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Supplementary material for

Unified Gold-Catalyzed Cyclization Approach towards Isothiazoles from Propargylic Sulfinamides

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Experimental details and characterization data for Compounds:

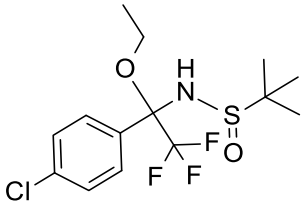
General Remarks

All chemicals and solvents were purchased from commercial suppliers and used without further purification unless specified.

Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR spectra were recorded at 25 °C using CDCl3 or DMSO-d6 as deuterated solvent. All chemical shifts are reported in δ-scale as parts per million [ppm] (multiplicity, coupling constant J, number of protons), relative to the solvent residual peaks as the internal standard. Coupling constants J are given in Hertz [Hz]. Besides 1H, 13C and 19F experiments. The following abbreviations were used to describe the signals: s (singlet), d (doublet), t (triplet), q (quartet), pent (pentet), sext (sextet), hept (heptet), m (multiplet), br (broad signal).

Substrates Preparation



2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-1-ethoxy-2,2,2-trifluoro-ethyl]-amide:

To a stirred solution of 4'-chloro-2,2,2-trifluoroacetophenone (3.0 g, 14 mmol) and $Ti(OEt)_4$ (9.3 mL, 40 mmol) in THF (110 mL) was added under argon *tert-butylsulfinamide* (3.50 g, 28 mmol). The reaction mixture was stirred at 50 °C over the week-end, then cooled to 0°C and poured into dichloromethane (250 mL) at 0°C. 10 mL of water was added slowly to the reaction mixture. During the addition, a large amount of precipitate was formed. The mixture was filtered, the filtrate was dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (cyclohexane/ethyl acetate = 4:1) gave 2.244 g of the title compound in 50% yield.

First diastereomer:

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.26 - 1.33 (s, 9 H) 1.34 - 1.38 (m, 3 H) 3.91 (s, 1 H) 4.65 (s, 1 H) 7.34 - 7.41 (m, 2 H) 7.62 (m, *J*=8.44 Hz, 2 H).

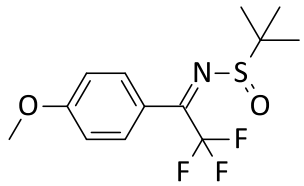
^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -77.70 (s, CF_3)

^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 15.02 (s, CH_3) 22.66 (s, CH_3) 57.44 (s, Cq) 60.41 (s, CH_2) 76.68 (s, C) 88.92-89.20 (q, Cq) 121.57-124.46 (q, Cq) 128.19 (s, CH) 130.59 (s, CH) 132.04 (s, Cq) 136.01 (s, Cq)

Second diastereomer:

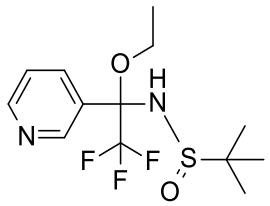
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.27 - 1.36 (m, 12 H) 3.40 (dd, *J*=8.44, 6.97 Hz, 1 H) 3.82 - 3.98 (m, 1 H) 4.24 (s, 1 H) 7.40 - 7.53 (m, 4 H)

^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -78.33 (s, CF_3)



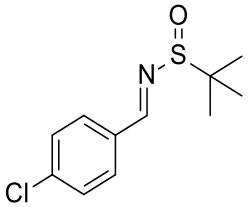
2-Methyl-propane-2-sulfinic acid [2,2,2-trifluoro-1-(4-methoxy-phenyl)-ethylidene]-amide

To a stirred solution of 4'-methoxy-2,2,2-trifluoroacetophenone (3.14 g, 14.7 mmol) and $Ti(OEt)_4$ (9.5 mL, 44.1 mmol) in THF (110 mL) was added under argon *tert-butylsulfinamide* (3.6 g, 29.4 mmol). The reaction mixture was stirred at 50 °C overnight, then cooled to 0°C and poured into dichloromethane (250 mL) at 0°C. 10 mL of water was added slowly to the reaction mixture. During the addition, a large amount of precipitate was formed. The mixture was filtered, the filtrate was dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (cyclohexane/ethyl acetate = 85:15) gave 1.500 g of the title compound in 30% yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.32 (s, 9 H) 3.85 (s, 3 H) 6.92 - 7.00 (m, 2 H) 7.49 (d, *J*=8.44 Hz, 2 H)
^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -69.16 (s, CF_3)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 22.56 (s, CH3) 55.33 (s, CH3) 59.28 (s, Cq) 113.51 (s, CH) 114.45 (q, Cq) 114.69-117.72 (q, Cq) 121.69 (s, Cq) 130.55 (s, CH) 161.99 (s, Cq)

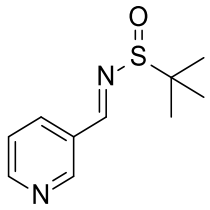


2-Methyl-propane-2-sulfinic acid (1-ethoxy-2,2,2-trifluoro-1-pyridin-3-yl-ethyl)-amide
To a stirred solution of 3-(Trifluoroacetyl) pyridine (4.7 g, 27 mmol) and $Ti(OEt)_4$ (28 g, 120 mmol) in THF (160 mL) was added under argon *tert-butylsulfinamide* (10 g, 80 mmol). The reaction mixture was stirred at 50 °C overnight, then cooled to 0°C and poured into dichloromethane (300 mL) at 0°C. 25 mL of water was added slowly to the reaction mixture. During the addition, a large amount of precipitate was formed. The mixture was filtered; the filtrate was dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (100 % of ethyl acetate) gave 1.136 g of the title compound in pure form (13% yield) and another 1.172 g as a mixture with the starting material (26% total yield).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.31 (s, 9 H) 1.36 (t, *J*=6.79 Hz, 3 H) 4.76 (s, 1 H) 7.30 - 7.40 (m, 1 H) 8.65 (dd, *J*=4.77, 1.47 Hz, 1 H) 8.83 - 8.89 (m, 1 H)
^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -69.16 (s, CF_3)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 14.15 (s, CH_3) 22.61 (s, CH_3) 57.57 (s, Cq) 60.36 (s, CH_2) 88.30-88.59 (q, Cq) 121.43-129.69 (q, Cq) 122.81 (s, CH) 136.88 (s, Cq) 150.43 (s, CH) 150.55 (s, CH)



2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-methylidene]-amide
To a stirred solution of 4'-chlorobenzaldehyde (11.2 g, 80 mmol) and $Ti(OEt)_4$ (35 mL, 160 mmol) in THF (160 mL) was added under argon *tert-butylsulfinamide* (11 g, 88 mmol). The reaction mixture was stirred at 50 °C for 1h, then cooled to 0°C and poured into dichloromethane (1L) at 0°C. 10 mL of water was added slowly to the reaction mixture. During the addition, a large amount of precipitate was formed. The mixture was filtered; the filtrate was dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (cyclohexane/ ethyl acetate = 7:3) gave 15.80 g of the title compound in 82% yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.27 (s, 9 H) 7.42 - 7.51 (m, 2 H) 7.76 - 7.84 (m, 2 H) 8.56 (s, 1 H)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 22.60 (s, CH3) 57.90 (s, Cq) 129.31 (s, CH) 130.50 (s, CH) 132.52 (s, Cq) 138.63 (s, Cq) 161.49 (s, CH)

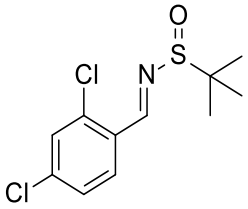


2-Methyl-propane-2-sulfinic acid [1-pyridin-3-yl-methylidene]-amide

To a stirred solution of 3-pyridinecarboxaldehyde (3.0 mL, 31 mmol) and $Ti(OEt)_4$ (12.5 mL, 59 mmol) in THF (200 mL) was added under argon tert-butylsulfinamide (4.22 g, 34.1 mmol). The reaction mixture was stirred at 50 °C for 1h30, then cooled to 0°C and poured into dichloromethane (400 mL) at 0°C. 15 mL of water was added slowly to the reaction mixture. During the addition, a large amount of precipitate was formed. The mixture was filtered; the filtrate was dried over $MgSO_4$ and concentrated in vacuo. Purification by chromatography on silica gel (100% ethyl acetate) gave 6.4 g of the title compound in 98% yield.

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.16 (s, 9 H) 7.32 (dd, *J*=8.07, 4.77 Hz, 1 H) 8.07 (dt, *J*=7.89, 2.11 Hz, 1 H) 8.54 (s, 1 H) 8.63 (dd, *J*=4.77, 1.83 Hz, 1 H) 8.92 (d, *J*=1.83 Hz, 1 H)

^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 22.33 (s, CH3) 57.80 (s, Cq) 123.66 (s, CH) 129.38 (s, Cq) 135.38 (s, CH) 150.72 (s, CH) 152.64 (s, CH) 160.15 (s, CH)

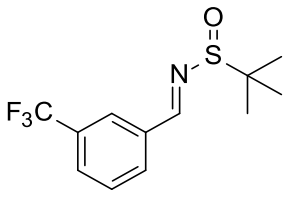


N-(2,4-dichlorobenzylidene)-2-methylpropane-2-sulfinamide

To a stirred solution of 2,4-dichlorobenzaldehyde (2.03 g, 11.6 mmol) in anhydrous THF (13 mL) was added under argon tert-butylsulfinamide (1.35 g, 11.1 mmol) and a solution of tetraethoxytitanium (5.34 g, 23.4 mmol) in anhydrous THF (10 mL). The reaction mixture was stirred at 50 °C for 4 h then it was cooled to room temperature and poured in 100 mL brine. A large amount of precipitate was formed. The mixture was filtered on a Celite pad and extracted once with ethyl acetate. The organic layer was washed once with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum to give 2.709 g of the title compound in 84 % yield.

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.28 (s, 9 H) 7.34 (d, J=8.44 Hz, 1 H) 7.49 (s, 1 H) 8.01 (d, J=8.44 Hz, 1 H) 8.98 (s, 1 H)

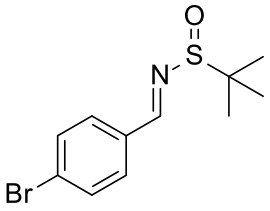
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 22.68 (s, 3 C) 58.14 (s, 1 C) 127.70 (s, 1 C) 129.96 (s, 1 C) 130.06 (s, 1 C) 130.16 (s, 1 C) 137.08 (s, 1 C) 138.81 (s, 1 C) 158.73 (s, 1 C)



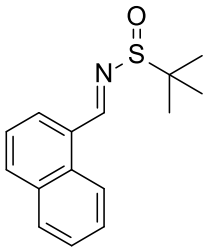
N-(3-trifluoromethylbenzylidene)-2-methylpropane-2-sulfinamide

To a stirred solution of 3-trifluoromethylbenzaldehyde (5.2 mL, 39 mmol) in anhydrous THF (10 mL) was added under argon tert-butylsulfinamide (4.68 g, 38.6 mmol) and a solution of tetraethoxytitanium (18.1 g, 79.3 mmol) in anhydrous THF (50 mL). The reaction mixture was stirred at 50 °C for 1 h then it was cooled to room temperature and poured in 200 mL brine. A large amount of precipitate was formed. The mixture was filtered on a Celite pad and extracted once with ethyl acetate. The organic layer was washed twice with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum to give 7.847 g of the title compound in 72 % yield.

