over Na₂SO₄, concentrated under reduced 
pressure and purified by column chromatography (hexane) to afford 2I (222 mg, 67%) as a 
colourless oil; ¹H NMR (300 MHz, CDCl₃): δ = 7.41 – 7.35 (m, 2H), 6.85 – 6.81 (m, 2H), 5.87 (ddt, 
J = 17.0, 10.2, 6.6 Hz, 1H), 5.15 (dd, J = 17.0, 1.6 Hz, 1H), 5.10 (dd, J = 10.2, 1.6 Hz, 1H), 3.81 (s, 
3H), 2.83 (t, J = 7.4 Hz, 2H), 2.55 (dt, J = 7.4, 6.6 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃): δ = 159.8 
(C), 135.9 (CH), 133.5 (2CH), 116.9 (CH₂), 115.7 (C), 114.1 (2CH), 93.2 (C), 55.4 (CH₃), 35.1 (CH₂), 
33.6 (CH₃); IR (neat): ν = 2933, 2837, 1604, 1505, 1289, 1245, 1171, 1030, 917, 829, 810, 777; 

Methyl-4-(((but-3-en-1-ythio)ethynyl)benzoate (S2I)

S2I was prepared according to GP2 using methyl 4-ethynylbenzoate (333 mg, 2.08 mmol), LiHMDS 1 M (2.08 mL, 
2.08 mmol), S1 (432 mg, 1.89 mmol) and THF (10 mL). The reaction time was 16 hours. Aqueous work-up and purification 
by column chromatography (hexane) provided S2I (428 mg, 92%) as a colourless oil; ¹H NMR (300 MHz, CDCl₃): δ = 7.96 (d, J = 8.2 
Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 5.87 (ddt, J = 17.0, 10.2, 6.6 Hz, 1H), 5.16 (dd, J = 17.0, 1.6 Hz, 1H), 5.11 (d, J = 10.2, 1.6 
Hz, 1H), 3.91 (s, 3H), 2.88 (t, J = 7.3 Hz, 2H), 2.63 – 2.51 (m, 2H); ¹³C NMR (101 MHz, CDCl₃): δ = 166.7 (C), 135.5 (CH), 131.0 (2CH), 129.6 (2CH), 129.1 (C), 128.3 (C), 117.2 (CH₂), 93.1 (C), 83.5 
(C), 52.3 (CH₃), 35.1 (CH₃), 33.6 (CH₃); IR (neat): ν = 2951, 2162, 1717, 1603, 1434, 1270, 1174, 
1270, 1174, 1105, 1017, 855, 766; HR-MS (ES-TOF): m/z: calcd for C₁₄H₁₄O₃S: 247.0793, found 
247.0789 [M + H]⁺.

But-3-en-1-yl(3-methoxyphenyl)ethynyl)sulfane (S2n)

S2n was prepared according to GP2 using 3-methoxyphenylacetylene 
(265 mg, 2.00 mmol), LiHMDS 1 M (2.00 mL, 2.00 mmol), S1 (415 mg, 
1.82 mmol) and THF (10 mL). The reaction time was 16 hours. Aqueous workup and purification by column chromatography (hexane) 
provided S2n (346 mg, 91%) as a colourless oil; ¹H NMR (300 MHz, 
CDCl₃): δ = 7.21 (t, J = 8.1 Hz, 1H), 7.04 – 6.98 (m, 1H), 6.94 (dd, J = 2.6, 1.4 Hz, 1H), 6.85 (dd, J = 8.1, 2.6, 1.0 Hz, 1H), 5.88 (ddt, J = 17.1, 10.2, 6.6 Hz, 1H), 5.16 (dd, J = 17.1, 1.6 Hz, 1H), 5.10 
(dd, J = 10.2, 1.6 Hz, 1H), 3.80 (s, 3H), 2.86 (t, J = 7.5 Hz, 2H), 2.57 (dt, J = 7.5, 6.6 Hz, 2H); ¹³C NMR 
(101 MHz, CDCl₃): δ = 159.4 (C), 135.8 (CH), 129.5 (CH₂), 124.3 (C), 124.1 (CH), 117.0 (CH₂), 
116.3 (CH), 114.8 (CH), 93.4 (C), 79.2 (C), 55.4 (CH₃), 35.0 (CH₂), 33.6 (CH₂); IR (neat): ν = 3076, 

((4-Bromophenyl)ethynyl)(but-3-en-1-yl)sulfane (S2o)

S2o was prepared according to GP2 using 4-bromophenylacetylene 
(240 mg, 1.32 mmol), LiHMDS 1 M (1.32 mL, 1.32 mmol), S1 (275 mg, 1.21 mmol) and THF (7 mL). The reaction time was 16 hours. 
Aqueous work-up and purification by column chromatography (hexane) provided 2o (190 mg, 59%) as a colourless oil; ¹H NMR (300 MHz, CDCl₃): δ = 7.25 (d, 
J = 8.6 Hz, 2H) 7.08 (d, J = 8.6 Hz, 2H), 5.68 (ddt, J = 17.0, 10.2, 6.6 Hz, 1H), 4.97 (dd, J = 17.0, 
1.6 Hz, 1H), 4.92 (dd, J = 10.2, 1.6 Hz, 1H), 2.68 (t, J = 7.4 Hz, 2H), 2.39 (dt, J = 7.4, 6.6 Hz, 2H);
C NMR (101 MHz, CDCl₃): δ = 135.6 (CH), 132.9 (2CH), 131.7 (2CH), 122.5 (C), 122.3 (C), 117.1 (CH₂), 92.4 (C), 80.8 (C), 35.0 (CH₂), 33.6 (CH₂); IR (neat): ν = 3078, 2978, 2925, 2164, 1640, 1583, 1483, 1393, 1069, 1009, 819; HR-MS (ES-TOF): m/z: calcd for C₁₂H₁₂S⁷9Br: 266.9843, found 266.9837 [M + H]+.

((2-Bromophenyl)ethynyl)(but-3-en-1-yl)sulfane (S₂p)

S₂p was prepared according to GP2 using 2-bromophenylacetylene (195 mg, 1.08 mmol), LiHMDS 1 M (1.08 mL, 1.08 mmol), S₁ (223 mg, 0.98 mmol) and THF (5 mL). The reaction time was 16 hours. Aqueous work-up and purification by column chromatography (hexane) provided S₂p (183 mg, 70%) as a colourless oil; ¹H NMR (300 MHz, CDCl₃): δ = 7.56 (dd, J = 8.0, 1.1 Hz, 1H), 7.42 (dd, J = 7.7, 1.7 Hz, 1H), 7.24 (app dt, J = 7.7, 1.4 Hz, 1H), 7.17 – 7.08 (m, 1H), 5.88 (ddt, J = 17.0, 1.6 Hz, 1H), 5.18 (dd, J = 17.0, 1.6 Hz, 1H), 5.11 (dd, J = 10.2, 1.6 Hz, 1H), 2.90 (t, J = 7.4 Hz, 2H), 2.63 (dt, J = 7.4, 6.6 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃): δ = 135.7 (CH), 132.8 (CH), 132.5 (CH), 129.0 (CH), 126.9 (CH), 125.7 (C), 125.0 (C), 117.1 (CH₂), 92.2 (C), 84.9 (C), 35.2 (CH₂), 33.7 (CH₂); IR (neat): ν = 3075, 2978, 2926, 2170, 1640, 1585, 1465, 1432, 1025, 918, 750; HR-MS for the corresponding sulfoxide was obtained.

But-3-en-1-yl((2-isopropylphenyl)ethynyl)sulfane (S₂q)

S₂q was prepared according to GP2 using 1-ethyl-1-isopropylbenzene (300 mg, 2.08 mmol), LiHMDS (1 M, 2.08 mL, 2.08 mmol), S₁ (431 mg, 1.89 mmol) and THF (10 mL). The reaction time was 20 hours. Aqueous work-up and purification by column chromatography (hexane) provided S₂q (350 mg, 80%) as a colourless oil; ¹H NMR (300 MHz, CDCl₃): δ = 7.39 (dd, J = 4.6, 3.6 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.12 (ddd, J = 7.7, 1.6 Hz, 1H), 5.16 (dd, J = 17.0, 1.6 Hz, 1H), 5.11 (dd, J = 10.2, 1.6 Hz, 1H), 3.51 – 3.35 (m, 1H), 2.87 (t, J = 7.4 Hz, 2H), 2.58 (dt, J = 7.4, 6.6 Hz, 2H), 1.28 (s, 3H), 1.25 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 150.5 (C), 135.8 (CH), 132.3 (CH), 129.0 (CH), 126.9 (CH), 125.7 (C), 125.0 (C), 117.1 (CH₂), 92.2 (C), 84.9 (C), 35.2 (CH₂), 33.7 (CH₂); IR (neat): ν = 3048, 2961, 2927, 2868, 2163, 1641, 916, 754. The mass ion could not be identified in order to obtain HRMS. HRMS for the corresponding sulfoxide was obtained.

But-3-en-1-yl(naphthalen-2-ylethynyl)sulfane (S₂r)

S₂r was prepared according to GP1 using 2-(2,2-dibromovinyl)naphthalene (550 mg, 1.76 mmol), n-BuLi (1.5 mL, 3.7 mmol) and S₁ (365 mg, 1.60 mmol). The reaction time was 18 hours. Aqueous work-up and purification by column chromatography (hexane) provided S₂r (248 mg, 65%) as a colourless oil; ¹H NMR (300 MHz, CDCl₃): δ = 7.94 (s, 1H), 7.86 – 7.73 (m, 3H), 7.51-7.45 (m, 3H), 5.91 (ddt, J = 17.0, 10.2, 6.6 Hz, 1H), 5.19 (dd, J = 17.0, 1.6 Hz, 1H), 5.10 (dd, J = 10.2, 1.6 Hz, 1H), 2.91 (t, J = 7.5 Hz, 2H), 2.61 (dt, J = 7.5, 6.6 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃): δ = 135.7 (CH), 133.1 (C), 132.8 (C), 131.3 (CH), 128.4 (CH), 128.1 (CH), 127.9 (CH), 127.8 (CH), 126.7 (2CH), 120.9 (C), 117.0 (CH₂), 93.9 (C), 79.7 (C), 35.1 (CH₂), 33.7 (CH₂); IR (neat): ν = 3057, 2979, 2928, 2156, 1640, 1626, 1596, 1501, 1272, 918, 857, 816, 746; HR-MS (ES-TOF): m/z: calcd for C₁₆H₁₅S⁷9Br: 239.0894, found 239.0899 [M + H]+.
2-((But-3-en-1-ythio)ethynyl)furan (S2s)

S2s was prepared according to GP1 using 2-(2,2-dibromovinyl)furan (670 mg, 2.66 mmol), n-BuLi (2.4 M in hexanes) (2.3 mL, 5.6 mmol) and S1 (552 mg, 2.42 mmol). The reaction time was 18 hours. Aqueous workup and purification by column chromatography (pentane) provided S2s (191 mg, 44%) as a colourless oil; 1H NMR (300 MHz, CDCl3): δ = 7.39 (dd, J = 1.9, 0.7 Hz, 1H), 6.64 (dd, J = 3.4, 0.7 Hz, 1H), 6.39 (dd, J = 3.4, 1.9 Hz, 1H), 5.85 (ddt, J = 17.0, 10.2, 6.6 Hz, 1H), 5.15 (dd, J = 17.0, 1.6 Hz, 1H), 5.09 (dd, J = 10.2, 1.6 Hz, 1H), 2.84 (t, J = 7.5 Hz, 2H), 2.53 (dt, J = 7.5, 6.6 Hz, 2H); 13C NMR (101 MHz, CDCl3): δ = 144.1 (CH), 137.4 (C), 135.6 (CH), 117.1 (CH2), 117.1 (CH), 111.2 (CH), 85.3 (C), 83.4 (C), 35.3 (CH2), 33.5 (CH3); IR (neat): ν = 3079, 2979, 2925, 2154, 1640, 1565, 1461, 1015, 917, 745; HR-MS (ES-TOF): m/z: calcd for C10H10OS: 178.0452, found 178.0454 [M + H]+.

3-Bromo-2-((but-3-en-1-ythio)ethynyl)thiophene (S2t)

S2t was prepared according to GP2 using 3-bromo-2-ethynlthiophene (335 mg, 1.78 mmol), LiHMDS (1 M, 1.78 mL, 1.78 mmol), S1 (369 mg, 1.62 mmol) and THF (9 mL). The reaction time was 16 hours. Aqueous work-up and purification by column chromatography (hexane) provided S2t (238 mg, 55%) as a yellow oil; 1H NMR (300 MHz, CDCl3): δ = 7.19 (d, J = 5.4 Hz, 1H), 6.95 (d, J = 5.4 Hz, 1H), 5.87 (ddt, J = 17.0, 10.2, 6.6 Hz, 1H), 5.18 (dd, J = 17.1, 1.6 Hz, 1H), 5.11 (dd, J = 10.2, 1.6 Hz, 1H), 2.87 (t, J = 7.4 Hz, 2H), 2.60 (dt, J = 7.4, 6.6 Hz, 2H); 13C NMR (101 MHz, CDCl3): δ = 135.6 (CH), 130.1 (CH), 127.4 (CH), 121.3 (C), 117.2 (CH2), 117.1 (C), 88.4 (C), 84.5 (C), 35.4 (CH2), 33.5 (CH3); IR (neat): ν = 3105, 3081, 2978, 2925, 2153, 1640, 1499, 1416, 917, 862, 708; HR-MS (ES-TOF): m/z: calcd for C10H8S5Br: 271.9329, found 271.9335 [M + H]+.