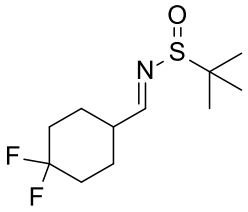
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.29 (s, 9 H) 7.63 – 7.68 (m, 1 H) 7.77 (d, J=7.70Hz, 1 H) 8.02 (d, J=7.70 Hz, 1 H) 8.14 (s, 1 H) 8.65 (s, 1 H)
^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -62.90 (s, 3 F)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 22.65 (s, 3 C) 58.11 (s, 1 C) 125.02 (q, J=272.48 Hz, 1 C) 125.68 (d, J=3.96 Hz, 1 C) 128.74 (d, J=3.96 Hz, 1 C) 129.59 (s, 1 C) 131.70 (q, J=32.70 Hz, 1 C) 132.62 (s, 1 C) 134.70 (s, 1 C) 161.47 (s, 1 C)



N-(4-bromobenzylidene)-2-methylpropane-2-sulfinamide
To a stirred solution of 4-bromobenzaldehyde (4.99 g, 27.0 mmol) in anhydrous THF (30 mL) was added under argon tert-butylsulfinamide (3.30 g, 27.2 mmol) and a solution of tetraethoxytitanium (12.7 g, 55.6 mmol) in anhydrous THF (18 mL). The reaction mixture was stirred at 50 °C for 2 h then it was cooled to room temperature and poured in 100 mL brine. A large amount of precipitate was formed. The mixture was filtered on a Celite pad and extracted once with ethyl acetate. The organic layer was washed twice with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. Purification by chromatography on silica gel (cyclohexane / ethyl acetate = 8:2) gave 7.204 g of the title compound in 92 % yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.27 (s, 9 H) 7.59 – 7.66 (m, 2 H) 7.69 – 7.76 (m, 2 H) 8.55 (s, 1 H)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 22.17 (s, 3 C) 57.34 (s, 1 C) 126.71 (s, 1 C) 130.19 (s, 2 C) 131.79 (s, 2 C) 132.43 (s, 1 C) 161.06 (s, 1 C)

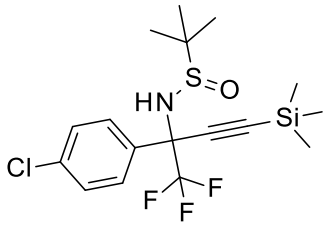


N-(naphthalene-1-ylmethylene)-2-methylpropane-2-sulfinamide
To a stirred solution of naphthalene-1-carbaldehyde (4.4 mL, 32 mmol) in anhydrous THF (20 mL) was added under argon tert-butylsulfinamide (3.87 g, 31.9 mmol) and a solution of tetraethoxytitanium (15 g, 65.8 mmol) in anhydrous THF (40 mL). The reaction mixture was stirred at 50 °C for 2 h then it was cooled to room temperature and poured in 200 mL brine. A large amount of precipitate was formed. The mixture was filtered on a Celite pad and extracted once with ethyl acetate. The organic layer was washed twice with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. Purification by chromatography on silica gel (cyclohexane / ethyl acetate = 9:1) gave 6.618 g of the title compound in 79 % yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.34 (s, 9 H) 7.56 – 7.62 (m, 2 H) 7.66 – 7.71 (m, 1 H) 7.94 (d, J=8.07 Hz, 1 H) 8.05 (dd, J=10.82 Hz, 7.52 Hz, 2 H) 9.05 (d, J=8.80 Hz, 1 H) 9.17 (s, 1 H)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 22.64 (s, 3 C) 57.68 (s, 1 C) 124.38 (s, 1 C) 125.23 (s, 1 C) 126.49 (s, 1 C) 128.01 (s, 1 C) 128.83 (s, 1 C) 129.47 (s, 1 C) 131.27 (s, 1C) 131.92 (s, 1 C) 133.26 (s, 1 C) 133.93 (s, 1 C) 162.50 (s, 1 C)

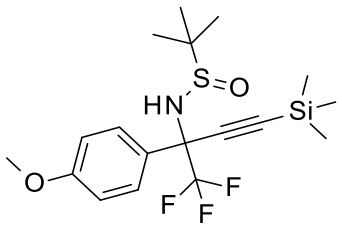


N-((4,4-difluorocyclohexyl)methylene)-2-methylpropane-2-sulfinamide
To a stirred solution of 4,4-difluorocyclohexanecarbaldehyde (3.16 g, 21 mmol) in anhydrous THF (21 mL) was added under argon tert-butylsulfinamide (2.70 g, 22.3 mmol) and a solution of tetraethoxytitanium (9.90 g, 43.4 mmol) in anhydrous THF (21 mL). The reaction mixture was stirred at 50 °C for 2 h then it was cooled to room temperature and poured in 100 mL brine. A large amount of precipitate was formed. The mixture was filtered on a Celite pad and extracted once with ethyl acetate. The organic layer was washed twice with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. Purification by chromatography on silica gel (cyclohexane / ethyl acetate = 8:2) gave 4.416 g of the title compound in 82 % yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.21 (s, 9 H) 1.66 – 1.94 (m, 4 H) 1.97 – 2.07 (m, 2 H) 2.09 – 2.23 (m, 2 H) 2.48 – 2.65 (m, 1 H) 8.02 (d, J=3.67 Hz, 1 H)
^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -100.04 (d, J=240.04 Hz, 1 F) -92.90 (d, J=240.04 Hz, 1 F)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 22.16 (s, 3 C) 24.84 – 25.34 (m, 2 C) 31.98 – 32.83 (m, 2 C) 41.15 (s, 1 C) 56.52 (s, 1 C) 119.98 – 125.19 (t, J=240.04 Hz, 1 C) 170.17 (s, 1 C)

Preparation of propargylsulfinamides

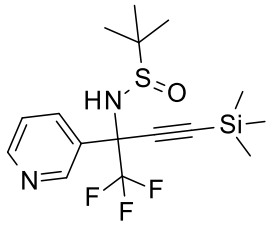


2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-1-trifluoromethyl-3-trimethylsilanyl-prop-2-ynyl]-amide
To a stirred suspension of Mg (500 mg) in anhydrous THF (50 mL) was added at 0°C under argon ethyl bromide (1.6 mL) and the suspension was stirred at room temperature until the solution has darkened and no Mg was left. The solution was then cooled at 0°C and ethynyltrimethylsilane (3.0 mL) was added. After 20 min of stirring at room temperature, a solution of 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-1-ethoxy-2,2,2-trifluoro-ethyl]-amide (2.24 g) in anhydrous THF (15 mL) was transferred using a cannula into the flask and the reaction mixture was stirred at 50 °C during 24h. The reaction mixture was then cooled to 0°C and a saturated solution of NH_4Cl was added. The solution was extracted with water; the organic layer was washed with brine and the aqueous layer with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (cyclohexane/ethyl acetate = 4:1) gave 2.20 g of the title compound in 88% yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 0.21 - 0.34 (s, 9 H) 1.23 (s, 9 H) 3.92 (s, 1 H) 7.36 - 7.45 (m, 2 H) 7.70 (m, *J*=8.80 Hz, 2 H)
^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -77.77 (s, CF_3)

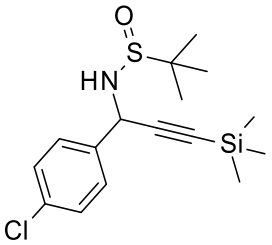


2-Methyl-propane-2-sulfinic acid [1-(4-methoxy-phenyl)-1-trifluoromethyl-3-trimethylsilanyl-prop-2-ynyl]-amide

To a stirred suspension of Mg (41 mg) in anhydrous THF (4 mL) was added at 0°C under argon ethyl bromide (0.12 mL) and the suspension was stirred at room temperature until the solution has darkened and no Mg was left. The solution was then cooled at 0°C and ethynyltrimethylsilane (0.23 mL) was added. After 20 min of stirring at room temperature, a solution of 2-Methyl-propane-2-sulfinic acid [2,2,2-trifluoro-1-(4-methoxy-phenyl)-ethylidene]-amide (150 mg) in anhydrous THF (1.5 mL) was transferred using a cannula into the flask and the reaction mixture was stirred at room temperature during 1h. The reaction mixture was then cooled to 0°C and a saturated solution of NH_4Cl was added. The solution was extracted with water; the organic layer was washed with brine and the aqueous layer with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (cyclohexane/ethyl acetate = 4:1) gave 91 mg of the title compound in 50% yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 0.24 - 0.31 (s, 9 H) 1.22 (s, 9 H) 1.27 (s, 1 H) 3.80 - 3.87 (m, 3 H) 3.94 (s, 1 H) 6.89 - 6.97 (m, 2 H) 7.67 (m, *J*=8.80 Hz, 2 H)
^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -76.75 (s, CF_3)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) -0.60 (s, CH3) 22.50 (s, CH3) 55.24 (s, CH3) 57.19 (s, Cq) 62.96 (q, Cq) 96.70 (s, Cq) 98.57 (s, Cq) 113.62 - 122.25 (q, Cq) 124.48 (s, Cq) 130.33 (s, CH) 160.52 (s, Cq).

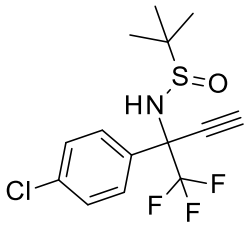


2-Methyl-propane-2-sulfinic acid (1-pyridin-3-yl-1-trifluoromethyl-3-trimethylsilanyl-prop-2-ynyl)-amide
To a stirred suspension of Mg (127 mg) in anhydrous THF (15 mL) was added at 0°C under argon ethyl bromide (0.38 mL) and the suspension was stirred at room temperature until the solution has darkened and no Mg was left. The solution was then cooled at 0°C and ethynyltrimethylsilane (0.72 mL) was added. After 20 min of stirring at room temperature, a solution of 2-Methyl-propane-2-sulfinic acid (1-ethoxy-2,2,2-trifluoro-1-pyridin-3-yl-ethyl)-amide (490 mg) in anhydrous THF (3 mL) was transferred using a cannula into the flask and the reaction mixture was stirred at room temperature during 30 min. The reaction mixture was then cooled to 0°C and a saturated solution of NH_4Cl was added. The solution was extracted with water; the organic layer was washed with brine and the aqueous layer with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (100% ethyl acetate) gave 499 mg of the title compound in 76% yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 0.19 - 0.29 (s, 9 H) 1.22 (s, 9 H) 4.06 (s, 1 H) 7.35 (dd, *J*=8.07, 4.77 Hz, 1 H) 8.05 (d, *J*=8.07 Hz, 1 H) 8.66 (dd, *J*=4.77, 1.47 Hz, 1 H) 8.94 - 9.05 (m, 1 H)
^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -76.74 (s, CF_3)