(3-(Allyloxy)prop-1-yn-1-yl)(but-3-en-1-yl)sulfane (S2u)

A flame dried (50 mL) 3-neck RBF was charged with 3-(prop-2-yn-1-olxy)prop-1-ene (60% in Et2O (760 µl, 4.00 mmol) and THF (20 mL). The mixture was cooled to -78 °C and n-BuLi (2.4 M in hexane) (1.8 mL, 1.2 equiv, 4.4 mmol) was added dropwise. On complete addition the mixture was stirred for an hour at -78 °C before the dropwise addition of 1 (827 mg, 3.63 mmol). The reaction mixture was allowed to warm to rt over 16 hours. The mixture was quenched NH4Cl (20 mL), the organic layer was removed and the aqueous layer extracted with Et2O (3 x 10 mL). The combined organic portions were washed with brine (20 mL), dried over Na2SO4, filtered, concentrated under reduced pressure and purified by column chromatography (hexane) providing S2u (376 mg, 57%) as a pale yellow oil; 1H NMR (300 MHz, CDCl3): δ = 5.99 – 5.74 (m, 2H), 5.38 – 5.03 (m, 4H), 4.26 (s, 2H), 4.06 (dt, J = 5.8, 1.3 Hz, 2H), 2.81 – 2.72 (m, 2H), 2.55 – 2.43 (m, 2H); 13C NMR (101 MHz, CDCl3): δ = 135.7 (CH), 134.2 (CH), 118.0 (CH2), 117.0 (CH2), 90.7 (C), 90.7 (C), 70.5 (CH2), 58.4 (CH2), 34.7 (CH3), 33.5 (CH3); IR (neat): ν = 3080, 2980, 2847, 2179, 1641, 1420, 1279, 1124, 1074, 991, 917; HR-MS (AP-TOF): m/z: calcd for C10H15OS: 183.0844, found 183.0852 [M + H]+.

But-3-en-1-yl(3-(cinnamylloxy)prop-1-yn-1-yl)sulfane (S2v)

A flame dried (50 mL) 3-neck RBF was charged with (E)-(3-(prop-2-yn-1-olxy)prop-1-en-1-yl)benzene (692 mg, 1.1 equiv, 4.00 mmol) and THF (20 mL). The mixture was
cooled to -78 °C and n-BuLi (2.35 M in hexane) (1.9 mL, 1.2 equiv, 4.4 mmol) was added dropwise. On complete addition the mixture was stirred for an hour at -78 °C before the dropwise addition of S1 (820 mg, 1.0 equiv, 3.6 mmol). The reaction mixture was allowed to warm to rt over 16 hours. The mixture was quenched NH₄Cl (20 mL), the organic layer was removed and the aqueous layer extracted with Et₂O (3 × 10 mL). The combined organics were washed with brine (20 mL), dried over Na₂SO₄, filtered, concentrated under reduced pressure and purified by column chromatography (hexane) providing S2v (683 mg, 66%) as a pale yellow oil; ¹H NMR (300 MHz, CDCl₃): δ = 7.29 (m, 5H), 6.67 (d, J = 15.9 Hz, 1H), 6.32 (dt, J = 15.9, 6.2 Hz, 1H), 5.87 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.23 – 5.07 (m, 2H), 4.34 (s, 2H), 4.27 (d, J = 6.2 Hz, 2H), 2.80 (t, J = 7.4 Hz, 2H), 2.55 – 2.45 (m, 2H); ¹³C NMR (101 MHz, CDCl₃): δ = 136.7 (C), 135.7 (CH), 133.4 (CH), 128.7 (2CH), 127.9 (CH), 126.7 (2CH), 125.3 (CH), 117.0 (CH₂), 90.7 (C), 70.1 (C), 58.3 (CH₂), 34.7 (CH₂), 33.5 (CH₂); IR (neat): ν = 3027, 2845, 2179, 1640, 1495, 1448, 1350, 1073, 966, 916, 744, 692; HR-MS (ES-TOF): m/z: calcd for C₁₆H₁₉OS: 259.1157, found 259.1159 [M + H]⁺.

((2-Isopropylphenyl)ethynyl)(methyl)sulfane (S3)

S3 was prepared according to GP2 using 1-ethynyl-2-isopropylbenzene (144 mg, 1.00 mmol), LiHMDS (1 M, 1.00 mL, 1.00 mmol), S₃-methyl benzenesulfonothioate (167 mg, 0.91 mmol) and THF (5 mL). The reaction time was 16 hours. Aqueous workup and purification by column chromatography (hexane) provided S3 (82 mg, 50%) as a colourless oil; ¹H NMR (300 MHz, CDCl₃): δ = 7.30 – 7.25 (m, 1H), 7.15 (dd, J = 2.6, 1.1 Hz, 1H), 7.14 (d, J = 1.0 Hz, 1H), 7.00 (ddd, J = 7.7, 5.3, 3.4 Hz, 1H), 3.30 (dt, J = 13.8, 6.9 Hz, 1H), 2.38 (s, 3H), 1.15 (d, J = 6.9 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃): δ = 150.4 (C), 132.2 (CH), 128.4 (CH), 125.5 (CH), 124.9 (CH), 122.2 (C), 90.7 (C), 84.1 (C), 31.6 (CH), 23.1 (2CH₃), 19.6 (CH₃); IR (neat): ν = 3062, 2961, 2927, 2868, 2164, 1596, 1481, 1444, 1312, 1082, 976, 754; HR-MS (EI-TOF): m/z: calcd for C₁₂H₁₄S: 245.1000, found 245.1004 [M + H]⁺.

(E)-(Cyclopropylethynyl)(4-phenylbut-3-en-1-yl)sulfone (S5)

S5 was prepared according to GP2 using cyclopropylacetylene (168 µl, 2.00 mmol), LiHMDS (1 M, 2.00 mL, 2.00 mmol), S₂ (554 mg, 1.82 mmol) and THF (10 mL). The reaction time was 16 hours. Aqueous workup and purification by column chromatography (hexane) provided S5 (308 mg, 74%) as a pale yellow oil; ¹H NMR (300 MHz, CDCl₃): δ = 7.42 – 7.27 (m, 4H), 7.25 – 7.18 (m, 1H), 6.48 (d, J = 15.8 Hz, 1H), 6.25 (dt, J = 15.8, 6.8 Hz, 1H), 2.78 (dd, J = 10.7, 4.1 Hz, 2H), 2.69 – 2.58 (m, 2H), 1.37 (tt, J = 8.3, 5.0 Hz, 1H), 0.85 – 0.70 (m, 4H); ¹³C NMR (101 MHz, CDCl₃): δ = 137.4 (C), 131.9 (CH), 128.7 (2CH₂), 127.7 (CH), 127.4 (CH), 126.2 (2CH), 98.8 (C), 64.0 (C), 35.2 (CH₂), 32.9 (CH₂), 9.1 (2CH₃), 0.9 (CH); IR (neat): ν = 3025, 2924, 2167, 1598, 1493, 1448, 1350, 1268, 1192, 1053, 1028, 987, 963, 839, 810, 740, 691; HR-MS (EI-TOF): m/z: calcd for C₁₅H₁₆S: 228.0977, found 228.0973 [M + H]⁺.

Alkynyl Sulfoxides

General Procedure 3: Preparation of alkynyl sulfoxides (GP 3)

A round-bottomed flask (RBF) equipped with a stirrer bar under argon was charged with alkynyl thioether (1.0 eq.) and CH₂Cl₂ (0.1 M). The mixture was cooled to 0 °C and mCPBA (1.0
(±)-1-(But-3-en-1-ylsulfinyl)hex-1-yn (9a)

9a was prepared according to GP3 using S2a (371 mg, 2.21 mmol), mCPBA (381.4 mg, 2.21 mmol) and CH₂Cl₂ (22 mL). The reaction time was 16 hours. Aqueous workup and purification by column chromatography (4:1 hexane:EtOAc) provided 9a as a pale yellow oil (308 mg, 76%); ¹H NMR (300 MHz CDCl₃): δ = 5.66 (ddt, J = 17.2, 10.3, 6.6, 1H), 5.17 (dd, J = 17.2, 1.4, 1H), 5.12 (dd, J = 10.3, 1.4, 1H), 3.09 (t, J = 7.7, 2H), 2.63 (m, 2H), 2.44 (t, J = 7.0, 2H), 1.60 – 1.37 (m, 4H), 0.93 (t, J = 7.3, 3H); ¹³C NMR (101 MHz CDCl₃): δ = 134.7 (CH), 117.4 (CH₂), 106.1 (C), 56.4 (C), 55.5 (CH₂), 29.8 (CH₂), 26.6 (CH₃), 22.1 (CH₂), 19.5 (CH₂), 13.6 (CH₃); IR (neat): ν = 2959, 2933, 2873, 2181, 1641, 1466, 1056, 916; HR-MS (ES-TOF): m/z: calcd for C₁₀H₁₀OSNa 207.0820, found 207.0825. [M + Na]⁺.

(±)-(4-(But-3-en-1-ylsulfinyl)but-3-yn-1-yl)benzene (9b)

9b was prepared according to GP3 using S2b (85.9 mg, 0.40 mmol), mCPBA (69.0 mg, 0.40 mmol) and CH₂Cl₂ (4 mL). The reaction time was 3.5 hours. Aqueous workup and purification by column chromatography (4:1 hexane:EtOAc) provided 9b as a pale yellow oil (67.4 mg, 73%). ¹H NMR (300 MHz CDCl₃): δ = 7.38 – 7.22 (m, 5H), 5.85 (ddt, J = 17.1, 10.2, 6.6, 1H), 5.17 (dd, J = 17.1, 1.4, 1H), 5.15 (dd, J = 10.2, 1.4, 1H), 3.07 (app t, J = 7.7, 2H), 2.94 (t, J = 7.2, 2H), 2.78 (t, J = 7.2, 2H), 2.70 – 2.44 (m, 2H); ¹³C NMR (101 MHz CDCl₃): δ = 140.8 (C), 136.1 (CH), 128.7 (2CH₂), 128.6 (2CH₂), 126.5 (CH), 116.8 (CH₃), 94.0 (C), 69.2 (C), 35.4 (CH₂), 34.7 (CH₂), 33.6 (CH₂), 22.5 (CH₂). IR: v_max (cm⁻¹) 3028, 2925, 2182, 1780, 1641, 1454, 1338, 1055, 994, 920, 748, 700, 626; HRMS (ES-TOF): m/z: calcd for C₂₉H₂₇OS 433.1712, found 433.1718. [M + H]⁺.

(4R)-1-((S)-but-3-en-1-ylsulfinyl)-4,8-dimethylnon-7-en-1-yn and (4R)-1-((R)-but-3-en-1-ylsulfinyl)-4,8-dimethylnon-7-en-1-yn (9c)

9c was prepared according to GP3 using S2c (156 mg, 0.66 mmol), mCPBA (113 mg, 0.66 mmol) and CH₂Cl₂ (7 mL). The reaction time was 19 hours. Aqueous workup and purification by column chromatography (9:1 hexane:EtOAc) afforded 9c (118 mg, 71%) as a colourless oil; ¹H NMR (300 MHz, CDCl₃): δ = 5.86 (ddt, J = 16.9, 10.1, 6.6 Hz, 1H), 5.23 – 4.99 (m, 3H), 3.09 (t, J = 7.7 Hz, 2H), 2.75 – 2.51 (m, 2H), 2.38 (qd, J = 17.2, 6.3 Hz, 2H), 2.07 – 1.90 (m, 2H), 1.76 (m, 1H), 1.68 (s, 3H), 1.60 (s, 3H), 1.43 (ddt, J = 13.5, 8.5, 6.5 Hz, 1H), 1.35 – 1.19 (m, 1H), 1.01 (d, J = 6.7 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 134.7 (CH), 132.0 (C), 124.1 (CH), 117.4 (CH₂), 104.9 (C), 78.0 (C), 55.5 (CH₂), 36.2 (CH₂), 31.8 (CH), 27.0 (CH₂), 26.6 (CH₂), 25.8 (CH₂), 25.5 (CH₂), 19.6 (CH₂), 17.8 (CH₃); IR (neat): ν = 2964, 2916, 2180, 1641,
(±)-(3,3-Dimethylbut-1-yn-1-yl)sulfinylbut-1-ene (9e)
9e was prepared according to GP3 using S2e (336 mg, 2.00 mmol), mCPBA (345 mg, 2.00 mmol) and CH₂Cl₂ (20 mL). The reaction time was 16 hours. Aqueous workup and purification by column chromatography (hexane to 4:1 hexane:EtOAc) provided 9e (190 mg, 52%) as a colourless oil; ¹H NMR (300 MHz, CDCl₃): δ = 5.81 (ddt, J = 17.2, 10.3, 6.6, 1H), 5.14 (dd, J = 17.2, 1.5 Hz, 1H), 5.08 (dd, J = 10.3, 1.4 Hz, 1H), 3.08 (td, J = 7.7, 2.1 Hz, 2H), 2.67 – 2.51 (m, 2H), 1.25 (s, 9H); ¹³C NMR (101 MHz, CDCl₃): δ = 134.7 (CH), 117.5 (CH₂), 112.9 (C), 73.2 (C), 55.5 (CH₂), 30.2 (3CH₃), 29.9 (C), 26.7 (2CH₂), 24.7 (CH₂); IR (neat): ν = 3078, 3012, 2920, 2178, 1641, 1441, 1348, 1277, 1052, 918, 838, 768, 752, 701; HRMS (ES-TOF) m/z calcd. for C₁₀H₁₇OS [M+H]+ 185.1002 found 185.1001.

(±)-(But-3-en-1-ylsulfanyl)ethynylcyclopropane (9f)
9f was prepared according to GP3 using sulfide S2f (91.4 mg, 0.60 mmol), mCPBA (104 mg, 0.60 mmol) and CH₂Cl₂ (6 mL). The reaction time was 16 hours. Aqueous workup and purification by column chromatography (4:1 hexane:EtOAc) provided 9f as a pale yellow oil (68.7 mg, 68%); ¹H NMR (300 MHz, CDCl₃): δ = 5.82 (ddt, J = 17.2, 10.3, 6.6, 1H), 5.14 (dd, J = 17.2, 1.5, 1H), 5.10 (dd, J = 10.3, 1.5, 1H), 3.04 (app t, J = 8.2, 5.1 Hz, 1H), 1.43 – 0.91 (m, 4H); ¹³C NMR (101 MHz, CDCl₃): δ = 134.7 (CH), 117.4 (CH₂), 109.6 (C), 72.1 (C), 55.5 (CH₂), 26.7 (CH₂), 9.6 (2CH₂), 0.33 (C); IR (neat): ν = 3080, 3012, 2920, 2178, 1641, 1441, 1348, 1277, 1052, 995, 916, 828, 781; HR-MS (ES-TOF): m/z: calcd for C₉H₁₃S 169.0687, found 169.0692 [M + H]^+.

(±)-(But-3-en-1-ylsulfanyl)benzene (9g)
9g was prepared according to GP3 using sulfide S2g (266 mg, 1.41 mmol), mCPBA (243 mg, 1.41 mmol) and CH₂Cl₂ (14 mL). The reaction time was 2 hours. Aqueous work-up and column chromatography (9:1 hexane:EtOAc) provided 9g (220 mg, 77%) as a colourless oil; ¹H NMR (300 MHz, CDCl₃): δ = 7.58 – 7.50 (m, 2H), 7.50
– 7.34 (m, 3H), 5.90 (ddt, $J = 17.0, 10.2, 6.6$ Hz, 1H), 5.21 (dd, $J = 17.0, 1.5$ Hz, 1H), 5.15 (dd, $J = 10.2, 1.5$ Hz, 1H), 3.23 (dd, $J = 8.0, 7.2, 1.0$ Hz, 2H), 2.82 – 2.60 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta = 134.6$ (CH), 132.4 (2CH), 130.8 (CH), 128.8 (2CH), 119.9 (C), 117.7 (CH$_2$), 102.7 (C), 85.1 (C), 55.4 (CH$_2$), 26.7 (CH$_2$); IR (neat): $\nu = 3068, 2920, 2164, 1719, 1574, 1282, 1244, 1057, 1023, 917, 832, 753, 688$; HRMS (ES) $m/z$ calcd. for C$_{12}$H$_{12}$OSNa 227.0507, found 227.0504 [M + Na]$^+$. 

(±) -1-(((But-3-en-1-yl)sulfinyl)ethynyl)-4-methylbenzene (9h)

9h was prepared according to GP3 using S2h (180 mg, 0.89 mmol), mCPBA (154 mg, 0.89 mmol) and CH$_2$Cl$_2$ (9 mL). The reaction time was 2 hours. Aqueous work-up and purification by column chromatography (9:1 hexane:EtOAc) provided 9h (143 mg, 74%) as a pale yellow oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.43$ (d, $J = 8.0$ Hz, 2H), 7.19 (d, $J = 8.0$ Hz, 2H), 5.89 (ddt, $J = 17.0, 10.1, 6.6$ Hz, 1H), 5.21 (dd, $J = 17.0, 1.5$ Hz, 1H), 5.14 (dd, $J = 10.2, 1.5$ Hz, 1H), 3.29 – 3.14 (m, 2H), 2.84 – 2.57 (m, 2H), 2.39 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta = 141.4$ (C), 134.6 (CH), 132.4 (2CH), 129.5 (2CH), 116.8 (C), 116.8 (C), 116.8 (C), 103.2 (C), 84.5 (C), 55.4 (CH$_2$), 26.7 (CH$_2$), 21.9 (CH$_3$); IR (neat): $\nu = 2923, 2243, 2162, 1605, 1508, 1055, 908, 817, 730$; HR-MS (ES-TOF): $m/z$: calcd for C$_{13}$H$_{14}$OSS: 241.0663, found 241.0670 [M + H]$^+$. 

(±) -1-(((But-3-en-1-yl)sulfinyl)ethynyl)-4-methoxybenzene (9i)

9i was prepared according to GP3 using S2i (151 mg, 0.69 mmol), mCPBA (120 mg, 0.69 mmol) and CH$_2$Cl$_2$ (7 mL). The reaction time was 2 hours. Aqueous work-up followed by column chromatography (4:1 hexane:EtOAc) provided 9i (124 mg, 75%) as a colourless oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.48$ (d, $J = 8.9$ Hz, 2H), 6.89 (d, $J = 8.9$ Hz, 2H), 5.89 (ddt, $J = 17.0, 10.1, 6.6$ Hz, 1H), 5.21 (dd, $J = 17.0, 1.5$ Hz, 1H), 5.15 (dd, $J = 10.1, 1.5$ Hz, 1H), 3.84 (s, 3H), 3.21 (t, $J = 7.2$ Hz, 2H), 2.79 – 2.61 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta = 161.6$ (C), 139.3 (C), 134.7 (CH), 134.7 (CH), 134.2 (2CH), 129.5 (2CH), 117.6 (CH$_2$), 116.8 (C), 103.4 (C), 84.1 (C), 55.4 (CH$_2$), 26.7 (CH$_2$), 21.9 (CH$_3$); IR (neat): $\nu = 3077, 2918, 2840, 2156, 1641, 1602, 1507, 1295, 1251, 1172, 1024, 832, 762$; HR-MS (ES-TOF): $m/z$: calcd for C$_{13}$H$_{15}$OSS: 235.0793, found 235.0799 [M + H]$^+$. 

(±) -N-(4-((but-3-en-1-yl)sulfinyl)phenyl)acetamide (9j)

A flame dried 2-neck RBF under argon was charged with N-(4-ethynylphenyl)acetamide (320 mg, 1.01 mmol, 1.1 eq.) and anhydrous THF (10 mL). The flask was cooled to -78 °C. LiHMDS (1 M in ethylbenzene) (4.02 mL, 4.02 mmol, 2.2 eq.) was added dropwise and on complete addition the mixture was stirred at -78 °C for an hour before S1 (417 mg, 1.83 mmol, 1.0 eq.) was added dropwise. The reaction was allowed to warm to rt for 16 hours. The reaction was quenched with NH$_4$Cl (10 mL of a saturated solution) and the mixture was extracted with Et$_2$O (3 × 10 mL), the organics were washed with brine (10 mL), dried over Na$_2$SO$_4$, filtered, concentrated under reduced pressure and most impurities were removed by column chromatography (7:3 hexane:EtOAc) to provide (370 mg) of a 1.8:1 ratio of sulfide S2j to N-(4-ethynylphenyl)acetamide. (S2j was used as a 1.8:1 mixture of alkynyl sulfide to alkyne) 9j was prepared according to GP3 using S2j (225 mg,
0.92 mmol), mCPBA (158 mg, 0.92 mmol) and CH$_2$Cl$_2$ (9 mL). The reaction time was 2 hours. Aqueous workup and purification by column chromatography (1:1 hexane:EtOAc to EtOAc provided 9j (176 mg, 74%) as a yellow solid; mp: 73-74 °C; $^1$H NMR (300 MHz, CDCl$_3$); δ = 8.17 (s, 1H), 7.57 (d, J = 8.6 Hz, 2H), 7.37 (d, J = 7.0 Hz, 2H), 5.89 (ddt, J = 16.8, 10.1, 6.6 Hz, 1H), 5.27 – 5.10 (m, 2H), 3.32 – 3.15 (m, 2H), 2.81 – 2.56 (m, 2H), 2.19 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$): δ = 169.0 (C), 140.7 (C), 134.4 (CH), 133.5 (2CH), 119.6 (2CH), 117.8 (CH$_2$), 114.4 (C), 103.7 (C), 84.3 (C), 55.3 (CH$_2$), 26.8 (CH$_2$), 24.8 (CH$_3$); IR (neat): ν = 3307, 3257, 3096, 2980, 2163, 1688, 1592, 1525, 1509, 1313, 1022, 839; HR-MS (ES-TOF): m/z: calcd for C$_{14}$H$_{16}$NO$_2$S: 262.0902, found 262.0900 [M + H]$^+$. 

(±)-1-((But-3-en-1-ylsulfinyl)ethynyl)-4-(trifluoromethyl)benzene (9k)

9k was prepared in 2 steps according to GP1 and GP3 starting from 1-(2,2-dibromovinyl)-4-(trifluoromethyl)benzene (825 mg, 2.50 mmol), n-BuLi (2.2 mL, 5.2 mmol), S1 (517 mg, 2.27 mmol) and THF (12 mL). The reaction time was 16 hours. Aqueous workup and removal of most impurities by column chromatography (hexane) provided the crude sulfide S2k (537 mg). Sulfide 2k (195 mg) was dissolved in CH$_2$Cl$_2$ (7 mL), the mixture was cooled to 0 °C and mCPBA (118 mg, 0.68 mmol) was added in 5 portions over 10 minutes. The reaction time was 2 hours. The mixture was washed with NaHCO$_3$ (10 mL) and the aqueous phase was extracted with CH$_2$Cl$_2$ (3 × 10 mL). The combined organic layers were dried over Na$_2$SO$_4$, filtered, concentrated and purified by column chromatography (9:1 hexane:EtOAc) to yield 9k (130 mg, 59% over 2 steps); $^1$H NMR (300 MHz, CDCl$_3$): δ = 7.65 (s, 4H), 5.89 (ddt, J = 16.9, 10.1, 6.6 Hz, 1H), 5.26 – 5.13 (m, 2H), 3.31 – 3.18 (m, 2H), 2.84 – 2.60 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$): δ = 134.3 (CH), 134.7 (q, J = 32.6 Hz, C) 132.6 (2CH), 125.8 (d, J = 3.2 Hz, 2CH), 123.6 (q, J = 271.4 Hz, C), 123.6 (C), 117.9 (CH$_2$), 100.6 (C), 87.4 (C), 55.3 (CH$_2$), 26.7 (CH$_3$); IR (neat): ν = 2981, 2170, 1643, 1615, 1321, 1241, 1128, 1065, 842, 655; HR-MS (ES-TOF): m/z: calcd for C$_{13}$H$_{11}$OF$_3$NaS: 295.0380, found 295.0371 [M + Na]$^+$. 

(±)-Methyl 4-((but-3-en-1-ylsulfinyl)ethynyl)benzoate (9l)

9l was prepared according to GP3 using S2l (246 mg, 1.00 mmol), mCPBA (173 mg, 1.00 mmol) and CH$_2$Cl$_2$ (10 mL). The reaction time was 2 hours. Aqueous work-up and purification by column chromatography (17:3 hexane:EtOAc) provided 9l (130 mg, 89%) as a pale orange oil; $^1$H NMR (300 MHz, CDCl$_3$); δ = 8.05 (d, J = 8.6 Hz, 2H), 7.60 (d, J = 8.6 Hz, 2H), 5.89 (ddt, J = 17.0, 10.2, 6.6 Hz, 1H), 5.22 (dd, J = 17.0, 1.5 Hz, 1H), 5.16 (dd, J = 10.2, 1.5 Hz, 1H), 3.93 (s, 3H), 3.30 – 3.19 (m, 2H), 2.83 – 2.59 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$): δ = 166.1 (C), 134.4 (CH), 132.3 (2CH), 131.8 (C), 129.8 (2CH), 124.2 (C), 117.8 (CH$_2$), 101.3 (C), 87.6 (C), 55.3 (CH$_2$), 52.6 (CH$_3$), 26.7 (CH$_3$); IR (neat): ν = 2952, 2166, 1436, 1275, 1107, 1060, 769; HR-MS (ES-TOF): m/z: calcd for C$_{14}$H$_{14}$O$_3$NaS: 285.0561, found 285.0567 [M + Na]$^+$. 

16
(±)-1-((But-3-en-1-ylsulfanyl)ethynyl)-4-fluorobenzene (9m)

9m was prepared in 2 steps from 1-(2,2-dibromovinyl)-4-fluorobenzene. Sulfide S2m was prepared according to GP1 using 1-(2,2-dibromovinyl)-4-fluorobenzene (840 mg, 3.0 mmol), n-BuLi (2.7 mL, 6.2 mmol), THF (15 mL) and S1 (616 mg, 2.7 mmol). The reaction time was 16 hours. Purification by column chromatography (hexane) afforded S2m (90% pure) 65%. 9m was prepared according to GP3 using S2m (97 mg, 0.47 mmol), mCPBA (81 mg, 0.47 mmol) and CH2Cl2 (5 mL). The reaction time was 2 hours. Aqueous workup and purification by column chromatography (9:1 hexane:EtOAc) provided 9m (76 mg, 73%) as a colourless oil; 'H NMR (300 MHz, CDCl3): δ = 7.65 – 7.46 (m, 2H), 7.17 – 7.00 (m, 2H), 5.89 (ddt, J = 17.0, 10.2, 6.6 Hz, 1H), 5.21 (dd, J = 17.0, 1.5 Hz, 1H), 5.15 (dd, J = 10.2, 1.5 Hz, 1H), 3.31 – 3.13 (m, 2H), 2.82 – 2.59 (m, 2H); 13C NMR (101 MHz, CDCl3): δ = 164.0 (d, J = 253.6 Hz, C), 134.6 (d, J = 8.8 Hz, 2CH), 134.4 (CH), 117.7 (CH2), 116.3 (d, J = 22.4 Hz, 2CH), 116.0 (d, J = 2.8 Hz, C), 101.6 (C), 85.0 (C), 55.3 (CH2); IR (neat): ν = 3077, 2981, 2919, 2165, 1641, 1598, 1505, 1233, 1216, 1157, 1054, 837, 775; HR-MS (ES-TOF): m/z: calcd for C12H12OSF: 223.0593, found 223.0601 [M + H]+.

(±)-1-((But-3-en-1-ylsulfanyl)ethyl)-3-methoxybenzene (9n)

9n was prepared according to GP3 using S2n (218 mg, 1.00 mmol), mCPBA (173 mg, 1.00 mmol) and CH2Cl2 (10 mL). The reaction time was 2 hours. Aqueous workup and purification by column chromatography (8:2 hexane:EtOAc) afforded 9n (170 mg, 72%) as a yellow oil; 'H NMR (300 MHz, CDCl3): δ = 7.32 – 7.25 (m, 1H), 7.16 – 7.09 (m, 1H), 7.08 – 6.96 (m, 2H), 5.89 (ddt, J = 16.8, 10.2, 6.6 Hz, 1H), 5.26 – 5.11 (m, 2H), 3.81 (s, 3H), 3.23 (ddd, J = 8.1, 7.1, 1.2 Hz, 2H), 2.85 – 2.58 (m, 2H); 13C NMR (101 MHz, CDCl3): δ = 159.5 (C), 134.5 (CH), 129.9 (CH), 124.8 (CH), 120.7 (C), 117.7 (CH2), 117.3 (CH), 117.0 (CH), 102.6 (C), 84.8 (C), 55.3 (CH2), 26.7 (CH3); IR (neat): ν = 3077, 2939, 2837, 2159, 1641, 1594, 1574, 1487, 1287, 1156, 1042, 683; HR-MS (ES-TOF): m/z: calcd for C13H15O2S: 235.0793, found 235.0796 [M + H]+.