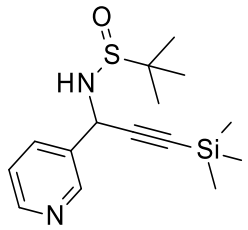


2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-3-trimethylsilanyl-prop-2-ynyl]-amide
To a stirred suspension of Mg (110 mg) in anhydrous THF (17 mL) was added at 0°C under argon ethyl bromide (0.32 mL) and the suspension was stirred at room temperature until the solution has darkened and no Mg was left. The solution was then cooled at 0°C and ethynyltrimethylsilane (0.61 mL) was added. After 20 min of stirring at room temperature, a solution of 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-methylidene]-amide (500 mg) in anhydrous THF (5 mL) was transferred using a cannula into the flask and the reaction mixture was stirred at room temperature for 4h. The reaction mixture was

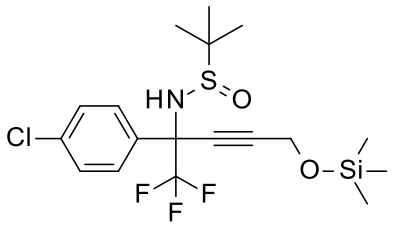
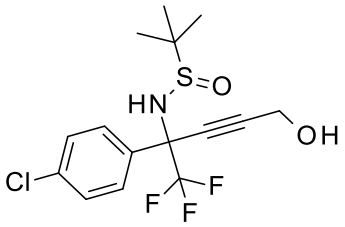
then cooled to 0°C and a saturated solution of NH_4Cl was added. The solution was extracted with water; the organic layer was washed with brine and the aqueous layer with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (cyclohexane/ethyl acetate = 4:1) gave 346 mg of the title compound in 48% yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 0.17 - 0.22 (m, 9 H) 1.21 (s, 9 H) 3.67 (d, 1 H) 5.22 (d, *J*=4.77 Hz, 1 H) 7.32 - 7.37 (m, 2 H) 7.41 - 7.46 (m, 2 H)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) -0.26 (s, CH3) 22.51 (s, CH3) 50.24 (s, CH) 56.37 (s, Cq) 91.77 (s, Cq) 103.35 (s, Cq) 128.81 (s, CH) 129.27 (s, CH) 134.21 (s, Cq) 137.49 (s, Cq)



2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-1-trifluoromethyl-prop-2-ynyl]-amide
To a solution of 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-3-trimethylsilanyl-prop-2-ynyl]-amide (100mg) in ethanol (2 mL) was added under argon a tip of spatula of $AgBF_4$. The reaction mixture was stirred at room temperature overnight, and then a tip of spatula of $AgBF_4$ was added twice (3h apart). The reaction mixture was quenched with a saturated solution of NH_4Cl. The solution was extracted with water; the organic layer was washed with brine and the aqueous layer with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (cyclohexane/ethyl acetate = 3:7) gave 65 mg of the title compound in 80% yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.23 - 1.27 (s, 9 H) 3.01 (s, 1 H) 4.02 (s, 1 H) 7.41 (m, *J*=8.80 Hz, 2 H) 7.72 (m, *J*=8.44 Hz, 2 H)
^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -77.18 (s, CF_3)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 22.48 (s, CH3) 57.54 (s, Cq) 62.64 - 62.95 (q, Cq) 79.83 (s, CH) 121.88-124.72 (q, Cq) 128.69 (s, CH) 130.17 (s, Cq) 130.70 (s, CH) 136.42 (s, Cq)



2-Methyl-propane-2-sulfinic acid (1-pyridin-3-yl-3-trimethylsilanyl-prop-2-ynyl)-amide
To a stirred suspension of Mg (342 mg) in anhydrous THF (80 mL) was added at 0°C under argon ethyl bromide (1.3 mL) and the suspension was stirred at room temperature until the solution has darkened and no Mg was left. The solution was then cooled at 0°C and ethynyltrimethylsilane (2.0 mL) was added. After 20 min of stirring at room temperature, a solution of 2-Methyl-propane-2-sulfinic acid [1-pyridin-3-yl-methylidene]-amide (2 g) in anhydrous THF (10 mL) was transferred using a cannula into the flask and the reaction mixture was stirred at room temperature during 3h. The reaction mixture was then cooled to 0°C and a saturated solution of NH_4Cl was added. The solution was extracted with water; the organic layer was washed with brine and the aqueous layer with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (100 % ethyl acetate) gave 877 mg of the title compound in 29% yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 0.17 - 0.21 (s, 9 H) 1.22 (s, 9 H) 3.74 - 3.81 (m, 1 H) 5.30 (d, *J*=5.13 Hz, 1 H) 7.31 - 7.38 (m, 1 H) 7.83 - 7.90 (m, 1 H) 8.59 (dd, *J*=4.77, 1.47 Hz, 1 H) 8.76 (d, *J*=2.20 Hz, 1 H)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) -0.30 (s, CH3) 22.50 (s, CH3) 48.82 (s, CH) 56.56 (s, Cq) 92.62 (s, Cq) 102.36 (s, Cq) 123.62 (s, CH) 135.01 (s, Cq) 135.92 (s, CH) 149.01 (s, CH) 149.12 (s, CH)

2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-1-trifluoromethyl-4-trimethylsilanyloxy-but-2-ynyl]-amide and 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-4-hydroxy-1-trifluoromethyl-but-2-ynyl]-amide

To a stirred suspension of Mg (36 mg) in anhydrous THF (4 mL) was added at 0°C under argon ethyl bromide (0.10 mL) and the suspension was stirred at room temperature until the solution has darkened and no Mg was left. The solution was then cooled at 0°C and 3-trimethylsiloxy-1-propyne (0.22 mL) was added. After 20 min of stirring at room temperature, a solution of 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-1-ethoxy-2,2,2-trifluoro-ethyl]-amide (153 mg) in anhydrous THF (1 mL) was transferred using a cannula into the flask and the reaction mixture was stirred at room temperature for 4h. The reaction mixture was then cooled to 0°C and a saturated solution of NH_4Cl was added. The solution was extracted with water; the organic layer was washed with brine and the aqueous layer with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (cyclohexane/ethyl acetate = 4:1 and 3:2) gave 67 mg of 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-1-trifluoromethyl-4-trimethylsilanyloxy-but-2-ynyl]-amide and 46 mg of 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-4-hydroxy-1-trifluoromethyl-but-2-ynyl]-amide for a total yield of 61 %.

Compound 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-1-trifluoromethyl-4-trimethylsilanyloxy-but-2-ynyl]-amide:

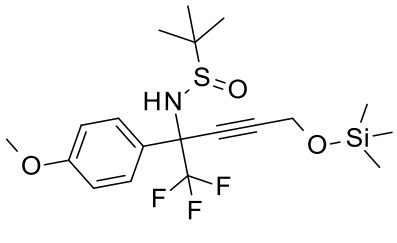
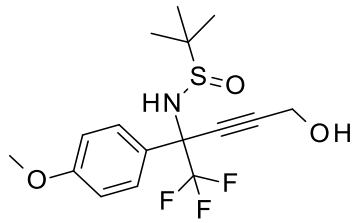
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 0.15 - 0.23 (s, 9 H) 1.19 - 1.27 (m, 9 H) 3.99 (s, 1 H) 4.45 - 4.53 (m, 2 H) 7.36 - 7.44 (m, 4 H) 7.70 (d, *J*=8.80 Hz, 4 H)

^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -76.75 (s, CF_3)

Compound 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-4-hydroxy-1-trifluoromethyl-but-2-ynyl]-amide

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.20 - 1.27 (s, 9 H) 4.19 (s, 1 H) 4.40 (s, 2 H) 7.37 - 7.43 (m, 2 H) 7.65 - 7.76 (m, 2 H)

^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -77.20 (s, CF_3)

N-[1-(4-methoxyphenyl)-1-(trifluoromethyl)-4-trimethylsilyloxy-but-2-ynyl]-2-methyl-propane-2-sulfinamide and N-[4-hydroxy-1-(4-methoxyphenyl)-1-(trifluoromethyl)but-2-ynyl]-2-methyl-propane-2-sulfinamide

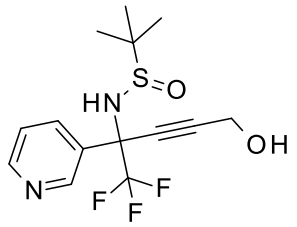
To a stirred suspension of Mg (41 mg) in anhydrous THF (4 mL) was added at 0°C under argon ethyl bromide (0.12 mL) and the suspension was stirred at room temperature until the solution has darkened and no Mg was left. The solution was then cooled at 0°C and 3-trimethylsiloxy-1-propyne (0.26 mL) was added. After 20 min of stirring at room temperature, a solution of 2-Methyl-propane-2-sulfinic acid [2,2,2-trifluoro-1-(4-methoxy-phenyl)-ethylidene]-amide (150 mg) in anhydrous THF (1.5 mL) was transferred using a cannula into the flask and the reaction mixture was stirred at room temperature during 30min. The reaction mixture was then cooled to 0°C and a saturated solution of NH_4Cl was added. The solution was extracted with water; the organic layer was washed with brine and the aqueous layer with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (cyclohexane/ethyl acetate = 4:1 and 1:1) gave N-[1-(4-methoxyphenyl)-1-(trifluoromethyl)-4-trimethylsilyloxy-but-2-ynyl]-2-methyl-propane-2-sulfinamide and N-[4-hydroxy-1-(4-methoxyphenyl)-1-(trifluoromethyl)but-2-ynyl]-2-methyl-propane-2-sulfinamide with total yield of 89 %.

Compound 2-Methyl-propane-2-sulfinic acid [1-(4-methoxy-phenyl)-1-trifluoromethyl-4-trimethylsilanyloxy-but-2-ynyl]-amide:

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.22 - 1.27 (s, 9 H) 3.82 - 3.85 (m, 3 H) 4.12 - 4.16 (m, 1 H) 4.40 (s, 2 H) 6.89 - 6.95 (m, 2 H) 7.67 (d, *J*=8.80 Hz, 2 H)

^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -77.35 (s, CF_3)

^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 22.52 (s, CH3) 50.56 (s, CH2) 55.25 (s, Cq) 57.40 (s, CH3) 62.91 - 63.21 (q, Cq) 79.82 (s, Cq) 90.06 (s, Cq) 113.63 (s, CH) 122.08 - 128.88 (q, Cq) 123.71 (s, Cq) 130.80 (s, CH) 160.71 (s, Cq)

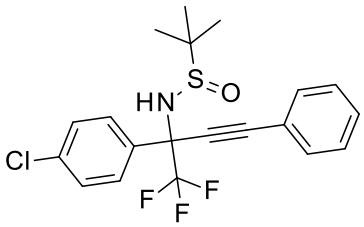


2-Methyl-propane-2-sulfinic acid (4-hydroxy-1-pyridin-3-yl-1-trifluoromethyl-but-2-ynyl)-amide

To a stirred suspension of Mg (56 mg) in anhydrous THF (5mL) was added at 0°C under argon ethyl bromide (0.17 mL) and the suspension was stirred at room temperature until the solution has darkened and no Mg was left. The solution was then cooled at 0°C and 3-trimethylsiloxy-1-propyne (0.35 mL) was added. After 20 min of stirring at room temperature, a solution of 2-Methyl-propane-2-sulfinic acid (1-ethoxy-2,2,2-trifluoro-1-pyridin-3-yl-ethyl)-amide (216 mg) in anhydrous THF (2 mL) was transferred using a cannula into the flask and the reaction mixture was stirred at room temperature during 1h30. The reaction mixture was then cooled to 0°C and a saturated solution of NH_4Cl was added. The solution was extracted with water; the organic layer was washed with brine and the aqueous layer with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (100 % ethyl acetate) gave the title compound with a yield of 48 %.

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.22 - 1.26 (s, 9 H) 4.40 (s, 2 H) 4.64 (br. s., 1 H) 7.30 - 7.43 (m, 1 H) 8.08 (d, *J*=8.07 Hz, 1 H) 8.67 (d, *J*=4.40 Hz, 1 H) 9.03 (s, 1 H)

^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -76.94 (s, CF_3)



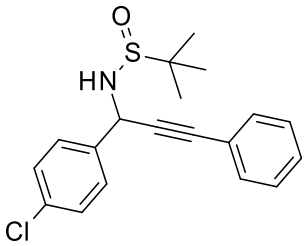
2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-3-phenyl-1-trifluoromethyl-prop-2-ynyl]-amide

To a solution of phenylacetylene (0.1 mL) in anhydrous THF (2.5 mL) was added at -78°C under argon a 1.6M-solution of n-BuLi (0.40 mL). After 30 min of stirring at -78°C, a solution of 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-1-ethoxy-2,2,2-trifluoro-ethyl]-amide (100 mg) in anhydrous THF (3 mL) was transferred using a cannula into the flask and the reaction mixture was stirred at -78°C during 1h. A saturated solution of NH_4Cl was then added at 0°C. The solution was extracted with water; the organic layer was washed with brine and the aqueous layer with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (cyclohexane/ethyl acetate = 4:1) gave 114 mg of the title compound in 98% yield.

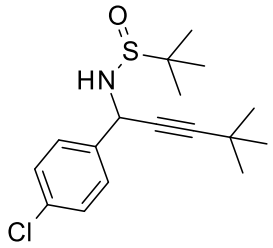
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.27 (s, 9 H) 4.09 (s, 1 H) 7.31 - 7.48 (m, 5 H) 7.55 - 7.67 (m, 2 H) 7.78 (d, *J*=8.44 Hz, 2 H)

^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -76.81 (s, CF_3)

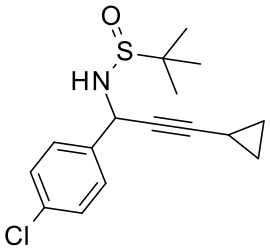
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 22.52 (s, CH3) 57.50 (s, Cq) 63.35 - 63.66 (q, Cq) 82.39 (s, Cq) 91.15 (s, Cq) 121.03 (s, Cq) 122.10 - 124.94 (q, Cq) 128.37 - 132.02 (s, 5 CH) 136.17 (s, Cq)



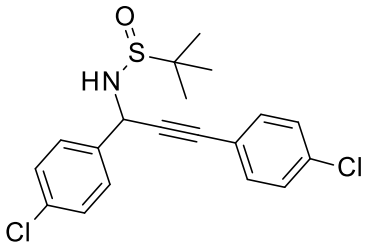
2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-3-phenyl-prop-2-ynyl]-amide
To a solution of phenylacetylene (0.14 mL) in anhydrous THF (4 mL) was added at -78°C under argon a solution of n-BuLi (0.51 mL, 1.6M in THF). After 30 min of stirring at -78°C, a solution of 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-methylidene]-amide (100 mg) in anhydrous THF (4 mL) was transferred using a cannula into the flask and the reaction mixture was stirred at -78°C for 4h and at room temperature overnight. A saturated solution of NH_4Cl was then added at 0°C. The solution was extracted with water; the organic layer was washed with brine and the aqueous layer with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (cyclohexane/ethyl acetate = 2:3) gave 84 mg of the title compound in 60% yield.
First diastereomer:
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.24 (s, 9 H) 3.79 - 3.84 (m, 1 H) 5.44 (d, *J*=5.50 Hz, 1 H) 7.31 - 7.38 (m, 5 H) 7.45 - 7.48 (m, 2 H) 7.50 - 7.54 (m, 2 H)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 22.49 (s, CH3) 50.50 (s, CH) 56.38 (s, Cq) 86.76 (s, Cq) 87.23 (s, Cq) 122.08 (s, Cq) 128.23 - 131.73 (s, 5 CH) 134.19 (s, Cq) 137.62 (s, Cq)
Second diastereomer:
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.26 (s, 9 H) 3.57 - 3.63 (m, 1 H) 5.50 (d, *J*=4.03 Hz, 1 H) 7.32 - 7.39 (m, 6 H) 7.45 - 7.48 (m, 2 H) 7.54 - 7.58 (m, 2 H)



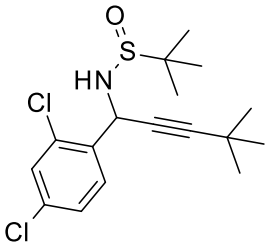
N-(1-(4-chlorophenyl)-4,4-dimethylpent-2-yn-1-yl)-2-methylpropane-2-sulfinamide
To a stirred solution of 3,3-dimethylbut-1-yne (3.1 mL, 25 mmol) in anhydrous THF (70 mL) was added at -78°C under argon n-butyllithium 1.0 M in hexanes (18 mL, 18 mmol). The reaction mixture was stirred at -78°C for 1h15 then at 0°C for 1h15. To this was added at 0°C under argon a solution of 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-methylidene]-amide (3.07 g, 12.6 mmol) in anhydrous THF (50 mL). The reaction mixture was stirred at 0°C for 1 h then it was warmed to room temperature, poured in 200 mL of a saturated solution of NH_4Cl and extracted once with ethyl acetate. The organic layer was washed twice with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum to give 4.155 g of the title compound. The crude was taken such in the next step.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.21 (s, 9 H) 1.25 (s, 9 H) 3.54 (d, J=5.50 Hz, 1 H) 5.18 (d, J=5.50 Hz, 1 H) 7.29 – 7.36 (m, 2 H) 7.39 – 7.46 (m, 2 H)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 22.52 (s, 3 C) 30.79 (s, 3 C) 50.06 (s, 1 C) 56.24 (s, 1 C) 95.87 (s, 1 C) 128.69 (s, 2 C) 129.18 (s, 2 C) 133.95 (s, 1 C) 138.49 (s, 1 C) 150.77 (s, 1 C) 173.83 (s, 1 C)



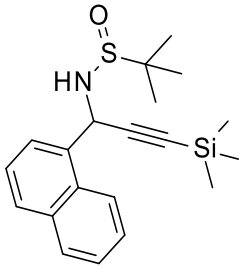
N-(1-(4-chlorophenyl)-3-cyclopropylprop-2-yn-1-yl)-2-methylpropane-2-sulfinamide
To a stirred solution of ethynylcyclopropane (0.28 mL, 3.3 mmol) in anhydrous THF (10 mL) was added at -78°C under argon n-butyllithium 1.0 M in hexanes (3.1 mL, 3.1 mmol). The reaction mixture was stirred at 0°C for 20 min then it was canulated at -78°C under argon to a solution of 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-methylidene]-amide (498 mg, 2.043 mmol) in anhydrous THF (10 mL). The reaction mixture was stirred at -78°C for 4 h then it was warmed to room temperature, poured in 50 mL of a saturated solution of NH_4Cl and extracted once with ethyl acetate. The organic layer was washed twice with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. Purification by chromatography on silica gel (cyclohexane / ethyl acetate = 75:25) gave 0.636 g of the title compound in 100 % yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 0.66 – 0.84 (m, 4 H) 1.20 (s, 9 H) 1.24 – 1.33 (m, 1 H) 3.56 (d, J=5.50 Hz, 1 H) 5.14 (d, J=5.50 Hz, 1 H) 7.29 – 7.36 (m, 2 H) 7.39 – 7.45 (m, 2 H)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) -0.43 (s, 1 C) 8.28 (s, 2 C) 22.53 (s, 3 C) 50.33 (s, 1 C) 56.25 (s, 1 C) 73.52 – 73.65 (m, 1 C) 90.72 – 90.83 (m, 1 C) 128.74 (s, 2 C) 129.12 (s, 2 C) 133.97 – 134.14 (m, 1 C) 138.24 – 138.32 (m, 1 C)



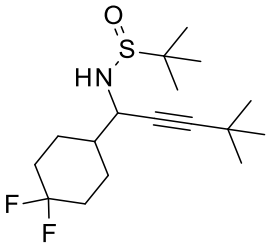
N-(1,3-bis(4-chlorophenyl)prop-2-yn-1-yl)-2-methylpropane-2-sulfinamide
To a stirred solution of 1-chloro-4-ethynylbenzene (1.01 g, 7.39 mmol) in anhydrous THF (20 mL) was added at -78°C under argon n-butyllithium 1.0 M in hexanes (5.6 mL, 5.6 mmol). The reaction mixture was stirred at 0°C for 3 h. To this was added at 0°C under argon a solution of 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-methylidene]-amide (902 mg, 3.70 mmol) in anhydrous THF (20 mL). The reaction mixture was stirred at 0°C for 30 min then it was warmed to room temperature, poured in 100 mL of a saturated solution of NH_4Cl and extracted once with ethyl acetate. The organic layer was washed twice with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. Purification by chromatography on silica gel (cyclohexane / ethyl acetate = 8:2) gave 1.150 g of the title compound in 81 % yield.
Main diastereomer:
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.22 – 1.31 (m, 9 H) 3.80 (d, J=5.87 Hz, 1 H) 5.44 (d, J=5.87 Hz, 1 H) 7.26 – 7.34 (m, 2 H) 7.36 – 7.45 (m, 4 H) 7.49 – 7.57 (m, 2 H)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 22.52 (s, 3 C) 50.67 (s, 1 C) 56.48 (s, 1 C) 85.77 (s, 1 C) 88.27 (s, 1 C) 120.64 (s, 1 C) 128.63 (s, 2 C) 128.91 (s, 2 C) 129.12 (s, 2 C) 133.00 (s, 2 C) 134.35 (s, 1 C) 134.82 (s, 1 C) 137.42 (s, 1 C)
Minor diastereomer:
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.22 – 1.26 (m, 9 H) 3.52 – 3.60 (d, J=4.40 Hz, 1 H) 5.46 – 5.49 (d, J=4.40 Hz, 1 H) 7.29 – 7.31 (m, 2 H) 7.36 – 7.41 (m, 4 H) 7.51 – 7.56 (m, 2 H)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 22.50 (s, 3 C) 51.12 (s, 1 C) 56.19 (s, 1 C) 86.04 (s, 1 C) 87.75 (s, 1 C) 120.80 (s, 1 C) 128.68 (s, 2 C) 129.10 (s, 2 C) 129.14 (s, 2 C) 132.96 (s, 2 C) 134.60 (s, 1 C) 134.81 (s, 1 C) 137.55 (s, 1 C)