(±)-1-Bromo-4-((but-3-en-1-ylsulfanyl)ethynyl)benzene (9o)

9o was prepared according to GP3 using S2o (180 mg, 0.67 mmol), mCPBA (117 mg, 0.67 mmol) and CH2Cl2 (7 mL). The reaction time was 2 hours. Aqueous work-up and purification by column chromatography (9:1 hexane:EtOAc) provided 9o (153 mg, 80%) as a yellow oil; 'H NMR (300 MHz, CDCl3): δ = 7.53 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 5.89 (ddt, J = 17.0, 10.2, 6.6 Hz, 1H), 5.21 (dd, J = 17.0, 1.4 Hz, 1H), 5.15 (dd, J = 10.2, 1.4 Hz, 1H), 3.34 – 3.12 (m, 2H), 2.85 – 2.55 (m, 2H); 13C NMR (101 MHz, CDCl3): δ = 134.4 (CH), 133.7 (2CH), 132.2 (2CH), 125.6 (C), 118.7 (C), 117.8 (CH2), 101.5 (C), 86.2 (C), 55.3 (CH2), 26.7 (CH3); IR (neat): ν = 3080, 2978, 2914, 2163, 1640, 1583, 1483, 1394, 1056, 762; HR-MS (ES-TOF): m/z: calcd for C12H11ONaSBr: 304.9612, found 304.9620 [M + Na]+.

17
(±)-1-Bromo-2-((but-3-en-1-yl)sulfinyl)ethynyl)benzene (9p)

9p was prepared according to GP3 using S2p (175 mg, 0.65 mmol), mCPBA (114 mg, 0.65 mmol) and CH₂Cl₂ (7 mL). The reaction time was 2 hours. Aqueous work-up and purification by column chromatography (9:1 hexane:EtOAc) provided 9p (157 mg, 85%) as a yellow oil; ¹H NMR (300 MHz, CDCl₃): δ = 7.68 – 7.54 (m, 2H), 7.40 – 7.26 (m, 2H), 5.90 (ddt, J = 17.0, 10.1, 6.6 Hz, 1H), 5.22 (dd, J = 17.0, 1.5 Hz, 1H), 5.15 (dd, J = 10.1, 1.5 Hz, 1H), 3.35 – 3.20 (m, 2H); ¹³C NMR (101 MHz, CDCl₃): δ = 134.5 (CH), 134.4 (CH), 132.9 (CH), 131.8 (CH), 127.5 (CH), 126.1 (C), 122.3 (C), 117.7 (CH₂), 100.0 (C), 89.2 (C), 55.4 (CH₂), 26.7 (CH₂); IR (neat): ν = 3077, 2979, 2917, 2167, 1675, 1640, 1584, 1057, 754; HR-MS (ES-TOF): m/z: calcd for C₁₉H₁₂OS²⁺Br: 282.9808, found 282.9792 [M + H]⁺.

(±)-1-((But-3-en-1-yl)sulfinyl)ethynyl)-2-isopropylbenzene (9q)

9q was prepared according to GP3 using S2q (230 mg, 1.00 mmol), mCPBA (173 mg, 1.00 mmol) and CH₂Cl₂ (10 mL). The reaction time was 2 hours. Aqueous work-up and purification by column chromatography (17:3 hexane:EtOAc) provided 9q (218 mg, 89%) as a yellow oil; ¹H NMR (300 MHz, CDCl₃): δ = 7.50 (dd, J = 7.7, 1.1 Hz, 1H), 7.41 (td, J = 7.7, 1.4 Hz, 1H), 7.32 (d, J = 6.7 Hz, 1H), 7.19 (td, J = 7.7, 1.4 Hz, 1H), 5.90 (ddt, J = 17.0, 10.2, 6.6 Hz, 1H), 5.21 (dd, J = 17.0, 1.5 Hz, 1H), 5.15 (dd, J = 10.2, 1.5 Hz, 1H), 3.39 (dt, J = 13.8, 6.9 Hz, 1H), 3.24 (t, J = 7.7 Hz, 2H), 2.87 – 2.58 (m, 2H), 1.27 (d, J = 6.9 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃): δ = 152.0 (C), 134.6 (CH), 133.4 (CH), 131.2 (CH), 126.0 (CH), 125.5 (CH), 118.6 (C), 117.6 (CH₂), 101.7 (C), 88.4 (C), 55.4 (CH₂), 32.0 (CH), 26.8 (CH₂), 23.3 (CH₃), 23.3 (CH₃); IR (neat): ν = 3067, 2963, 2870, 2157, 1641, 1484, 1444, 1056, 758; HR-MS (ES-TOF): m/z: calcd for C₁₅H₁₀OS: 247.1155, found 247.1155 [M + H]⁺.

(±)-2-((But-3-en-1-yl)sulfinyl)ethynyl)naphthalene (9r)

9r was prepared according to GP3 using sulfide S2r (90 mg, 0.38 mmol), mCPBA (65 mg, 0.38 mmol) and CH₂Cl₂ (4 mL). The reaction time was 2 hours. Aqueous work-up and purification by column chromatography (9:1 hexane:EtOAc) provided 9r as a colourless oil (73 mg, 79%); ¹H NMR (300 MHz, CDCl₃): δ = 8.10 (d, J = 0.9 Hz, 1H), 7.85 (dd, J = 7.2, 3.7 Hz, 3H), 7.56 (app tdd, J = 8.7, 6.9, 1.8 Hz, 3H), 5.92 (ddt, J = 17.0, 10.2, 6.6 Hz, 1H), 5.24 (dd, J = 17.0, 1.5 Hz, 1H), 5.17 (dd, J = 10.2, 1.5 Hz, 1H), 3.35 – 3.20 (m, 2H), 2.89 – 2.62 (m, 2H); ¹³C NMR (101 MHz, CDCl₃): δ = 134.6 (CH), 133.9 (C), 133.5 (CH), 132.7 (C), 128.6 (CH), 128.3 (CH), 128.1 (C), 127.8 (CH), 127.2 (CH), 117.7 (CH₂), 117.0 (C), 103.2 (C), 85.3 (C), 55.4 (CH₂), 26.8 (CH₂); IR (neat): ν = 3057, 2924, 2154, 1720, 1641, 1277, 1056, 916, 818, 749; HR-MS (ES-TOF): m/z: calcd for C₁₆H₁₄OS²⁺: 255.0844, found 255.0841 [M + H]⁺.

(±)-2-((But-3-en-1-yl)sulfinyl)ethynyl)furan (9s)

9s was prepared according to GP3 from S2s (54.3 mg, 0.30 mmol), mCPBA (52.0 mg, 0.30 mmol) and CH₂Cl₂ (3 mL). The reaction time was 16 hours. Aqueous workup and purification by column chromatography (4:1 hexane:EtOAc) provided 9s (41.4 mg, 70%) as a colourless oil. The product was seen to degrade when neat and so was used directly in the catalysis reaction on its preparation.
(±)-3-Bromo-2-((but-3-en-1-ylsulfinyl)ethynyl)thiophene (9t)

9t was prepared according to GP3 from S2t (82.0 mg, 0.30 mmol), mCPBA (52.0 mg, 0.30 mmol) and CH₂Cl₂ (3 mL). The reaction time was 16 hours. Aqueous workup and purification by column chromatography (4:1 hexane:EtOAc) provided 9t (60.7 mg, 70%) as a colourless oil. The product was seen to degrade when neat and so was used directly in the catalysis reaction on its preparation.

(±)-4-((3-(Allyloxy)prop-1-yn-1-yl)sulfinyl)but-1-ene (9u)

9u was prepared according to GP3 using S2u (249 mg, 1.36 mmol), mCPBA (233 mg, 1.36 mmol) and CH₂Cl₂ (13 mL). The reaction time was 2 hours. Aqueous workup and purification by column chromatography (4:1 hexane:EtOAc) provided 9u (217 mg, 80%) as a colourless oil; ¹H NMR (300 MHz, CDCl₃): δ = 5.95 – 5.76 (m, 2H), 5.36 – 5.08 (m, 4H), 4.34 (s, 2H), 4.06 (dt, J = 5.8, 1.3 Hz, 2H), 3.14 (dd, J = 11.6, 4.1 Hz, 2H), 2.76 – 2.51 (m, 2H); ¹³C NMR (101 MHz, CDCl₃): δ = 134.3 (CH), 133.3 (CH), 118.7 (CH₂), 117.7 (CH₃), 99.7 (C), 82.9 (C), 71.3 (CH₂), 57.3 (CH₂), 55.1 (CH₂), 26.5 (CH₂); IR (neat): ν = 3081, 2850, 2181, 1641, 1435, 1351, 1058, 990, 919; HR-MS (ES-TOF): m/z: calcd for C₁₀H₁₅O₂S: 199.0793, found 199.0799 [M + H]+.

(±)-(E)-3-((3-(But-3-en-1-ylsulfinyl)prop-2-yn-1-yl)oxy)prop-1-en-1-yl)benzene (9v)

9v was prepared according to GP3 using S2v (500 mg, 1.93 mmol), mCPBA (333 mg, 1.93 mmol) and CH₂Cl₂ (19 mL). The reaction time was 16 hours. Aqueous workup and purification by column chromatography (4:1 hexane:EtOAc) provided 9v (353 mg, 66%) as a colourless oil; ¹H NMR (300 MHz, CDCl₃): δ = 7.44 – 7.21 (m, 5H), 6.65 (d, J = 15.9 Hz, 1H), 6.25 (dt, J = 15.9, 6.3 Hz, 1H), 5.85 (ddt, J = 16.9, 10.1, 6.6 Hz, 1H), 5.25 – 5.09 (m, 2H), 4.41 (s, 2H), 4.25 (dd, J = 6.3, 1.3 Hz, 2H), 3.28 – 3.06 (m, 2H), 2.79 – 2.52 (m, 2H); This compound proved unstable and prevented collection of useful ¹³C NMR data. IR (neat): ν = 2850, 2180, 1641, 1599, 1495, 1448, 1352, 1057, 990, 968, 918, 744, 692; HR-MS (ES-TOF): m/z: calcd for C₁₆H₁₉O₂S: 275.1106, found 275.1113 [M + H]+.

(E)-(4-((Cyclopropylethynyl)sulfinyl)but-1-en-1-yl)benzene (14)

14 was prepared according to GP3 using S5 (280 mg, 1.23 mmol), mCPBA (212 mg, 1.23 mmol) and CH₂Cl₂ (12 mL). The reaction time was 2 hours. Aqueous workup and purification by column chromatography (4:1 hexane:EtOAc) provided 14 (208 mg, 69%) as a colourless oil; ¹H NMR (300 MHz, CDCl₃): δ = 7.39 – 7.18 (m, 5H), 6.52 (d, J = 15.8 Hz, 1H), 6.21 (dt, J = 15.8, 7.0 Hz, 2H), 3.14 (t, J = 7.6 Hz, 2H), 2.89 – 2.66 (m, 2H), 1.51 – 1.41 (m, 1H), 1.03 – 0.85 (m, 4H); ¹³C NMR (101 MHz, CDCl₃): δ = 137.0 (C), 132.7 (CH), 128.7 (2CH), 127.6 (CH), 126.2 (2CH), 126.1 (CH), 109.8 (C), 72.0 (C), 55.8 (CH₂), 26.0 (CH₃), 9.7 (CH), 0.3 (2CH₂); IR (neat): ν = 3025, 2179, 1598, 1493, 1444, 1059, 967, 829, 745, 694; HR-MS (ES-TOF): m/z: calcd for C₁₅H₁₇O₂S: 245.1000, found 245.1004 [M + H]+.
(±)-(Hex-5-en-1-yn-1-ylsulfinyl)benzene (17)

17 was prepared according to an adapted literature procedure.²⁶ Mg turnings (1.73 g, 72.0 mmol, 2.3 eq.) and a pellet of iodine were added to a two-neck RBF fitted with a condenser and the mixture was purged with argon. Et₂O (30 mL) was added followed by slow addition of allyl bromide (6.14 mL, 72.0 mmol, 2.3 eq.). The solution was stirred for 2 hours at rt. The reaction mixture was cooled to -10 °C, propargyl chloride (3.45 mL, 30 mmol, 1.0 eq.) was added and the solution was stirred for 5 hours allowing to warm to rt. After cooling to 0 °C, methyl benzenesulfinate (9.37 g, 60 mmol, 2.0 eq.) was added dropwise and the solution was stirred at rt for 16 hours. The reaction was quenched by the addition of sat. NH₄Cl solution (30 mL) at 0 °C and the aqueous layer was extracted with Et₂O (5 × 20 mL), washed with brine (20 mL) and the organic layers were dried over Na₂SO₄, filtered, concentrated under reduced pressure and purified by column chromatography (9:1 hexane:EtOAc) affording 17 as a yellow oil (1.23 g, 26%); ¹H NMR (300 MHz, CDCl₃): δ = 7.85 – 7.75 (m, 2H), 7.59 – 7.50 (m, 3H), 5.79 (ddt, J = 17.0, 10.2, 6.6 Hz, 1H), 5.06 (dd, J = 17.0, 1.4 Hz, 1H), 5.06 (dd, J = 10.2, 1.4 Hz, 1H), 2.52 (t, J = 7.2 Hz, 2H), 2.31 (dt, J = 7.2, 6.6 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃): δ = 144.4 (C), 135.7 (CH), 131.7 (CH), 129.6 (2CH), 125.1 (2CH), 116.8 (CH₂), 106.2 (C), 78.2 (C), 31.7 (CH₂), 19.7 (CH₂); IR (neat): ν = 3078, 2981, 2913, 2180, 1643, 1581, 1476, 1444, 1188, 1086, 1052, 985, 917, 885, 788, 749, 687; HR-MS (ES-TOF): m/z: calcd for C₁₂H₁₂ONaS: 227.0507, found 227.0502 [M + Na]⁺.