N-(1-(2,4-dichlorophenyl)-4,4-dimethylpent-2-yn-1-yl)-2-methylpropane-2-sulfinamide
To a stirred solution of 3,3-dimethylbut-1-yne (0.90 mL, 7.3 mmol) in anhydrous THF (20 mL) was added at -78°C under argon n-butyllithium 1.0 M in hexanes (5.5 mL, 5.5 mmol). The reaction mixture was stirred at -78°C for 2 h then at 0°C for 2 h. To this was added at 0°C under argon a solution of N-(2,4-dichlorobenzylidene)-2-methylpropane-2-sulfinamide (1.00 g, 3.60 mmol) in anhydrous THF (15 mL). The reaction mixture was stirred at 0°C for 1 h then it was warmed to room temperature, poured in 100 mL of a saturated solution of NH_4Cl and extracted once with ethyl acetate. The organic layer was washed once with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. Purification by chromatography on silica gel (cyclohexane / ethyl acetate = 85:15) gave 1.278 g of the title compound in 98 % yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.16 – 1.21 (m, 9 H) 1.23 – 1.27 (m, 9 H) 3.50 (d, J=5.87 Hz, 1 H) 5.55 (d, J=5.87 Hz, 1 H) 7.30 (d, J = 2.20 Hz, 1 H) 7.39 (d, J=2.20 Hz, 1 H) 7.66 (d, J=8.07 Hz, 1 H)

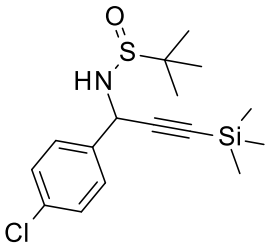


N-(1-(naphthalene-1-yl)-3-(trimethylsilyl)prop-2-yn-1-yl)-2-methylpropane-2-sulfinamide
To a stirred solution of ethynyltrimethylsilane (7.25 mL, 51.3 mmol) in anhydrous THF (60 mL) was added at -78°C under argon n-butyllithium 1.5 M in hexanes (29 mL, 44 mmol). The reaction mixture was stirred at -78°C for 20 min then at 0°C for 2 h. To this was added at 0°C under argon a solution of N-(naphthalene-1-ylmethylene)-2-methylpropane-2-sulfinamide (6.618 g, 25.51 mmol) in anhydrous THF (20 mL). The reaction mixture was stirred at 0°C for 30 min then it was warmed to room temperature, poured in 200 mL of a saturated solution of NH_4Cl and extracted once with ethyl acetate. The organic layer was washed once with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. Purification by chromatography on silica gel (cyclohexane / ethyl acetate = 9:1) gave 8.922 g of the title compound in 97 % yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 0.19 (s, 9 H) 1.16 (s, 9 H) 3.71 (d, J=5.50 Hz, 1 H) 5.87 (d, J=5.50 Hz, 1 H) 7.45 – 7.57 (m, 3 H) 7.78 – 7.82 (m, 1 H) 7.84 – 7.91 (m, 2 H) 8.25 – 8.31 (m, 1 H)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) -0.23 (s, 3 C) 22.55 (s, 3 C) 49.53 (s, 1 C) 56.32 (s, 1 C) 91.96 (s, 1 C) 103.99 (s, 1 C) 124.26 (s, 1 C) 125.24 (s, 1 C) 125.86 (s, 1 C) 126.06 (s, 1 C) 126.63 (s, 1 C) 128.77 (s, 1 C) 129.43 (s, 1 C) 130.50 (s, 1 C) 133.88 (s, 1 C) 134.18 (s, 1 C)

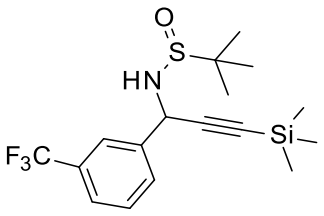


N-(1-(4,4-difluorocyclohexyl)-4,4-dimethylpent-2-yn-1-yl)-2-methylpropane-2-sulfinamide

To a stirred solution of 3,3-dimethylbut-1-yne (3.0 mL, 24 mmol) in anhydrous THF (75 mL) was added at -78°C under argon n-butyllithium 1.0 M in hexanes (20 mL, 20 mmol). The reaction mixture was stirred at -78°C for 1 h then at 0°C for 1 h. To this was added at 0°C under argon a solution of N-((4,4-difluorocyclohexyl)methylene)-2-methylpropane-2-sulfinamide (2.99 g, 11.9 mmol) in anhydrous THF (75 mL). The reaction mixture was stirred at 0°C for 1 h then it was warmed to room temperature, poured in 300 mL of a saturated solution of NH_4Cl and extracted once with ethyl acetate. The organic layer was washed once with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. Purification by chromatography on silica gel (cyclohexane / ethyl acetate = 8:2) gave 3.003 g of the title compound in 60 % yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.22 (s, 9 H) 1.24 (s, 9 H) 1.47 – 2.21 (m, 9 H) 3.16 – 3.26 (m, 1 H) 3.94 – 4.01 (m, 1 H)
^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -103.10 (d, J=235.32 Hz, 1 F) -91.69 (d, J=235.32 Hz, 1 F)

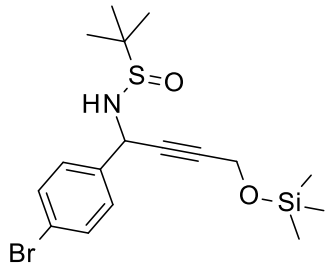


N-(1-(4-chlorophenyl)-3-(trimethylsilyl)prop-2-yn-1-yl)-2-methylpropane-2-sulfinamide
To a stirred suspension of magnesium (114 mg, 4.69 mmol) in anhydrous THF (15 mL) was added at 0°C under argon bromoethane (0.35 mL, 4.7 mmol). The reaction mixture was stirred at room temperature for 30 min then ethynyltrimethylsilane (0.60 mL, 4.2 mmol) was added at 0°C under argon. The reaction mixture was stirred at room temperature for another 30 min. To this was added under argon a solution of 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-methylidene]-amide (509 mg, 2.088 mmol) in anhydrous THF (6 mL). The reaction mixture was stirred at room temperature for 2 h then it was poured in 50 mL of a saturated solution of NH_4Cl and extracted once with ethyl acetate. The organic layer was washed once with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. Purification by chromatography on silica gel (cyclohexane / ethyl acetate = 8:2) gave 0.536 g of the title compound in 75 % yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 0.12 – 0.22 (m, 9 H) 1.21 (s, 9 H) 3.67 (d, J=4.77 Hz, 1 H) 5.22 (d, J=4.77 Hz, 1 H) 7.31 – 7.38 (m, 2 H) 7.40 – 7.50 (m, 2 H)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) -0.26 (s, 3 C) 22.51 (s, 3 C) 50.24 (s, 1 C) 56.37 (s, 1 C) 91.77 (s, 1 C) 103.35 (s, 1 C) 128.81 (s, 2 C) 129.27 (s, 2 C) 134.21 (s, 1 C) 137.49 (s, 1 C)



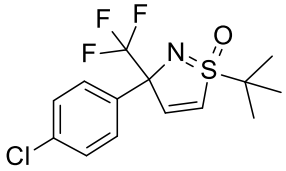
N-(1-(3-(trifluoromethyl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-yl)-2-methylpropane-2-sulfinamide
To a stirred suspension of magnesium (462 mg, 19.01 mmol) in anhydrous THF (40 mL) was added at 0°C under argon bromoethane (1.4 mL, 19 mmol). The reaction mixture was stirred at room temperature for 30 min then ethynyltrimethylsilane (3.1 mL, 22 mmol) was added at 0°C under argon. The reaction mixture was stirred at room temperature for another 1 h. To this was added at 0°C under argon a solution of N-(3-trifluoromethylbenzylidene)-2-methylpropane-2-sulfinamide (2.98 g, 10.7 mmol) in anhydrous THF (15 mL). The reaction mixture was stirred at 0°C for 30 min then at room temperature for 2 h 30 then it was poured in 50 mL of a saturated solution of NH_4Cl and extracted once with ethyl acetate. The organic layer was washed twice with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. Purification by chromatography on silica gel (cyclohexane / ethyl acetate = 9:1) gave 1.457 g of the title compound in 36 % yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 0.21 (s, 9 H) 1.23 (s, 9 H) 3.67 – 3.75 (m, 1 H) 5.26 – 5.36 (m, 1 H) 7.46 – 7.55 (m, 1 H) 7.57 – 7.62 (m, 1 H) 7.67 – 7.73 (m, 1 H) 7.78 – 7.83 (m, 1 H)

^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -63.71 (s, 3 F)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) -0.35 (s, 3 C) 22.47 (s, 3 C) 50.42 (s, 1 C) 56.51 (s, 1 C) 92.38 (s, 1 C) 102.94 (s, 1 C) 122.58 (q, J=272.48 Hz, 1 C) 124.57 – 124.78 (m, 1 C) 125.00 – 125.24 (m, 1 C) 129.09 (s, 1 C) 130.86 (s, 1 C) 131.27 (s, 1 C) 140.15 (s, 1 C)



N-(1-(4-bromophenyl)-4-((trimethylsilyl)oxy)but-2-yn-1-yl)-2-methylpropane-2-sulfinamide
To a stirred suspension of magnesium (887 mg, 36.48 mmol) in anhydrous THF (40 mL) was added at 0°C under argon bromoethane (2.6 mL, 35 mmol). The reaction mixture was stirred at room temperature for 30 min then propargyloxytrimethylsilane (5.3 mL, 35 mmol) was added at 0°C under argon. The reaction mixture was stirred at room temperature for another 30 min. To this was added under argon a solution of N-(4-bromobenzylidene)-2-methylpropane-2-sulfinamide (2.99 g, 10.4 mmol) in anhydrous THF (10 mL). The reaction mixture was stirred at room temperature for another 1 h then it was poured in 100 mL of a saturated solution of NH_4Cl and extracted once with ethyl acetate. The organic layer was washed twice with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. Purification by chromatography on silica gel (cyclohexane / ethyl acetate = 9:1) gave 2.682 g of the title compound in 46 % yield.

Cyclizations under basic condition



1-tert-butyl-3-(4-chlorophenyl)-3-(trifluoromethyl)isothiazole 1-oxide
(i) To a stirred solution of 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-1-trifluoromethyl-3-trimethylsilanyl-prop-2-ynyl]-amide (130 mg) in ethyl acetate (2.5 mL) under argon was added at 0°C a solution of TBAF (0.33mL i.e. 1 equivalent, 1M in THF). The reaction mixture was stirred at 0°C during 15 min and then quenched with water. The solution was extracted with water; the organic layer was washed with brine and the aqueous layer with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (cyclohexane/ethyl acetate = 1:1) gave 98mg of the title compound in 88% yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.33 (s, 9 H) 6.91 (d, *J*=5.14 Hz, 1 H) 7.35 - 7.40 (m, 2 H) 7.66 (m, *J*=8.44 Hz, 2 H) 7.77 (d, *J*=5.50 Hz, 1 H)
^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -75.71 (s, CF_3)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 23.98 (s, CH3) 61.07 (s, Cq) 126.92 (s, CH) 128.54 (s, CH) 129.63 (s, CH) 134.08 (s, Cq) 135.01 (s, Cq) 148.13 (s, CH). *Note: fluorine-coupling carbons were not visible.*

(ii) To a stirred solution of 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-1-trifluoromethyl-3-trimethylsilanyl-prop-2-ynyl]-amide (38 mg) in ethyl acetate (1 mL) under argon was added at 0°C a solution of TBAF (0.01mL i.e. 0.1 equivalent, 1M in THF). The reaction mixture was stirred at 0°C during 15 min and then quenched with water. The solution was extracted with water; the organic layer was washed with brine and the aqueous layer with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. Analysis on the crude show only the title compound is present.