((But-3-en-1-ylsulfonyl)ethynyl)benzene

A RBF under argon was charged with 2b (130 mg, 0.69 mmol), and CH₂Cl₂ (10 mL). The mixture was cooled to 0 °C and mCPBA (238 mg, 1.38 mmol, 2.0 eq.) was added in 5 portions over 10 mins. The mixture was stirred for 3 hours allowing to warm to rt. The mixture was cooled to 0 °C and mCPBA (59 mg, 0.35 mmol, 0.5 eq.) was added in one portion. The reaction was stirred for a further hour. The mixture was washed with NaHCO₃ (3 × 10 mL) and the aqueous phase was extracted with CH₂Cl₂ (3 × 10 mL). The combined organic layers were dried over Na₂SO₄, filtered, concentrated and purified by column chromatography (9:1 hexane:EtOAc) providing 4b (129 mg, 85%) as a viscous colourless oil; ¹H NMR (300 MHz, CDCl₃): δ = 7.69 – 7.60 (m, 2H), 7.59 – 7.51 (m, 1H), 7.50 – 7.40 (m, 2H), 5.89 (ddt, J = 16.8, 10.2, 6.5 Hz, 1H), 5.30 – 5.14 (m, 2H), 3.44 – 3.34 (m, 2H), 2.83 – 2.70 (m, 2H); ¹³C NMR (101 MHz, CDCl₃): δ = 133.4 (CH), 133.0 (2CH), 131.9 (CH), 129.0 (2CH), 117.8 (CH₂), 117.7 (C), 92.8 (C), 83.3 (C), 57.5 (CH₂), 27.3 (CH₂); IR (neat): ν = 3082, 2922, 2181, 1643, 1490, 1444, 1319, 1232, 1136, 847, 756, 687; HR-MS (AP-TOF): m/z: calcd for C₁₂H₁₃O₂S: 221.0636, found 221.0630 [M + H]*.
Catalysis Reactions

Table of catalysis results at room temperature

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Reactions were run on a 0.3 mmol scale. ᵃ 0.2 mmol scale. ᵇ 19 h. ᶜ 20 h.

Structural assignment of major and minor diastereomers 10a-t.

Fig S1. ¹H NMR chemical shifts in catalysis product 10g and 10g′

The structure of the major diastereomer 10g was determined by X-ray crystallography. The structures of major diastereomers 10a-f and 10h-t were assigned by analogous key characteristic chemical shifts in the ¹H NMR spectra, which remain consistent across the series 10a-t. In every case, for the major diastereomer a distinctive proton α to the sulfoxide resonates between 3.52 and 3.58 ppm, 0.4 ppm downfield of the same proton in the ¹H NMR spectrum of the minor diastereomer. The methylene cyclopropyl hydrogens in the major diastereomer are are shifted downfield compared to the analogous protons in the minor diastereomer, presumably due to the anisotropic effect exerted by the proximal sulfanyl group (Fig S1). ²² Data is reported for the major diastereomer the structures of which are shown in the inserts.
Cyclopropanation products

General procedure 4 (GP4) Gold catalysed reactions of alkynyl sulfoxides

A Radleys tube under argon was charged with 3,5-dichloropyridine-N-oxide (1.2 eq.) and alkynyl sulfoxide (1.0 eq.) in 1,4-dioxane (¾ of the total solvent volume). SPhosAuNTf₂ (2.5 to 5 mol%) was added followed by 1,4-dioxane (¾ of the total solvent volume, the final concentration is 0.05 M) and the tube was heated at the specified temperature and with stirring until completion or no further reaction was observed by TLC analysis. The mixture was filtered through a pad of silica, washing with EtOAc, concentrated and purified by column chromatography.

(±)-1-(2-Oxido-2-thiabicyclo[3.1.0]hexan-1-yl)pentan-1-one (10a)

10a was prepared according to GP4 using 9a (36.8 mg, 0.20 mmol), 3,5-dichloropyridine-N-oxide (39.4 mg, 0.24 mmol), SPhosAuNTf₂ (8.8 mg, 5 mol%) and 1,4-dioxane (4 mL). The reaction time was 17 hours. Purification by column chromatography (EtOAc to 95:5 EtOAc:MeOH) afforded 10a (29.4 mg, 72%) a pale yellow oil as a 6:1 mixture of diastereomers; ¹H NMR (300 MHz CDCl₃): δ 3.57 – 3.47 (m, 1H), 2.85 (t, J = 7.4 Hz, 2H), 2.54 – 2.45 (m, 1H), 2.44 – 2.36 (m, 1H), 2.33 – 2.25 (m, 2H), 2.04 (app t, J = 5.7 Hz, 1H), 1.83 (dd, J = 8.4, 5.7 Hz, 1H), 1.59 (tt, J = 7.5, 7.4 Hz, 2H), 1.31 (app q, J = 7.5 Hz, 2H), 0.89 (t, J = 7.3 Hz, 3H); ¹³C NMR (101 MHz CDCl₃): δ 203.7 (C), 171.5 (C), 149.7 (C), 140.4 (C), 128.6 (CH₂), 128.5 (2CH), 126.3 (CH), 58.6 (C), 50.7 (CH₂), 40.7 (CH₃), 35.2 (CH), 25.5 (CH₂), 22.1 (CH₂), 17.7 (CH₃), 13.8 (CH₃). IR (neat): ν = 2957, 2933, 2871, 1687, 1450, 1375, 1260, 1055, 1031, 992, 875. HR-MS (ES-TOF): m/z calcd. for C₁₀H₁₃O₂S 201.0949, found 201.0950 [M + Na⁺].

(±)-1-(2-Oxido-2-thiabicyclo[3.1.0]hexan-1-yl)-3-phenylpropan-1-one (10b)

10b was prepared according to GP4 using 9b (23.2 mg, 0.10 mmol), 3,5-dichloropyridine-N-oxide (19.7 mg, 0.12 mmol), SPhosAuNTf₂ (4.4 mg, 5 mol%) and 1,4-dioxane (2 mL). The reaction time was 3.5 hours. Purification by column chromatography (EtOAc:MeOH) afforded 10b (15.7 mg, 63%) as a pale yellow oil as a 6:1 mixture of diastereomers; ¹H NMR (300 MHz CDCl₃): δ = 3.50 (ddd, J = 13.2, 6.9, 2.9 Hz, 1H), 3.20 – 3.17 (m, 2H), 2.97 (t, J = 7.4 Hz, 2H), 2.55 – 2.45 (m, 1H), 2.45 – 2.35 (m, 1H), 2.31 – 2.24 (m, 2H), 2.07 (app t, J = 5.9 Hz, 1H), 1.86 (ddd, J = 8.4, 5.9 Hz, 1H); ¹³C NMR (101 MHz CDCl₃): δ = 202.9 (C), 140.4 (C), 128.6 (2CH), 128.5 (2CH), 126.3 (CH), 58.9 (C), 50.9 (CH₂), 42.9 (CH₃), 35.6 (CH), 29.7 (CH₂), 25.4 (CH₃), 18.1 (CH₃); IR (neat): ν = 3410, 3028, 2931, 1689, 1584, 1536, 1400, 1372, 1251, 1107, 1058, 967, 842, 730, 699, 615; HR-MS (ES-TOF): m/z calcd. for C₁₄H₁₃O₂S 249.0949, found 249.0952 [M + Na⁺].

(3S)-3,7-Dimethyl-1-(2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl)oct-6-en-1-one (10c)

10c was prepared according to GP4 using 9c (50.4 mg, 0.20 mmol), 3,5-dichloropyridine-N-oxide (39.4 mg, 0.24 mmol), SPhosAuNTf₂ (8.8 mg, 5 mol%) and 1,4-dioxane (4 mL). The reaction time was 21 hours. Purification by column chromatography (1:1 hexane:EtOAc to EtOAc) afforded 10c (37.8 mg, 70%) as a colourless oil (d.r. ratio 10:10:1:1, assignment of the two major diastereomers is observed in the ¹³C NMR); ¹H NMR (300 MHz,
CDCl$_3$): $\delta$ = 5.08 (dtd, $J$ = 7.0, 2.7, 1.3 Hz, 1H), 3.58 – 3.45 (m, 1H), 2.93 – 2.62 (m, 2H), 2.59 – 2.38 (m, 2H), 2.37 – 2.25 (m, 2H), 2.19-2.05 (m, 1H), 2.10 – 2.04 (m, 1H), 1.97 (td, $J$ = 14.0, 7.1 Hz, 2H), 1.85 (dd, $J$ = 7.9, 5.8 Hz, 1H), 1.67 (s, 3H), 1.59 (s, 4H), 1.43 – 1.15 (m, 3H), 0.93 (dd, $J$ = 6.6, 2.0 Hz, 3H); Major diastereomer 1; $^{13}$C NMR (101 MHz, CDCl$_3$): 203.5 (C), 131.7 (C), 124.3 (CH), 59.3 (C), 51.3 (CH$_3$), 50.1 (CH$_2$), 48.6 (CH$_3$), 37.0 (CH$_2$), 35.5 (CH), 28.8 (CH), 25.8 (CH$_3$), 25.6 (CH$_3$), 19.9 (CH$_3$), 18.1 (CH$_3$), 17.8 (CH$_3$); Major diastereomer 2 $\delta$ = 203.5 (C), 131.7 (C), 124.3 (CH), 59.2 (C), 51.1 (CH$_3$), 50.1 (CH$_2$), 48.6 (CH$_3$), 36.9 (CH$_2$), 35.4 (CH), 28.8 (CH), 25.8 (CH$_3$), 25.6 (CH$_3$), 19.8 (CH$_3$), 18.0 (CH$_3$), 17.8 (CH$_3$); IR (neat): $\nu$ = 3458, 2961, 2924, 1688, 1446, 1375, 1287, 1241, 1100, 1057, 1031, 989; HR-MS (ES-TOF): $m/z$: calcd for C$_{13}$H$_{22}$O$_3$NaS: 291.1395, found 291.1393 [M + Na]$^+$. 

(±)-Cyclohexyl[2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl]methylone (10d)

10d was prepared according to GP4 using 9d (42.7 mg, 0.20 mmol), 3,5-dichloropyridine-N-oxide (39.4 mg, 0.24 mmol), SPhosAuNTf$_2$ (8.8 mg, 5 mol%) and 1,4-dioxane (4 mL). The reaction time was 24 hours. Purification by column chromatography (1:1 hexane:EtOAc to EtOAc) afforded 10d (20.6 mg, 45%) as a white solid as a 7:1 mixture of diastereomers; mp: 86-87 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 3.60 – 3.48 (ddd, $J$ = 10.2, 6.2, 4.8, 1H), 3.17 – 3.01 (m, 1H), 2.59 – 2.47 (m, 1H), 2.45 – 2.36 (m, 1H), 2.34 – 2.27 (m, 2H), 2.08 – 2.02 (m, 1H), 2.02 – 1.95 (m, 1H), 1.85 (dd, $J$ = 8.5, 5.6 Hz, 1H), 1.80 (dd, $J$ = 9.1, 3.2 Hz, 2H), 1.75 – 1.63 (m, 2H), 1.56 – 1.11 (m, 5H); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ = 207.1 (C), 58.3 (C), 51.8 (CH$_2$), 48.7 (CH), 36.2 (CH), 28.8 (CH$_2$), 28.5 (CH$_3$), 25.8 (CH$_2$), 25.7 (CH$_2$), 25.5 (2CH$_3$), 18.0 (CH$_3$); IR (neat): $\nu$ = 2980, 2925, 2853, 1667, 1442, 1382, 1332, 1267, 1259, 1057, 1041, 980, 874; HR-MS (ES-TOF): $m/z$: calcd for C$_{12}$H$_{18}$O$_2$NaS: 249.0925, found 249.0920 [M + Na]$^+$. 

(±)-2,2-Dimethyl-1-[(1S,2R)-2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl]propan-1-one (10e)

10e was prepared according to GP4 using 9e (36.9 mg, 0.20 mmol), 3,5-dichloropyridine-N-oxide (39.4 mg, 0.24 mmol), SPhosAuNTf$_2$ (8.8 mg, 5 mol%) and 1,4-dioxane (4 mL). The reaction time was 25 hours. $^1$H NMR analysis using 1,2,4,5-tetramethyl benzene as internal standard showed a d.r. of 12:1. Purification by column chromatography (EtOAc) afforded 10e (28.0 mg, 70%) as a colourless oil as a 12:1 mixture of diastereomers; $^1$H NMR (300 MHz CDCl$_3$): $\delta$ = 3.51 (ddd, $J$ = 13.2, 6.8, 4.9 Hz, 1H), 2.65 (ddd, $J$ = 13.2, 6.8, 4.9 Hz, 1H), 2.48 – 2.39 (m, 1H), 2.38 – 2.29 (m, 2H), 2.03 (app t, $J$ = 5.7 Hz, 1H), 1.78 (dd, $J$ = 8.6, 5.7 Hz, 1H), 1.36 (s, 9H); $^{13}$C NMR (101 MHz CDCl$_3$): $\delta$ = 207.0 (C), 58.3 (C), 53.7 (CH$_2$), 45.4 (C), 36.6 (CH), 26.7 (3CH$_3$), 25.9 (CH$_3$), 18.5 (CH$_2$); IR (neat): $\nu$ = 3470, 2971, 2871, 1768, 1478, 1367, 1225, 1169, 1091, 1057, 994. HR-MS (ES-TOF): $m/z$: calcd. for C$_{16}$H$_{18}$O$_2$S: 249.0871, found 200.0879 [M + H]$^+$. 