NaOMe in MeOH conditions
To a stirred solution of 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-1-trifluoromethyl-3-

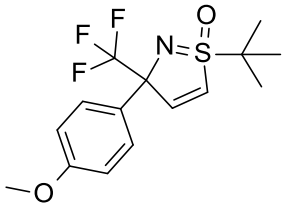
trimethylsilanyl-prop-2-ynyl]-amide (100 mg) in methanol (2 mL) under argon was added a solution of MeONa (0.05 mL, 5.4M in methanol). The reaction mixture was stirred at room temperature during 30 min and then quenched with a saturated solution of NH_4Cl. The solution was extracted with water; the organic layer was washed with brine and the aqueous layer with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (cyclohexane/ethyl acetate = 2:3) gave 72mg of the title compound in 86% yield.

NaH in DMF conditions

To a stirred solution of 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-1-trifluoromethyl-3-trimethylsilanyl-prop-2-ynyl]-amide (100 mg) in DMF (2.5 mL) under argon was added sodium hydride (10 mg, 60% dispersion in mineral oil). The reaction mixture was stirred at room temperature during 30 min and then quenched with a saturated solution of NH_4Cl. The solution was extracted with water; the organic layer was washed with brine and the aqueous layer with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. The remaining DMF was extracted with a hydrochloride solution (pH=3) and ethyl acetate. The organic layer was then dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (cyclohexane/ethyl acetate = 2:3) gave 58mg of the title compound in 69% yield.

KO^tBu in THF conditions

To a stirred solution of 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-1-trifluoromethyl-3-trimethylsilanyl-prop-2-ynyl]-amide (100 mg) in THF (2 mL) under argon was added a solution of KO^tBu (0.25 mL, 1M in THF). The reaction mixture was stirred at room temperature during 20 min and then quenched with a saturated solution of NH_4Cl. The solution was extracted with water; the organic layer was washed with brine and the aqueous layer with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (cyclohexane/ethyl acetate = 2:3) gave 54mg of the title compound in 64% yield.



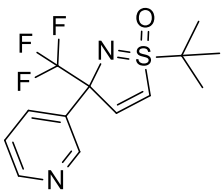
1-tert-butyl-3-(4-methoxyphenyl)-3-(trifluoromethyl)isothiazole 1-oxide

To a stirred solution of 2-Methyl-propane-2-sulfinic acid [1-(4-methoxy-phenyl)-1-trifluoromethyl-3-trimethylsilanyl-prop-2-ynyl]-amide **(**90 mg) in ethyl acetate (1.5 mL) under argon was added at 0°C a solution of TBAF (0.22 mL, 1M in THF). The reaction mixture was stirred at 0°C during 30 min and then quenched with water. The solution was extracted with water; the organic layer was washed with brine and the aqueous layer with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (cyclohexane/ethyl acetate = 1:1) gave 39 mg of the title compound in 53% yield.

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.32 (s, 9 H) 3.82 (s, 3 H) 6.86 (d, *J*=5.14 Hz, 1 H) 6.89 - 6.95 (m, 2 H) 7.62 (m, *J*=8.44 Hz, 2 H) 7.79 (d, *J*=5.50 Hz, 1 H)

^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -75.93 (s, CF_3)

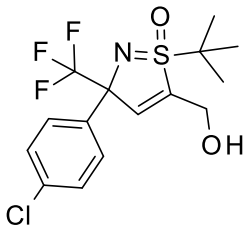
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 23.98 (s, CH3) 55.23 (s, CH3) 60.99 (s, Cq) 113.63 (s, CH) 126.15 (s, CH) 127.48 (s, Cq) 129.43 (s, CH) 148.81 (s, CH) 159.85 (s, Cq). *Note: fluorine-coupling carbons were not visible.*



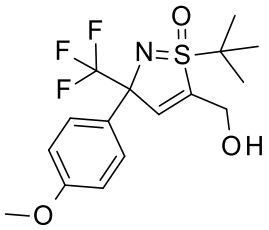
1-tert-butyl-3-(3-pyridyl)-3-(trifluoromethyl)isothiazole 1-oxide

To a stirred solution of 2-Methyl-propane-2-sulfinic acid (1-pyridin-3-yl-1-trifluoromethyl-3-trimethylsilanyl-prop-2-ynyl)-amide (446 mg) in ethyl acetate (10 mL) under argon was added at 0°C a solution of TBAF (1.2 mL, 1M in THF). The reaction mixture was stirred at 0°C during 15 min and then

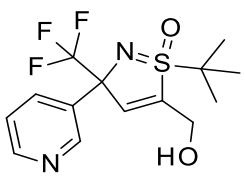
quenched with water. The solution was extracted with water; the organic layer was washed with brine and the aqueous layer with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (100 % ethyl acetate) gave 338 mg of the title compound in 90% yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.32 (s, 9 H) 6.98 (d, *J*=5.13 Hz, 1 H) 7.31 - 7.41 (m, 1 H) 7.84 (d, *J*=5.14 Hz, 1 H) 8.04 - 8.15 (m, 1 H) 8.54 - 8.72 (m, 1 H) 8.81 - 8.96 (m, 1 H)
^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -75.76 (s, CF_3)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 23.94 (s, CH3) 61.13 (s, Cq) 81.68-81.97 (q, Cq) 122.57-128.24 (q, Cq) 123.37 (s, CH) 127.62 (s, C) 131.81 (s, Cq) 136.21 (s, CH) 147.47 (s, CH) 149.00 (s, CH) 150.06 (s, CH)



[1-tert-butyl-3-(4-chlorophenyl)-1-oxo-3-(trifluoromethyl)isothiazol-5-yl]methanol
To a stirred solution of 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-1-trifluoromethyl-4-trimethylsilanyloxy-but-2-ynyl]-amide and 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-4-hydroxy-1-trifluoromethyl-but-2-ynyl]-amide (67 mg) in ethyl acetate (1 mL) under argon was added at 0°C a solution of TBAF (0.15 mL, 1M in THF). The reaction mixture was stirred at 0°C during 1h30 and then quenched with water. The solution was extracted with water; the organic layer was washed with brine and the aqueous layer with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (cyclohexane/ethyl acetate = 3:7) gave 23 mg of the title compound in 42% yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.34 (s, 9 H) 4.55 - 4.61 (m, 1 H) 4.69 - 4.77 (m, 1 H) 7.35 - 7.40 (m, 2 H) 7.58 (t, *J*=1.65 Hz, 1 H) 7.65 (d, *J*=8.44 Hz, 2 H)
^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -75.88 (s, CF_3)

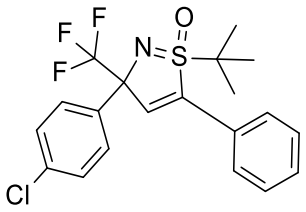


[1-tert-butyl-3-(4-methoxyphenyl)-1-oxo-3-(trifluoromethyl)isothiazol-5-yl]methanol
To a stirred solution of 2-Methyl-propane-2-sulfinic acid [1-(4-methoxy-phenyl)-1-trifluoromethyl-4-trimethylsilanyloxy-but-2-ynyl]-amide and 2-Methyl-propane-2-sulfinic acid [1-(4-methoxy-phenyl)-1-trifluoromethyl-4-trimethylsilanyloxy-but-2-ynyl]-amide (107 mg) in ethyl acetate (2 mL) under argon was added at 0°C a solution of TBAF (0.25 mL, 1M in THF). The reaction mixture was stirred at 0°C during 1h and then quenched with water. The solution was extracted with water; the organic layer was washed with brine and the aqueous layer with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (cyclohexane/ethyl acetate = 1:4) gave 32 mg of the title compound in 35% yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.34 (s, 9 H) 2.83 - 2.90 (m, 1 H) 3.82 (s, 3 H) 4.51 - 4.60 (m, 1 H) 4.64 - 4.71 (m, 1 H) 6.88 - 6.93 (m, 2 H) 7.57 - 7.64 (m, 3 H)
^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -76.06 (s, CF_3)



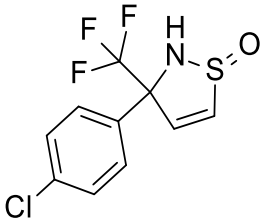
[1-tert-butyl-1-oxo-3-(3-pyridyl)-3-(trifluoromethyl)isothiazol-5-yl]methanol

To a stirred solution of 2-Methyl-propane-2-sulfinic acid (4-hydroxy-1-pyridin-3-yl-1-trifluoromethyl-but-2-ynyl)-amide (129 mg) in ethyl acetate (4 mL) under argon was added at 0°C a solution of TBAF (0.39 mL, 1M in THF). The reaction mixture was stirred at 0°C during 25 min and then quenched with water. The solution was extracted with water; the organic layer was washed with brine and the aqueous layer with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (100 % ethyl acetate) gave 83 mg of the title compound in 64% yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.31 (s, 9 H) 4.50 - 4.58 (m, 1 H) 4.68 - 4.76 (m, 1 H) 7.32 - 7.38 (m, 1 H) 7.66 - 7.71 (m, 1 H) 8.09 - 8.14 (m, 1 H) 8.54 - 8.58 (m, 1 H) 8.79 - 8.83 (m, 1 H)
^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -76.06 (s, CF_3)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 23.91 (s, CH3) 56.49 (s, CH2) 62.00 (s, Cq) 78.39-78.66 (q, Cq) 122.74-125.68 (q, Cq) 123.46 (s, CH) 132.53 (s, Cq) 136.56 (s, CH) 141.71 (s, CH) 145.23 (s, Cq) 148.72 (s, CH) 149.60 (s, CH)

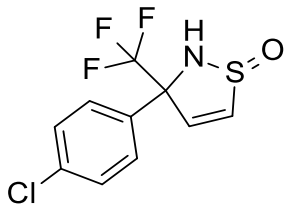


1-tert-butyl-3-(4-chlorophenyl)-5-phenyl-3-(trifluoromethyl)isothiazole 1-oxide
To a stirred solution of 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-3-phenyl-1-trifluoromethyl-prop-2-ynyl]-amide (75 mg) in methanol (2 mL) under argon was added a solution of MeONa (0.03 mL, 5.4M in methanol). The reaction mixture was stirred at room temperature during 30 min and then quenched with a saturated solution of NH_4Cl. The solution was extracted with water; the organic layer was washed with brine and the aqueous layer with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (cyclohexane/ethyl acetate = 2:3) gave 64mg of the title compound in 85% yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.18 (s, 9 H) 7.37 - 7.50 (m, 6 H) 7.69 (d, *J*=6.97 Hz, 2 H) 7.74 (d, *J*=8.44 Hz, 2 H)
^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -75.92 (s, CF_3)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 24.18 (s, CH3) 63.20 (s, Cq) 78.71 - 79.00 (q, Cq) 122.89 - 125.73 (q, Cq) 127.84 (s, CH) 128.56 (s, CH) 128.98 (s, CH) 129.20 (s, CH) 129.71 (s, CH) 130.40 (s, CH) 134.65 (s, Cq) 134.90 (s, Cq) 141.66 (s, Cq) 142.41 (s, Cq)

Au and Ag catalysis for the cyclization



3-(4-chlorophenyl)-3-(trifluoromethyl)-2H-isothiazole 1-oxide
To a solution of 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-1-trifluoromethyl-3-trimethylsilanyl-prop-2-ynyl]-amide (300mg) in ethanol (6 mL) was added 13 mg of $AgSbF_6$. The reaction mixture was stirred at room temperature overnight, and then for a day. During this day, a tip of spatula of $AgSbF_6$ was added three times (2-3h apart). The following morning, the solution was quenched with a saturated solution of NH_4Cl. The solution was extracted with water; the organic layer was washed with brine and the aqueous layer with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (cyclohexane/ethyl acetate = 3:7) gave 168 mg of the title compound in 82% yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 5.13 (s, 1 H) 6.95 (d, *J*=6.24 Hz, 1 H) 7.02 (d, *J*=6.24 Hz, 1 H) 7.35 - 7.40 (m, 2 H) 7.41 - 7.45 (m, 2 H)
^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -73.78 (s, CF_3)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 79.90-80.20 (q, Cq) 122-124.83 (q, Cq) 127.93 (s, CH) 129.49 (s, CH) 132.41 (s, Cq) 135.95 (s, CH) 136.06 (s, Cq) 138.50 (s, CH)



3-(4-chlorophenyl)-3-(trifluoromethyl)-2H-isothiazole 1-oxide

(i) To a solution of 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-1-trifluoromethyl-3-trimethylsilanyl-prop-2-ynyl]-amide (100mg) in ethanol (2 mL) was added under argon a tip of spatula of AgOTf. The reaction mixture was stirred at room temperature overnight, and then another tip of spatula of AgOTf was added. The reaction mixture was stirred at room temperature for 4h, and then quenched with a saturated solution of NH_4Cl. The solution was extracted with water; the organic layer was washed with brine and the aqueous layer with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (cyclohexane/ethyl acetate = 3:7) gave 7 mg of the title compound as isomer 1 in 10% yield and 48 mg of the title compound as isomer 2 in 71% yield.

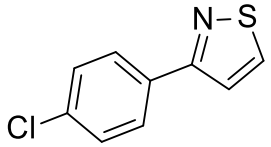
(ii) To a solution of **1** (100 mg) in ethanol (2 mL) was added under argon 4 mg of $AgSbF_6$ and 6 mg of $AuPPh_3Cl$. A white precipitate of AgCl appears as $AuPPh_3SbF_6$ is formed. The reaction mixture was stirred at room temperature overnight, and then another tip of spatula of $AgSbF_6$ and $AuPPh_3Cl$ was added. The reaction mixture was stirred at room temperature for 7h, and then quenched with a saturated solution of NH_4Cl. The solution was extracted with water; the organic layer was washed with brine and the aqueous layer with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (cyclohexane/ethyl acetate = 3:7) gave 10 mg of the title compound as isomer 1 in 13% yield and 39 mg of the title compound as isomer 2 in 58% yield.

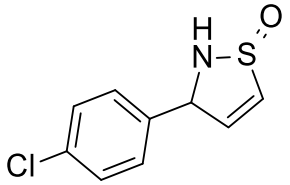
isomer 1:

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 5.32 (s, 1 H) 6.84 - 6.90 (m, 2 H) 7.38 - 7.43 (m, 2 H) 7.59 (d, *J*=8.07 Hz, 2 H)

^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -73.83 (s, CF_3)

^{13}C NMR ($CDCl_3$, 125 MHz, δ ppm) 81.194-81.431 (q, Cq) 122.939-125.212 (q, Cq) 128.317 (s, CH) 129.217 (s, CH) 132.719 (s, Cq) 135.076 (s, CH) 135.686 (s, Cq) 138.067(s, CH)





3-(4-Chloro-phenyl)-isothiazole and 3-(4-chlorophenyl)-2,3-dihydroisothiazole 1-oxide

Conditions 1: To a solution of 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-3-trimethylsilanyl-prop-2-ynyl]-amide (1 g) in dichloromethane (10 mL) was added under argon 74 mg of AgOTf. The reaction mixture was stirred at room temperature for 6h, and then a tip of spatula of AgOTf was added. The reaction mixture was stirred at room temperature overnight, and then the reaction mixture was quenched with a saturated solution of NH_4Cl. The solution was extracted with water; the organic layer was washed with brine and the aqueous layer with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (cyclohexane/ethyl acetate = 1:4 to 100% ethyl acetate) gave 89 mg of 3-(4-Chloro-phenyl)-isothiazole in 17% yield and 167 mg of 3-(4-chlorophenyl)-2,3-dihydroisothiazole 1-oxide in 27% yield (the yields given were calculated after recrystallisation).

3-(4-Chloro-phenyl)-isothiazole:

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 7.39 - 7.48 (m, 2 H) 7.60 (d, *J*=4.77 Hz, 1 H) 7.89 - 7.96 (m, 2 H) 8.73 (d, *J*=4.40 Hz, 1 H)

^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 121.08 (s, CH) 128.24 (s, CH) 129.03 (s, CH) 133.11 (s, Cq) 135.16 (s, Cq) 149.30 (s, CH) 166.44 (s, Cq)

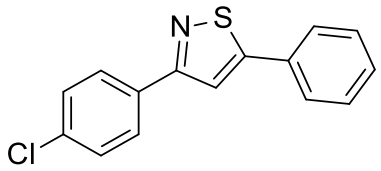
3-(4-chlorophenyl)-2,3-dihydroisothiazole 1-oxide:

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 5.43 - 5.48 (s, 1 H) 6.65 - 6.70 (m, 2 H) 7.32 - 7.38 (m, 2 H) 7.38 - 7.44 (m, 2 H)

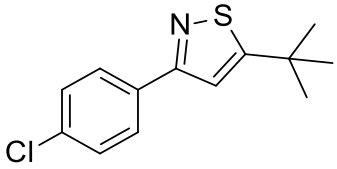
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 128.76 (s, CH) 129.07 (s, CH) 133.66 (s, Cq) 134.21 (s, CH) 136.43 (s, Cq) 139.99 (s, CH)

Conditions 2: To a solution of 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-3-trimethylsilanyl-prop-2-ynyl]-amide (100 mg) in dichloromethane (2 mL) was added under argon 5 mg of $AgSbF_6$ and 7mg of $AuPPh_3Cl$. A white precipitate of AgCl appears as $AuPPh_3SbF_6$ is formed. The reaction mixture was stirred at room temperature for 6h, and then a tip of spatula of $AgSbF_6$ and $AuPPh_3Cl$ was added. The reaction mixture was stirred at room temperature overnight, and then the reaction mixture was quenched with a saturated solution of NH_4Cl. The solution was extracted with water; the organic layer was washed with brine and the aqueous layer with ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel (cyclohexane/ethyl acetate = 1:4 to 100% ethyl acetate) gave 20 mg of 3-(4-Chloro-phenyl)-isothiazole in 33% yield and 32mg of 3-(4-chlorophenyl)-2,3-dihydroisothiazole 1-oxide in 52% yield.

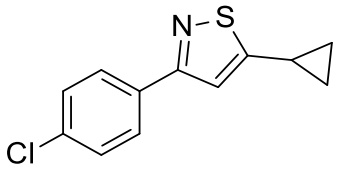
Conditions 3**.** To a stirred solution of 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-3-trimethylsilanyl-prop-2-ynyl]-amide (108 mg, 0.22 mmol) in acetic acid (3 mL) were added chlorotriphenylphosphine gold (11 mg, 0.022 mmol) and silver hexafluoroantimonate (7 mg, 0.022 mmol). The reaction mixture was stirred at 80°C for 30 min then was cooled to room temperature, poured in 2 mL of a saturated solution of NH_4Cl and extracted once with ethyl acetate. The organic layer was washed twice with brine, dried over $MgSO_4$, filtered and concentrated under vacuum. Purification by chromatography on silica gel (cyclohexane / ethyl acetate = 9:1) gave 23 mg of 3-(4-Chloro-phenyl)-isothiazole in 53.2 % yield.



3-(4-Chloro-phenyl)-5-phenyl-isothiazole
To a solution of 2-Methyl-propane-2-sulfinic acid [1-(4-chloro-phenyl)-3-phenyl-prop-2-ynyl]-amide (42 mg) in 1,2-dichloroethane (2 mL) was added under argon a tip of spatula of $AgSbF_6$ and $AuPPh_3Cl$. A white precipitate of AgCl appears as $AuPPh_3SbF_6$ is formed. The reaction mixture was stirred at room temperature for 4h. A tip of spatula of $AgSbF_6$ and $AuPPh_3Cl$ was then added and the suspension was stirred at 50 °C for 45 min. The reaction mixture was quenched with water, extracted with brine (3x) and the aqueous layer was washed with ethyl acetate. The organic layers were combined, dried over $MgSO_4$, filtered on a pad of Celite and concentrated *in vacuo*. Purification by chromatography on silica gel (cyclohexane/ethyl acetate = 1:4) gave 19 mg of the title compound in 58% yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 7.42 - 7.51 (m, 5 H) 7.64 - 7.68 (m, 2 H) 7.73 (s, 1 H) 7.91 - 7.98 (m, 2 H)



5-(tert-butyl)-3-(4-chlorophenyl)isothiazole
To a stirred solution of N-(1-(4-chlorophenyl)-4,4-dimethylpent-2-yn-1-yl)-2-methylpropane-2-sulfinamide (105 mg, 0.32 mmol) in acetic acid (3 mL) were added chlorotriphenylphosphine gold (16 mg, 0.032 mmol) and silver hexafluoroantimonate (12 mg, 0.035 mmol). The reaction mixture was stirred at 80°C for 45 min then it was cooled to room temperature, poured in 2 mL of a saturated solution of NH_4Cl and extracted once with ethyl acetate. The organic layer was washed twice with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. Purification by chromatography on silica gel (cyclohexane / ethyl acetate = 9:1) gave 52 mg of the title compound in 61 % yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.41 – 1.50 (m, 9 H) 7.32 (s, 1 H) 7.38 – 7.45 (m, 2 H) 7.82 – 7.93 (m, 2 H)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 32.12 (s, 3 C) 34.58 (s, 1 C) 117.11 (s, 1 C) 128.06 (s, 2 C) 128.90 (s, 2 C) 133.65 (s, 1 C) 134.87 (s, 1 C) 166.28 (s, 1 C) 182.72 (s, 1 C)

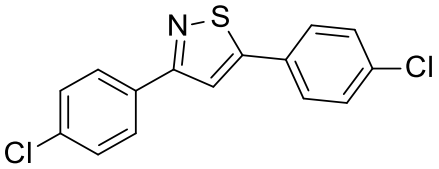


5-cyclopropyl-3-(4-chlorophenyl)isothiazole

To a stirred solution of N-(1-(4-chlorophenyl)-3-cyclopropylprop-2-yn-1-yl)-2-methylpropane-2-sulfinamide (95 mg, 0.31 mmol) in acetic acid (3 mL) were added chlorotriphenylphosphine gold (15 mg, 0.031 mmol) and silver hexafluoroantimonate (10 mg, 0.031 mmol). The reaction mixture was stirred at 80°C for 2h15 then it was cooled to room temperature, poured in 2 mL of a saturated solution of NH_4Cl and extracted once with ethyl acetate. The organic layer was washed twice with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. Purification by chromatography on silica gel (cyclohexane / ethyl acetate = 9:1) gave 43 mg of the title compound in 59 % yield.