(±)-Cyclopropyl[2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl]methylone (10f)

10f was prepared according to GP4 using 9f (17.0 mg, 0.10 mmol), 3,5-dichloropyridine-N-oxide (19.7 mg, 0.12 mmol), SPhosAuNTf$_2$ (4.4 mg, 5 mol%) and 1,4 dioxane (2 mL). The reaction time was 17 hours. Purification by column chromatography (EtOAc to 95:5 EtOAc:MeOH) afforded 10f (15.8 mg, 86%) a pale yellow oil as a 10:1 mixture of diastereomers; $^1$H NMR (300 MHz CDCl$_3$): $\delta$ =3.55 (app dt, $J$ = 13.5, 4.8 Hz, 1H), 2.56 – 2.50 (m, 1H), 2.50 – 2.46 (m, 1H), 2.43 – 2.38 (m, 1H), 2.38 – 2.29 (m, 2H), 2.12 (app t, $J$ = 6.1 Hz, 1H), 1.88 (dd, $J$ = 8.6, 6.1 Hz, 1H), 1.22 – 1.13 (m, 2H), 1.09 – 0.99
(m, 2H); $^{13}$C NMR (101 MHz CDCl$_3$): $\delta = 203.8$ (C), 59.3 (C), 50.6 (CH$_3$), 34.5 (CH), 25.5 (CH$_2$), 18.7 (CH), 17.8 (CH$_2$), 12.8 (2CH$_2$); IR (neat): $\nu = 3412, 2934, 1167, 1445, 1394, 1250, 1057, 1022, 988, 872, 885, 677$; HR-MS (ES-TOF): $m/z$ calcd. for C$_9$H$_{12}$O$_2$SNa 207.0456, found 207.0461 [M + Na]$^+$. 

$(\pm)$-(2-Oxido-2-thiabicyclo[3.1.0]hexan-1-yl)(phenyl)methanone (10g)

10g was prepared according to GP4 using 9g (61.2 mg, 0.30 mmol), SPhosAuNTf$_2$ (13.2 mg, 5 mol%) and 1,4-dioxane (6 mL). The reaction time was 45 min. $^1$H NMR analysis showed a d.r. ratio of 8:1. Purification by column chromatography (3:7 hexane:EtOAc) afforded 10g (52.8 mg, 80%) as an off-white solid as a single diastereomer. When run on the same scale with SPhosAuNTf$_2$ (6.6 mg, 2.5 mol%), 10g was obtained as a single diastereomer (48.2 mg, 73%) as an off white solid after 28 hours; mp: 77-78 $^\circ$C (Et$_2$O); $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 8.06 - 7.92$ (m, 2H), 7.65 - 7.56 (m, 1H), 7.50 (t, $J = 7.4$ Hz, 2H), 3.53 (ddd, $J = 12.9, 7.7, 4.3$ Hz, 1H), 2.79 - 2.64 (m, 2H), 2.56 - 2.34 (m, 2H), 2.26 (t, $J = 5.9$ Hz, 1H), 1.82 (dd, $J = 8.7, 5.9$ Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta = 196.5$ (C), 136.9 (C), 133.5 (CH), 129.5 (2CH), 128.8 (2CH), 59.7 (C), 54.4 (CH$_2$), 34.0 (CH), 26.5 (CH$_2$), 19.5 (CH$_3$); IR (neat): $\nu = 3078, 3006, 2989, 2934, 2860, 1611, 1600, 1449, 1442, 1060, 754, 692, 662$; HR-MS (ES-TOF): $m/z$: calcd for C$_{12}$H$_{16}$O$_2$NaS: 243.0456, found 243.0458 [M + Na]$^+$. 

$(\pm)$-(2-Oxido-2-thiabicyclo[3.1.0]hexan-1-yl)(phenyl)methanone (10g$'$)

The minor diastereomer 10g$'$ was isolated from a separate reaction run; mp: 129-130 $^\circ$C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.10 - 8.02$ (m, 2H), 7.60 (t, $J = 7.4$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 2H), 3.12 (dd, $J = 14.4, 7.1$ Hz, 1H), 3.02 - 2.85 (m, 2H), 2.67 (ddd, $J = 14.4, 12.4, 7.1$ Hz, 1H), 2.40 (dd, $J = 13.2, 7.0$ Hz, 1H), 1.43 (dd, $J = 8.2, 6.6$ Hz, 1H), 1.14 (app t, $J = 6.2$ Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta = 194.0$ (C), 137.3 (C), 133.6 (CH), 129.0 (2CH), 128.8 (2CH), 58.7 (C), 50.4 (CH$_2$), 27.5 (CH), 25.5 (CH$_2$), 18.4 (CH$_3$); IR (neat): $\nu = 3082, 3009, 2990, 2934, 2865, 1667, 1597, 1286, 1022, 989, 775$; HR-MS (EI-TOF): $m/z$: calcd for C$_{12}$H$_{16}$O$_2$S: 220.0558 found 220.0556 [M + H]$^+$. 

$(\pm)$-(2-Oxido-2-thiabicyclo[3.1.0]hexan-1-yl)(p-toly)methanone (10h)

10h was prepared according to GP4 using 9h (65.4 mg, 0.30 mmol), SPhosAuNTf$_2$ (6.6 mg, 2.5 mol%) and 1,4-dioxane (6 mL). The reaction time was 28 hours. $^1$H NMR analysis using 1,2,4,5-tetramethylbenzene as internal standard showed a d.r. of 8:1. Purification by column chromatography (3:7 hexane:EtOAc) afforded 10h (53.0 mg, 75%) as a colourless oil as a single diastereomer after 28 hours; $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.87$ (d, $J = 8.1$ Hz, 2H), 7.27 (d, $J = 8.1$ Hz, 2H), 3.49 (ddd, $J = 13.1, 7.7, 4.3$ Hz, 1H), 2.73 - 2.62 (m, 2H), 2.52 - 2.29 (m, 2H), 2.39 (s, 3H), 2.24 - 2.17 (t, $J = 5.9$ Hz, 1H), 1.75 (dd, $J = 8.7, 5.9$ Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta = 195.8$ (C), 144.4 (C), 134.2 (C), 129.6 (2CH), 129.4 (2CH), 59.4 (C), 54.5 (CH$_2$), 33.3 (CH), 26.4 (CH$_2$), 21.8 (CH$_3$), 19.1 (CH$_3$); IR (neat): $\nu = 3463, 2926, 1760, 1660, 1605, 1571, 1281, 1180, 1055, 1029, 734$; HR-MS (ES-TOF): $m/z$: calcd for C$_{13}$H$_{14}$O$_2$NaS: 257.0612, found 257.0605 [M + Na]$^+$. 

24
(±)-(4-Methoxyphenyl)(2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl)methanone (10i)

10i was prepared according to GP4 using 9i (70.2 mg, 0.30 mmol), 3,5-dichloropyridine-N-oxide (59.1 mg, 0.36 mmol), SPhosAuNTf₂ (13.2 mg, 5 mol%) and 1,4-dioxane (6 mL). The reaction time was 1 hour. ¹H NMR analysis showed a d.r. of 8:1. Purification by column chromatography (1:1 hexane:EtOAc to EtOAc) afforded 10i (58.5 mg, 78%) as a colourless oil as a single diastereomer. When run on the same scale with SPhosAuNTf₂ (6.6 mg, 2.5 mol%), 10i was obtained as a single diastereomer (53.0 mg, 72%) after 19 hours. ¹H NMR (300 MHz, CDCl₃): δ = 8.08 – 7.99 (m, 2H), 7.04 – 6.95 (m, 2H), 3.53 (dd, J = 13.1, 7.8, 4.3 Hz, 1H), 2.77 – 2.64 (m, 2H), 2.55 – 2.31 (m, 2H), 2.22 (t, J = 5.9 Hz, 1H), 1.71 (dd, J = 8.7, 5.9 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃): δ = 194.2 (C), 164.1 (C), 132.3 (2CH), 129.6 (C), 114.1 (2CH), 59.1 (C), 55.7 (CH₂), 54.7 (CH), 32.4 (CH₂), 18.8 (CH₃); IR (neat): ν = 3452, 2934, 1731, 1655, 1597, 1579, 1285, 1258, 1170, 1024, 841; HR-MS (ES-TOF): m/z: calcd for C₁₃H₁₂O₃NaS: 273.0561, found 273.0570 [M + Na]+.

(±)-N-(4-(2-Oxido-2-thiabicyclo[3.1.0]hexane-1-carbonyl)phenyl)acetamide (10j)

10j was prepared according to GP4 using 9j (78.3 mg, 0.30 mmol), 3,5-dichloropyridine-N-oxide (59.1 mg, 0.36 mmol), SPhosAuNTf₂ (6.6 mg, 2.5 mol%) and 1,4-dioxane (6 mL). The reaction time was 20 hours. ¹H NMR analysis showed a d.r. of 8:1. Purification by column chromatography (3:7 hexane:EtOAc) afforded 10j (66.0 mg, 79%) as a white solid as a single diastereomer. When run on 0.2 mmol scale with SPhosAuNTf₂ (8.8 mg, 5 mol%), 10j (44.0 mg, 79%) was obtained as a single diastereomer after 4 hours. mp: 170-172 °C; ¹H NMR (300 MHz, CDCl₃): δ = 8.48 (s, 1H), 7.99 (d, J = 8.6 Hz, 2H), 7.71 (d, J = 8.6 Hz, 2H), 3.58 (dd, J = 12.9, 7.8, 4.0 Hz, 1H), 2.81 – 2.64 (m, 2H), 2.59 – 2.34 (m, 2H), 2.22 (t, J = 6.0 Hz, 1H), 2.18 (s, 3H), 1.77 (dd, J = 8.6, 6.0 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃): δ = 194.3 (C), 169.1 (C), 143.6 (C), 131.8 (C), 131.1 (2CH), 119.0 (2CH), 59.1 (C), 54.4 (CH₂), 33.0 (CH₃), 26.4 (CH₂), 24.8 (CH), 18.9 (CH₃); IR (neat): ν = 3086, 3039, 2958, 1678, 1662, 1597, 1579, 1286, 1117, 885; HR-MS (ES-TOF): m/z: calcd for C₁₃H₁₂O₃NaS: 300.0670, found 300.0658 [M + Na]+.

(±)-(2-Oxido-2-thiabicyclo[3.1.0]hexan-1-yl)-(4-(trifluoromethyl)phenyl)methanone (10k)

10k was prepared according to GP4 using 9k (54.4 mg, 0.20 mmol), 3,5-dichloropyridine-N-oxide (39.4 mg, 0.24 mmol), SPhosAuNTf₂ (8.8 mg, 5 mol%) and 1,4-dioxane (4 mL). The reaction time was 17 hours. ¹H NMR analysis showed a d.r. of 8:1; Purification by column chromatography (1:1 hexane:EtOAc to EtOAc) afforded 10k (35.6 mg, 63%) as a colourless oil, as a single diastereomer. When run on 0.3 mmol scale with SPhosAuNTf₂ (6.6 mg, 2.5 mol%), 10k (26.0 mg, 30%) was obtained as a single diastereomer after 28 hours. ¹H NMR (300 MHz, CDCl₃): δ = 8.09 (d, J = 8.2 Hz, 2H), 7.77 (d, J = 8.2 Hz, 2H), 3.57 (dd, J = 13.2, 7.3, 4.2 Hz, 1H), 2.82 – 2.64 (m, 2H), 2.55 – 2.36 (m, 2H), 2.31 (t, J = 5.9 Hz, 1H), 1.85 (dd, J = 8.7, 5.9 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃): δ = 196.2 (C), 139.8 (C), 134.7 (q, J = 32.7 Hz, C), 129.8 (2CH), 125.8 (d, J = 3.2 Hz, 2CH), 123.4 (q, J = 272.4 Hz, C), 59.4 (C), 53.8 (CH₃), 34.4 (CH), 26.2 (CH₂), 19.8 (CH₂); IR (neat): ν = 2937, 1673, 1409, 1323, 1279, 1167, 1112, 1063, 855; HR-MS (ES-TOF): m/z: calcd for C₁₃H₁₂O₃NaSF₃: 311.0330, found 311.0327 [M + Na]+.
(t)-Methyl 4-(2-oxido-2-thiabicyclo[3.1.0]hexane-1-carbonyl)benzoate (10l)

10l was prepared according to GP4 using 9l (52.5 mg, 0.20 mmol), 3,5-dichloropyridine-N-oxide (39.4 mg, 0.24 mmol), SPhosAuNTf₂ (8.8 mg, 5 mol%) and 1,4-dioxane (4 mL). The reaction time was 20 hours. ¹H NMR analysis showed a d.r. of 8:1. Purification by column chromatography (3:7 hexane:EtOAc) afforded 10l (35.6 mg, 64%) as an off white solid. When run on 0.3 mmol scale with SPhosAuNTf₂ (6.6 mg, 2.5 mol%), 10l (38.5 mg, 54%) was obtained as a single diastereomer after 28 hours. mp: 63-64 °C; ¹H NMR (300 MHz, CDCl₃): δ = 8.18 – 8.12 (m, 2H), 8.04 – 7.98 (m, 2H), 3.94 (s, 3H), 3.55 (dd, J = 13.2, 7.5, 4.2 Hz, 1H), 2.80 – 2.62 (m, 2H), 2.54 – 2.38 (m, 2H), 2.33 – 2.26 (t, J = 5.9 Hz, 1H), 1.86 (dd, J = 8.7, 5.9 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃): δ = 196.6 (C), 166.2 (C), 140.3 (C), 134.1 (C), 129.9 (2CH), 129.3 (2CH), 59.7 (C), 54.7 (CH₃), 26.3 (CH₂), 19.7 (CH₂); IR (neat): ν = 3493, 3094, 3022, 2960, 2936, 1716, 1665, 1436, 1273, 1031, 763; HR-MS (ES-TOF): m/z: calcd for C₁₃H₁₂O₃NaS: 301.0510, found 301.0500 [M + Na]⁺.

(±)-(4-Fluorophenyl)[2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl)methanone (10m)

10m was prepared according to GP4 using 9m (66.6 mg, 0.30 mmol), 3,5-dichloropyridine-N-oxide (59.1 mg, 0.36 mmol), SPhosAuNTf₂ (13.2 mg, 5 mol%) and 1,4-dioxane (6 mL). The reaction time was 17 hours. ¹H NMR analysis showed a d.r. ratio of 8:1. Purification by column chromatography (3:7 hexane:EtOAc) afforded 10m (53.6 mg, 68%) as a colourless viscous oil, as a single diastereomer. When run on 0.3 mmol scale with SPhosAuNTf₂ (6.6 mg, 2.5 mol%), 10m (38.5 mg, 54%) was obtained as a single diastereomer after 28 hours. ¹H NMR (300 MHz, CDCl₃): δ = 8.15 – 7.99 (m, 2H), 7.23 – 7.10 (m, 2H), 3.56 (dd, J = 13.2, 7.6, 4.1 Hz, 1H), 2.78 – 2.64 (m, 2H), 2.54 – 2.33 (m, 2H), 2.25 (t, J = 5.9 Hz, 1H), 1.76 (dd, J = 8.7, 5.9 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃): δ = 194.8 (C), 166.1 (d, J = 255.8 Hz, C), 133.1 (C), 132.5 (d, J = 9.4 Hz, 2CH), 116.0 (d, J = 22.1 Hz, 2CH), 59.1 (C), 54.2 (CH₃), 33.2 (CH), 26.3 (CH₂), 19.2 (CH₂); IR (neat): ν = 3070, 2937, 1663, 1596, 1506, 1280, 1230, 1027, 844, 609; HR-MS (ES-TOF): m/z: calcd for C₁₂H₁₄O₃FS: 239.0542, found 239.0547 [M + H]⁺.

(±)-3-Methoxyphenyl)[2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl)methanone (10n)

10n was prepared according to GP4 using 9n (46.9 mg, 0.20 mmol), 3,5 dichloropyridine-N-oxide (39.4 mg, 0.24 mmol), SPhosAuNTf₂ (8.8 mg, 5 mol%) and 1,4-dioxane (4 mL). The reaction time was 18 hours. ¹H NMR analysis showed a d.r. ratio of 8:1. Purification by column chromatography (3:7 hexane:EtOAc) afforded 10n (35.0 mg, 70%) as colourless oil as a single diastereomer. When run on 0.3 mmol scale with SPhosAuNTf₂ (6.6 mg, 2.5 mol%), 10n (40.0 mg, 54%) was obtained as a single diastereomer after 28 hours. ¹H NMR (300 MHz, CDCl₃): δ = 7.61 – 7.54 (m, 1H), 7.49 (dd, J = 2.4, 1.7 Hz, 1H), 7.40 (t, J = 7.9 Hz, 1H), 7.13 (dd, J = 8.2, 2.6, 0.9 Hz, 1H), 3.85 (s, 3H), 3.53 (dd, J = 13.2, 7.6, 4.1 Hz, 1H), 2.76 – 2.61 (m, 2H), 2.52 – 2.32 (m, 2H), 2.25 (t, J = 5.9 Hz, 1H), 1.80 (dd, J = 8.7, 5.9 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃): δ = 196.4 (C), 159.8 (C), 138.1 (C), 129.8 (CH), 122.0 (CH), 120.4 (CH), 113.4 (CH), 59.5 (C), 55.6 (CH₃), 54.2 (CH₃), 34.0 (CH), 26.3 (CH₂), 19.4 (CH₂); IR (neat): ν = 2939, 1722, 1663, 1596, 1580, 1279, 1030, 787; HR-MS (ES-TOF): m/z: calcd for C₁₃H₁₄O₃NaS: 273.0561, found 273.0563 [M + Na]⁺.
(±)-4-Bromophenyl)(2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl)methanone (10o)

10o was prepared according to GP4 using 9o (56.6 mg, 0.20 mmol), 3,5-dichloropyridine-N-oxide (39.4 mg, 0.24 mmol), SPhosAuNTf₂ (8.8 mg, 5 mol%) and 1,4-dioxane (4 mL). The reaction time was 3 hours. ¹H NMR analysis showed a d.r. of 8:1. Purification by column chromatography (3:7 hexane:EtOAc) afforded 10o (42.0 mg, 74%) as a white solid as a single diastereomer. When run on 0.3 mmol scale with SPhosAuNTf₂ (6.6 mg, 2.5 mol%), 10o (49.3 mg, 54%) was obtained as a single diastereomer after 28 hours. mp: 78-80 °C; ¹H NMR (300 MHz, CDCl₃): δ = 7.89 – 7.82 (m, 2H), 7.67 – 7.59 (m, 2H), 3.54 (ddd, J = 13.2, 7.5, 4.1 Hz, 1H), 2.78 – 2.61 (m, 2H), 2.53 – 2.32 (m, 2H), 2.25 (t, J = 6.0 Hz, 1H), 1.76 (dd, J = 8.7, 6.0 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃): δ = 195.5 (C), 135.5 (C), 132.1 (2CH), 131.1 (2CH), 128.8 (C), 59.2 (C), 54.0 (CH₂), 33.6 (CH), 26.2 (CH₃), 19.3 (CH₃); IR (neat): ν = 3082, 3068, 2991, 1647, 1410, 1275, 1013, 874, 756; HR-MS (ES-TOF): m/z: calcd for C₁₃H₁₁O₃SNa⁺Br: 320.9561, found 320.9550 [M + Na]⁺.

(±)-2-Bromophenyl)(2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl)methanone (10p)

10p was prepared according to GP4 using 9p (85.0 mg, 0.30 mmol), 3,5-dichloropyridine-N-oxide (59.1 mg, 0.36 mmol), SPhosAuNTf₂ (6.6 mg, 2.5 mol%) and 1,4-dioxane (5 mL). The reaction time was 28 hours. ¹H NMR analysis using 1,2,4,5 tetramethyl benzene as internal standard showed a d.r. of 8:1; Purification by column chromatography (3:7 hexane:EtOAc) afforded 10p (44.3 mg, 50%) as a white solid as a single diastereomer after 28 hours. mp: 120-122 °C; ¹H NMR (300 MHz, CDCl₃): δ = 7.65 – 7.70 (m, 1H), 7.49 – 7.41 (m, 1H), 7.41 – 7.32 (m, 2H), 3.60 – 3.48 (m, 1H), 2.73 – 2.63 (m, 1H), 2.59 – 2.39 (m, 3H), 2.31 – 2.16 (m, 2H); ¹³C NMR (101 MHz, CDCl₃): δ = 199.2 (C), 140.2 (C), 133.0 (CH), 131.9 (CH), 128.4 (CH), 128.0 (CH), 118.4 (C), 60.4 (C), 52.4 (CH₃), 40.2 (CH), 26.6 (CH₃), 19.1 (CH₃); IR (neat): ν = 3049, 3006, 2924, 1662, 1589, 1426, 1326, 1054, 1026, 754; HR-MS (ES-TOF): m/z: calcd for C₁₃H₁₁O₃SNa⁺Br: 320.9561, found 320.9551 [M + Na]⁺.

(±)-2-Isopropylphenyl)(2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl)methanone (10q)

10q was prepared according to GP4 using 9q (49.3 mg, 0.20 mmol), 3,5-dichloropyridine-N-oxide (39.4 mg, 0.24 mmol), SPhosAuNTf₂ (8.8 mg, 5 mol%) and 1,4-dioxane (4 mL). The reaction time was 28 hours. Purification by column chromatography (3:7 hexane:EtOAc) afforded 10q (27.5 mg, 52%) as a colourless oil, as a 7:1 mixture of diastereomers. When run on 0.3 mmol scale with SPhosAuNTf₂ (6.6 mg, 2.5 mol%), 10q (39.4 mg, 50%) was obtained as a 7:1 mixture of diastereomers after 28 hours. ¹H NMR (300 MHz, CDCl₃): δ = 7.41 – 7.32 (m, 2H), 7.29 – 7.24 (m, 1H), 7.21 (dd, J = 6.0, 2.2 Hz, 1H), 3.45 – 3.35 (m, 1H), 3.03 – 2.87 (m, 1H), 2.64 – 2.45 (m, 2H), 2.36 – 2.28 (m, 2H), 2.25 – 2.15 (m, 1H), 1.96 (dd, J = 8.7, 5.7 Hz, 1H), 1.19 (d, J = 6.8 Hz, 3H), 1.14 (d, J = 6.8 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 201.7 (C), 146.4 (C), 137.2 (C), 130.9 (CH), 126.6 (CH), 126.3 (CH), 125.7 (CH), 61.1 (C), 52.4 (CH₂), 37.2 (CH), 30.5 (CH), 26.1 (CH₂), 24.2 (CH₃), 24.0 (CH₃), 19.1 (CH₃); IR (neat): ν = 3039, 3084, 2959, 1677, 1663, 1597, 1579, 1286, 1263, 1056, 762; HR-MS (ES-TOF): m/z: calcd for C₁₅H₁₆O₃SNa⁺Br: 285.0925, found 285.0932 [M + Na]⁺.
(±)-Naphthalen-2-yl(2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl)methanone (10r)

10r was prepared according to GP4 using 9r (50.9 mg, 0.20 mmol), 3,5-dichloropyridine-N-oxide (39.4 mg, 0.24 mmol), SPhosAuNTf₂ (8.8 mg, 5 mol%) and 1,4-dioxane (4 mL). The reaction time was 28 hours. ¹H NMR analysis showed a d.r. ratio of 8:1. Purification by column chromatography (3:7 hexane:EtOAc) afforded 10r (37.7 mg, 70%) as a white solid as a single diastereomer. When run on the same scale with SPhosAuNTf₂ (4.4 mg, 2.5 mol%), 10r (35.1 mg, 65%) was obtained as a single diastereomer after 28 hours. mp: 108-109 °C; ¹H NMR (300 MHz, CDCl₃): δ = 8.65 (s, 1H), 8.09 – 7.83 (m, 4H), 7.67 – 7.52 (m, 2H), 3.56 (dd, J = 13.0, 7.7, 4.2 Hz, 1H), 2.85 – 2.61 (m, 2H), 2.62 – 2.38 (m, 2H), 2.33 (dt, J = 5.9 Hz, 1H), 1.86 (dd, J = 8.6, 5.9 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃): δ = 186.8 (C), 135.8 (C), 132.4 (C), 132.1 (CH), 130.1 (CH), 128.9 (CH), 128.7 (CH), 127.9 (CH), 127.1 (CH), 124.7 (CH), 59.6 (C), 54.5 (CH₂), 33.8 (CH₂), 18.3 (CH₂); HR-MS (ES-TOF): m/z: calcd for C₁₆H₁₃O₂S: 271.0793, found 271.0798 [M + H]⁺.

(±)-Furan-2-yl(2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl)methanone (10s)

10s was prepared according to GP4 using 9s (41.4 mg, 0.21 mmol), 3,5-dichloropyridine-N-oxide (41.0 mg, 0.25 mmol), SPhosAuNTf₂ (9.0 mg, 5 mol%) and 1,4-dioxane (4.2 mL). The reaction time was 28 hours. Purification by column chromatography (1:4 hexane:EtOAc) afforded 10s (33.3 mg, 74%) as a colourless oil; ¹H NMR (300 MHz, CDCl₃): δ = 7.67 – 7.58 (m, 2H), 6.58 (dd, J = 3.7, 1.7 Hz, 1H), 3.57 (dt, J = 13.1, 5.0 Hz, 1H), 2.88 – 2.77 (m, 1H), 2.68 – 2.53 (m, 1H), 2.44 – 2.33 (m, 2H), 2.18 (t, J = 6.1 Hz, 1H), 1.91 (dd, J = 8.6, 6.1 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃): δ = 182.5 (C), 151.5 (C), 147.4 (CH), 120.9 (CH), 112.8 (CH), 58.1 (C), 52.0 (CH₃), 33.8 (CH), 25.5 (CH₂), 18.3 (CH₂); HR-MS (AP-TOF): m/z: calcd for C₁₆H₁₃O₂S: 211.0429, found 211.0425 [M + H]⁺.

(±)-(5-Bromothiophen-2-yl)(2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl)methanone (10t)

10t was prepared according to GP4 using 9t (60.7 mg, 0.21 mmol), 3,5-dichloropyridine-N-oxide (41.0 mg, 0.25 mmol), SPhosAuNTf₂ (9.0 mg, 5 mol%) and 1,4-dioxane (4.2 mL). The reaction time was 28 hours. Purification by column chromatography (1:4 hexane:EtOAc) afforded 10t (44.4 mg, 73%) as a white solid, as a single diastereomer; mp: 116-118 °C; ¹H NMR (300 MHz, CDCl₃): δ = 7.58 (d, J = 5.1 Hz, 1H), 7.13 (d, J = 5.1 Hz, 1H), 3.68 – 3.52 (m, 1H), 2.72 – 2.39 (m, 4H), 2.13 (t, J = 6.2 Hz, 1H), 2.07 (dd, J = 8.3, 6.2 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃): δ = 187.2 (C), 135.1 (C), 132.9 (CH), 132.1 (CH), 115.2 (C), 60.8 (C), 54.5 (CH₂), 36.6 (CH), 27.8 (CH₂), 16.8 (CH₂); IR (neat): ν = 3082, 3068, 2989, 1650, 1411, 1277, 1011, 755; HR-MS (ES-TOF): m/z: calcd for C₁₆H₁₃O₂SBr₂: 326.9125, found 326.9129 [M + Na]⁺.

(±)-2-(Allyloxy)-1-(2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl)ethan-1-one (10u)

10u was prepared according to GP4 using 9u (39.7 mg, 0.20 mmol), 3,5-dichloropyridine-N-oxide (39.4 mg, 0.24 mmol), SPhosAuNTf₂ (8.8 mg, 5 mol%) and 1,4-dioxane (4 mL). The reaction time was 21 hours. Purification by column chromatography (EtOAc to 1:9 MeOH:EtOAc) afforded 10u (27.0
mg, 63%) as a colourless oil as a 10:1 mixture of diastereomers; 1H NMR (300 MHz, CDCl3): δ = 5.92 (ddt, J = 17.0, 10.4, 5.8 Hz, 1H), 5.37 – 5.17 (m, 2H), 4.64 (d, J = 17.0 Hz, 1H), 4.52 (d, J = 17.0 Hz, 1H), 4.11 – 4.05 (m, 2H), 3.52 (dt, J = 13.1, 5.2 Hz, 1H), 2.63 – 2.48 (m, 2H), 2.32 (dd, J = 5.9, 4.4, 2.0 Hz, 2H), 2.14 – 2.06 (m, 1H), 1.94 (dd, J = 8.6, 5.7 Hz, 1H); 13C NMR (101 MHz, CDCl3): δ = 200.4 (C), 133.5 (CH), 118.8 (CH2), 74.4 (CH2), 72.7 (CH2), 58.1 (C), 52.3 (CH3), 36.9 (CH), 25.9 (CH2), 18.6 (CH3); IR (neat): ν = 3451, 2935, 1703, 1423, 1250, 1140, 1092, 992, 730; HR-MS (AP-TOF): m/z: calcd for C10H15O2S: 215.0742, found 215.0746 [M + H]+.

(±)-2-(Cinnamylxoy)-1-(2-oxido-2-thiabicyclo[3.1.0]hexan-1-yl)ethan-1-one (10v)

10v was prepared according to GP4 using 9v (54.8 mg, 0.20 mmol), 3,5-dichloropyridine-N-oxide (39.4 mg, 0.24 mmol), SPhosAuNTf2 (8.8 mg, 5 mol%) and 1,4-dioxane (4 mL). The reaction time was 21 hours. Purification by column chromatography (EtOAc to 1:19 MeOH:EtOAc) afforded 10v (38.0 mg, 65%) as a white semi-solid, as a 10:1 mixture of diastereomers; 1H NMR (300 MHz, CDCl3): δ = 7.46 – 7.22 (m, 5H), 6.64 (d, J = 16.0 Hz, 1H), 6.30 (dt, J = 16.0, 6.3 Hz, 1H), 4.71 (d, J = 17.0 Hz, 1H), 4.60 (d, J = 17.0 Hz, 1H), 4.36 – 4.19 (m, 2H), 3.59 – 3.48 (m, 1H), 2.65 – 2.50 (m, 2H), 2.38 – 2.26 (m, 2H), 2.16 – 2.07 (m, 1H), 1.95 (dd, J = 8.6, 5.7 Hz, 1H); 13C NMR (101 MHz, CDCl3): δ = 200.5 (C), 136.3 (C), 134.1 (CH), 128.7 (2CH2), 128.1 (CH), 126.7 (2CH), 124.7 (CH), 74.4 (CH2), 72.4 (CH2), 58.1 (C), 52.2 (CH2), 37.0 (CH), 25.9 (CH2), 18.8 (CH3); IR (neat): ν = 2934, 1704, 1495, 1449, 1248, 1137, 1093, 1058, 1031, 968, 872, 735, 693; HR-MS (AP-TOF): m/z: calcd for C16H19O3S: 291.0555, found 291.0559 [M + H]+.

1-Isopropyl-2-((methylsulfinyl)ethyl)benzene (12)

1-Isopropyl-2-((methylsulfinyl)ethyl)benzene (12) was prepared according to GP3 from S3 (74.1 mg, 0.39 mmol), mCPBA (67.3 mg, 0.39 mmol) and CH2Cl2 (4 mL). The reaction time was 2 hours. Aqueous workup and purification by column chromatography (4:1 hexane:EtOAc) provided 12 (60.3 mg, 75%) as a colourless oil which was used directly in the catalysis according to GP4: 12 (41.2 mg, 0.20 mmol), 3,5-dichloropyridine-N-oxide (39.4 mg, 0.24 mmol), SPhosAuNTf2 (4.4 mg, 2.5 mol%) and 1,4-dioxane (4 mL). The reaction time was 24 hours. Purification by column chromatography (7:3 hexane:EtOAc) afforded 13 (9.0 mg, 22%) as an off white solid; mp: 104-106 °C; 1H NMR (300 MHz, CDCl3): δ = 7.51 (ddd, J = 15.2, 7.6, 1.3 Hz, 2H), 7.42 – 7.30 (m, 2H), 5.29 – 5.26 (m, 1H), 4.90 (d, J = 0.5 Hz, 1H), 4.33 (d, J = 14.3 Hz, 1H), 4.14 (d, J = 14.8 Hz, 1H), 2.76 (s, 3H), 2.18 (dd, J = 1.3, 0.9 Hz, 3H); 13C NMR (101 MHz, CDCl3): δ = 197.2 (C), 144.8 (C), 143.2 (C), 137.9 (C), 132.2 (CH), 128.8 (CH), 128.7 (CH), 127.9 (CH), 118.2 (CH2), 65.4 (CH2), 40.0 (CH2), 24.0 (CH3); IR (neat): ν = 2916, 1679, 1594, 1288, 1039, 770; HR-MS (ES-TOF): m/z: calcd for C12H14O2S: 222.0715, found 222.0713 [M + H]+.

(±)-Cyclopropyl(2-oxido-2-phenyl-2-thiabicyclo[3.1.0]hexan-1-yl)methane (15)

Prepared according to GP4 using sulfoxide 14 (97.7 mg, 0.40 mmol), 3,5-dichloropyridine-N-oxide (78.6 mg, 0.48 mmol), SPhosAuNTf2 (17.6 mg, 5 mol%) and dioxane (8 mL). The reaction time was 3 hours. Purification by column chromatography (1:1 hexane:EtOAc) to (2:1 hexane:EtOAc) afforded 15 (41.6 mg, 40%) as a white solid, stereochemistry is undefined; mp: 107-108 °C; 1H NMR (400 MHz, CDCl3): δ = 7.35 – 7.22 (m, 5H), 3.77 (d, J = 6.8 Hz, 1H), 3.58 (dt, J = 13.1, 5.8 Hz, 1H), 3.17 (dt, J = 6.8, 3.3 Hz, 1H), 2.83 – 2.70 (m, 1H), 2.61 – 2.50 (m, 2H), 2.39 – 2.28 (m, 1H), 1.07
- 0.94 (m, 1H), 0.92 – 0.83 (m, 1H), 0.82 – 0.71 (m, 1H), 0.67 – 0.58 (m, 1H); 
13C NMR (101 MHz, CDCl3): δ = 201.1 (C), 133.3 (C), 129.2 (2CH), 128.4 (CH), 127.7 (2CH), 68.3 (C), 53.6 (CH3), 35.4 (CH), 33.9 (CH), 27.1 (CH2), 21.3 (CH), 12.6 (CH2), 12.2 (CH3); IR (neat): ν = 2983, 2941, 2871, 1659, 1601, 1497, 1447, 1396, 1249, 1218, 1058, 1032, 968, 896, 747, 702; HR-MS (ES-TOF): m/z: calcd for C9H11O4NaS: 283.0769, found 283.0775 [M + Na]+.

(±)-Cyclopropyl[3-(hydroxy(phenyl)methyl)-1-oxidotetrahydrothiophen-2-yl)methanone (16)

The relative stereochemistry of 16 at the benzylic position was assigned assuming a stereospecific hydrative cyclisation of the alkene which appears consistent with the data. Prepared from the same reaction eluting with (EtOAc) yielding 16 (24.5 mg, 22%); mp: 94-95 °C; 1H NMR (400 MHz, CDCl3): δ = 7.37 (dt, J = 15.1, 7.4 Hz, 4H), 7.27 (t, J = 6.3 Hz, 1H), 4.86 (t, J = 5.1 Hz, 1H), 4.24 (dd, J = 4.7, 1.5 Hz, 1H), 3.74 (d, J = 4.7 Hz, 1H), 3.22 – 3.05 (m, 2H), 2.78 – 2.60 (m, 2H), 2.44 – 2.29 (m, 1H), 1.69 (dd, J = 12.4, 7.8, 4.6 Hz, 1H), 1.00 – 0.80 (m, 4H); 13C NMR (101 MHz, CDCl3): δ = 205.4 (C), 143.7 (C), 128.8 (2CH), 127.9 (CH), 126.0 (2CH), 80.0 (CH), 74.8 (CH), 53.1 (CH3), 52.2 (CH), 29.6 (CH2), 21.3 (CH), 12.4 (CH3), 12.3 (CH2); IR (neat): ν = 3314, 3063, 3011, 2935, 1677, 1604, 1380, 1063, 1028, 1041, 998, 760, 703; HR-MS (ES-TOF): m/z: calcd for C16H16O6SNa: 301.0874, found 301.0878 [M + Na]+.

(±)-1-(Phenylsulfinyl)bicyclo[3.1.0]hexan-2-one (18 and 18’)

18/18’ were prepared according to GP4 using 17 (40.8 mg, 0.20 mmol), 3,5-dichloropyridine-N-oxide (39.4 mg, 0.12 mmol), SPhosAuNTf2 (8.8 mg, 5 mol%) and 1,4-dioxane (4 mL). The reaction time was 20 hours. 1H NMR analysis using 1,2,4,5-tetramethylbenzene as internal standard showed the formation of 18/18’ (62%) as a 1:6:1 mixture of diastereomers. Structure elucidation of 18/18’ was achieved by separation of mixed fractions using column chromatography (2:1 hexane:EtOAc) to afford: diastereomer 1 as an oily solid; 1H NMR (300 MHz, CDCl3): δ = 7.82 – 7.74 (m, 2H), 7.50 (dd, J = 5.0, 1.9 Hz, 3H), 2.80 – 2.70 (m, 2H), 2.38 – 2.23 (m, 6H), 2.13 – 2.01 (m, 2H), 1.75 (dd, J = 8.6, 5.3 Hz, 2H), 1.24 (t, J = 5.3 Hz, 3H); 13C NMR (101 MHz, CDCl3): δ = 208.4 (C), 143.5 (C), 131.3 (CH), 129.1 (2CH), 124.7 (2CH), 54.3 (C), 34.3 (CH2), 30.3 (CH), 21.5 (CH3), 15.4 (CH2); IR (neat): ν = 3059, 2946, 2879, 1718, 1582, 1477, 1443, 1276, 1083, 1041, 1022, 749, 689; HR-MS (ES-TOF): m/z: calcd for C12H13O2S: 221.0636, found 221.0638 [M + H]+; and then diastereomer 2 as a colourless oil; 1H NMR (300 MHz, CDCl3): δ = 7.68 – 7.58 (m, 2H), 7.52 – 7.46 (m, 3H), 2.44 (dt, J = 8.7, 5.0 Hz, 1H), 2.29 – 1.91 (m, 4H), 1.90 – 1.74 (m, 1H), 1.48 (t, J = 5.3 Hz, 1H); 13C NMR (101 MHz, CDCl3): δ = 208.5 (C), 143.2 (C), 131.5 (CH), 129.2 (2CH), 124.6 (2CH), 55.4 (C), 33.6 (CH2), 26.5 (CH), 21.1 (CH3), 18.8 (CH2); IR (neat): ν = 3060, 2944, 2880, 1721, 1582, 1476, 1443, 1274, 1084, 1030, 956, 748, 690; HR-MS (ES-TOF): m/z: calcd for C12H13O2S: 221.0636, found 221.0631 [M + H]+.

(±)-(2,2-Dioxido-2-thiabicyclo[3.1.0]hexan-1-yl)(phenyl)methanone (6b)

6b was prepared according to GP4 using 4b (66.0 mg, 0.30 mmol), 3,5-dichloropyridine-N-oxide (59.1 mg, 0.36 mmol), SPhosAuNTf2 (6.6 mg, 2.5 mol%) and 1,4-dioxane (6 mL). The reaction time was 28 hours. Purification by column chromatography (7:3 hexane:EtOAc), followed by recrystallisation from hot EtOH afforded 6b (56.0 mg, 79%) as a white solid; mp: 118-119 °C (EtOH); 1H NMR (300 MHz, CDCl3): δ = 8.18 – 8.09 (m, 2H), 7.68 – 7.58 (m, 1H), 7.56 – 7.46 (m, 2H), 3.34 – 3.03 (m,
2H), 2.79 (dt, J = 8.6, 5.7 Hz, 1H), 2.63 – 2.46 (m, 1H), 2.32 (dd, J = 13.7, 7.7 Hz, 1H), 1.85 (t, J = 6.6 Hz, 1H), 1.77 – 1.68 (m, 1H); 13C NMR (101 MHz, CDCl₃): δ = 190.7 (C), 136.5 (C), 134.3 (CH), 129.7 (2CH), 128.8 (2CH), 50.6 (C), 48.6 (CH₂), 25.4 (CH), 19.7 (CH₂), 18.4 (CH₃); IR (neat): ν = 3039, 3086, 2958, 1678, 1662, 1597, 1452, 1302, 1286, 1117, 885; HR-MS (ES-TOF): m/z: calcd for C₁₂H₁₂O₃NaS: 259.0405, found 259.0416 [M + Na]⁺.

**Crystal Structure Determination of 10g:**

**Crystal Data** for C₁₂H₁₂O₃S (M = 220.28 g/mol): triclinic, space group P-1 (no. 2), a = 6.2782(3) Å, b = 7.1917(3) Å, c = 12.4920(6) Å, α = 86.275(4)°, β = 75.966(4)°, γ = 66.086(4)°, V = 499.87(4) Å³, Z = 2, T = 100.01(11) K, μ(CuKα) = 2.667 mm⁻¹, Dcalc = 1.463 g/cm³, 7653 reflections measured (7.3° ≤ 2θ ≤ 144.236°), 1939 unique (Rint = 0.0218, Rsigma = 0.0170) which were used in all calculations. The final R1 was 0.0390 (I > 2σ(I)) and wR2 was 0.0963 (all data).

![Structure of 10g](image)

**Fig. S1:** Crystal structure of 10g with ellipsoids drawn at the 50% probability level.

The dataset was measured on an Agilent SuperNova diffractometer using an Atlas detector. The data collection was driven and processed and an absorption correction was applied using CrysAlisPro.²⁴ The structure was solved using ShelXS²⁵ and refined by a full-matrix least-squares procedure on F² in ShelXL.²⁵ All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on the equivalent isotropic displacement parameter (Ueq) of the parent atom. Figures and reports were produced using OLEX2.²⁶

The CIF for the crystal structure of 10g has been deposited with the CCDC and have been given the deposition number CCDC 1528851. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
References

$^1\text{H NMR and }^{13}\text{C NMR Spectra of New Compounds}$
Alkynyl Thioethers
MeO

S

S2n
Alkynyl Sulfoxides

Diagram of 9a
18/18' Diastereomer 1
18/18' Diastereomer 2
Reaction of an Alkynyl Sulfone