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 0.80 – 0.94 (m, 2 H) 1.15 – 1.25 (m, 2 H) 2.21 (tt, J=8.34 Hz, 4.86 Hz, 1 H) 7.22 (s, 1 H) 7.37 – 7.45 (m, 2 H) 7.81 – 7.89 (m, 2 H)

^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 9.72 (s, 1 C) 11.38 (s, 2 C) 117.36 (s, 1 C) 128.00 (s, 2 C) 128.88 (s, 2 C) 133.44 (s, 1 C) 134.90 (s, 1 C) 166.35 (s, 1 C) 174.17 (s, 1 C)

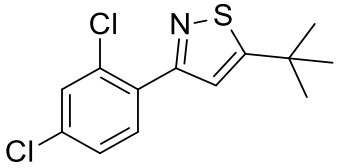


3,5-bis(4-chlorophenyl)isothiazole

To a stirred solution of N-(1,3-bis(4-chlorophenyl)prop-2-yn-1-yl)-2-methylpropane-2-sulfinamide (115 mg, 0.30 mmol) in acetic acid (3 mL) were added chlorotriphenylphosphine gold (15 mg, 0.031 mmol) and silver hexafluoroantimonate (10 mg, 0.031 mmol). The reaction mixture was stirred at 80°C for 2h15 then it was cooled to room temperature, poured in 2 mL of a saturated solution of NH_4Cl and extracted once with ethyl acetate. The organic layer was washed twice with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. Purification by chromatography on silica gel (cyclohexane / ethyl acetate = 9:1) gave 67 mg of the title compound in 72 % yield.

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 7.41 – 7.50 (m, 4 H) 7.54 – 7.63 (m, 2 H) 7.70 (s, 1 H) 7.88 – 7.99 (m, 2 H)

^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 117.64 (s, 1 C) 127.81 (s, 2 C) 128.11 (s, 2 C) 129.06 (s, 2 C) 129.28 (s, 1 C) 129.53 (s, 2 C) 133.12 (s, 1 C) 135.35 (s, 1 C) 135.70 (s, 1 C) 167.15 (s, 1 C) 167.27 (s, 1 C).

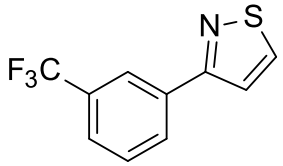


5-(tert-butyl)-3-(2,4-dichlorophenyl)isothiazole

To a stirred solution of N-(1-(2,4-dichlorophenyl)-4,4-dimethylpent-2-yn-1-yl)-2-methylpropane-2-sulfinamide (49 mg, 0.12 mmol) in acetic acid (1 mL) were added chlorotriphenylphosphine gold (7 mg, 0.012 mmol) and silver hexafluoroantimonate (4 mg, 0.012 mmol). The reaction mixture was stirred at 80°C for 5 h then it was cooled to room temperature, poured in 2 mL of a saturated solution of NH_4Cl and extracted once with ethyl acetate. The organic layer was washed twice with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. Purification by chromatography on silica gel (cyclohexane / ethyl acetate = 9:1) gave 25 mg of the title compound in 71 % yield.

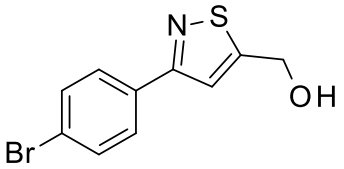
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.47 (s, 9 H) 7.33 (dd, J=8.44 Hz, 2.20 Hz, 1 H) 7.42 (s, 1 H) 7.49 (d, J=2.20 Hz, 1 H) 7.71 (d, J=8.44 Hz, 1 H)

^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 32.14 (s, 3 C) 34.61 (s, 1 C) 120.72 (s, 1 C) 127.33 (s, 1 C) 129.98 (s, 1 C) 132.34 (s, 1 C) 132.67 (s, 1 C) 133.26 (s, 1 C) 135.08 (s, 1 C) 164.34 (s, 1 C) 181.74 (s, 1 C)

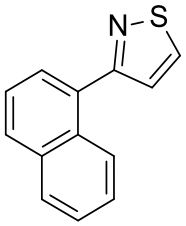


3-(3-trifluoromethylphenyl)isothiazole
To a stirred solution of N-(1-(3-(trifluoromethyl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-yl)-2-methylpropane-2-sulfinamide (108 mg, 0.29 mmol) in acetic acid (3 mL) were added chlorotriphenylphosphine gold (15 mg, 0.031 mmol) and silver hexafluoroantimonate (10 mg, 0.031 mmol). The reaction mixture was stirred at 80°C for 5 h then it was cooled to room temperature, poured in 2 mL of a saturated solution of NH_4Cl and extracted once with ethyl acetate. The organic layer was washed twice with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. Purification by chromatography on silica gel (cyclohexane / ethyl acetate = 9:1) gave 115 mg of the title compound in 78 % yield.

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 7.57 – 7.63 (m, 1 H) 7.65 – 7.70 (m, 2 H) 8.17 (d, J=7.70 Hz, 1 H) 8.26 (s, 1 H) 8.78 (d, J=4.40 Hz, 1 H)
^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -62.74 (s, 3 F)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 121.19 (s, 1 C) 122.66 (q, J=272.48 Hz, 1 C) 123.68 – 123.95 (m, 1 C) 125.59 - 125.78 (m, 1 C) 129.33 (s, 1 C) 130.12 (s, 1 C) 130.66 – 131.95 (m, 1 C) 135.29 (s, 1 C) 149.64 (s, 1 C) 166.05 (s, 1 C)

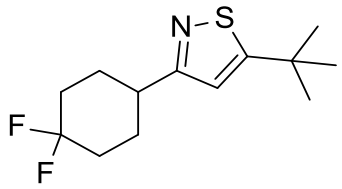


(3-(4-bromophenyl)isothiazol-5-yl)methanol
To a stirred solution of N-(1-(4-bromophenyl)-4-((trimethylsilyl)oxy)but-2-yn-1-yl)-2-methylpropane-2-sulfinamide (119 mg, 0.29 mmol) in acetic acid (3 mL) were added chlorotriphenylphosphine gold (15 mg, 0.031 mmol) and silver hexafluoroantimonate (10 mg, 0.031 mmol). The reaction mixture was stirred at 80°C for 1 h then it was cooled to room temperature, poured in 2 mL of a saturated solution of NH_4Cl and extracted once with ethyl acetate. The organic layer was washed twice with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. Purification by chromatography on silica gel (cyclohexane / ethyl acetate = 9:1) gave 47 mg of the title compound in 60% yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 5.06 (d, J=0.73 Hz, 2 H) 7.44 – 7.48 (m, 1 H) 7.55 – 7.61 (m, 2 H) 7.77 – 7.85 (m, 2 H)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 58.85 (s, 1 C) 118.27 (s, 1 C) 123.46 (s, 1 C) 128.35 (s, 2 C) 131.98 (s, 2 C) 133.65 (s, 1 C) 166.55 (s, 1 C) 169.73 (s, 1 C)



3-(naphthalen-1-yl)isothiazole
To a stirred solution of N-(1-(naphthalene-1-yl)-3-(trimethylsilyl)prop-2-yn-1-yl)-2-methylpropane-2-sulfinamide (108 mg, 0.30 mmol) in acetic acid (3 mL) were added chlorotriphenylphosphine gold (15 mg, 0.031 mmol) and silver hexafluoroantimonate (10 mg, 0.031 mmol). The reaction mixture was stirred at 80°C for 6 h then it was cooled to room temperature, poured in 2 mL of a saturated solution

of NH_4Cl and extracted once with ethyl acetate. The organic layer was washed twice with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. Purification by chromatography on silica gel (cyclohexane / ethyl acetate = 9:1) gave 38 mg of the title compound in 59 % yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 7.46 – 7.61 (m, 4 H) 7.72 (dd, J=6.97 Hz, 1.10 Hz, 1 H) 7.87 – 7.99 (m, 2 H) 8.29 – 8.41 (m, 1 H) 8.82 (d, J=4.40 Hz, 1 H)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 125.16 (s, 1 C) 125.65 (s, 1 C) 126.03 (s, 1 C) 126.73 (s, 1 C) 127.58 (s, 1 C) 128.35 (s, 1 C) 129.42 (s, 1 C) 131.17 (s, 1 C) 132.22 (s, 1 C) 133.00 (s, 1 C) 133.88 (s, 1 C) 148.27 (s, 1 C) 168.07 (s, 1 C)



5-(tert-butyl)-3-(4,4-difluorocyclohexyl)isothiazole
To a stirred solution of N-(1-(4,4-difluorocyclohexyl)-4,4-dimethylpent-2-yn-1-yl)-2-methylpropane-2-sulfinamide (103 mg, 0.22 mmol) in acetic acid (2 mL) were added chlorotriphenylphosphine gold (11 mg, 0.022 mmol) and silver hexafluoroantimonate (7 mg, 0.022 mmol). The reaction mixture was stirred at 80°C for 2 h then it was cooled to room temperature, poured in 2 mL of a saturated solution of NH_4Cl and extracted once with ethyl acetate. The organic layer was washed twice with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. Purification by chromatography on silica gel (cyclohexane / ethyl acetate = 9:1) gave 38 mg of the title compound in 68 % yield.
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.41 (s, 9 H) 1.69 – 1.97 (m, 4 H) 2.02 – 2.27 (m, 4 H) 2.81 – 2.95 (m, 1 H) 6.83 (s, 1 H)
^{19}F NMR ($CDCl_3$, 376 MHz, δ ppm) -101.18 (d, J=236.17 Hz, 1 F) -92.41 (d, J=236.17 Hz, 1 F)
^{13}C NMR ($CDCl_3$, 101 MHz, δ ppm) 28.44 (d, J=9.91 Hz, 2 C) 32.16 (s, 3 C) 32.87 – 33.80 (m, 2 C) 40.09 (s, 1 C) 47.99 (s, 1 C) 117.40 (s, 1 C) 138.49 (s, 1 C) 173.26 (s, 1 C) 181.85 (s, 1 C)

Crystallographic information for X-ray structure

Structure of N-[4-hydroxy-1-(4-methoxyphenyl)-1-(trifluoromethyl)but-2-ynyl]-2-methyl-propane-2-sulfinamide

A single crystal was selected for X-ray data analysis. The crystal sample mounted had dimensions of 0.4 mm x 0.4 mm x 0.2 mm and was a yellow prism. Data collection was performed on an Oxford Diffraction Xcalibur diffractometer at 100 K. The unit cell was determined to be monoclinic (space group *Cc*), and the structure contained one molecule in the crystal asymmetric unit (Figure 1). The relative stereochemistry of the molecules in the crystal unit cell is depicted in Figure 2. Crystallographic data is summarized in Table 1 and selected geometric parameters are listed in Table 2. Coordinates and structure factors have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2556113).

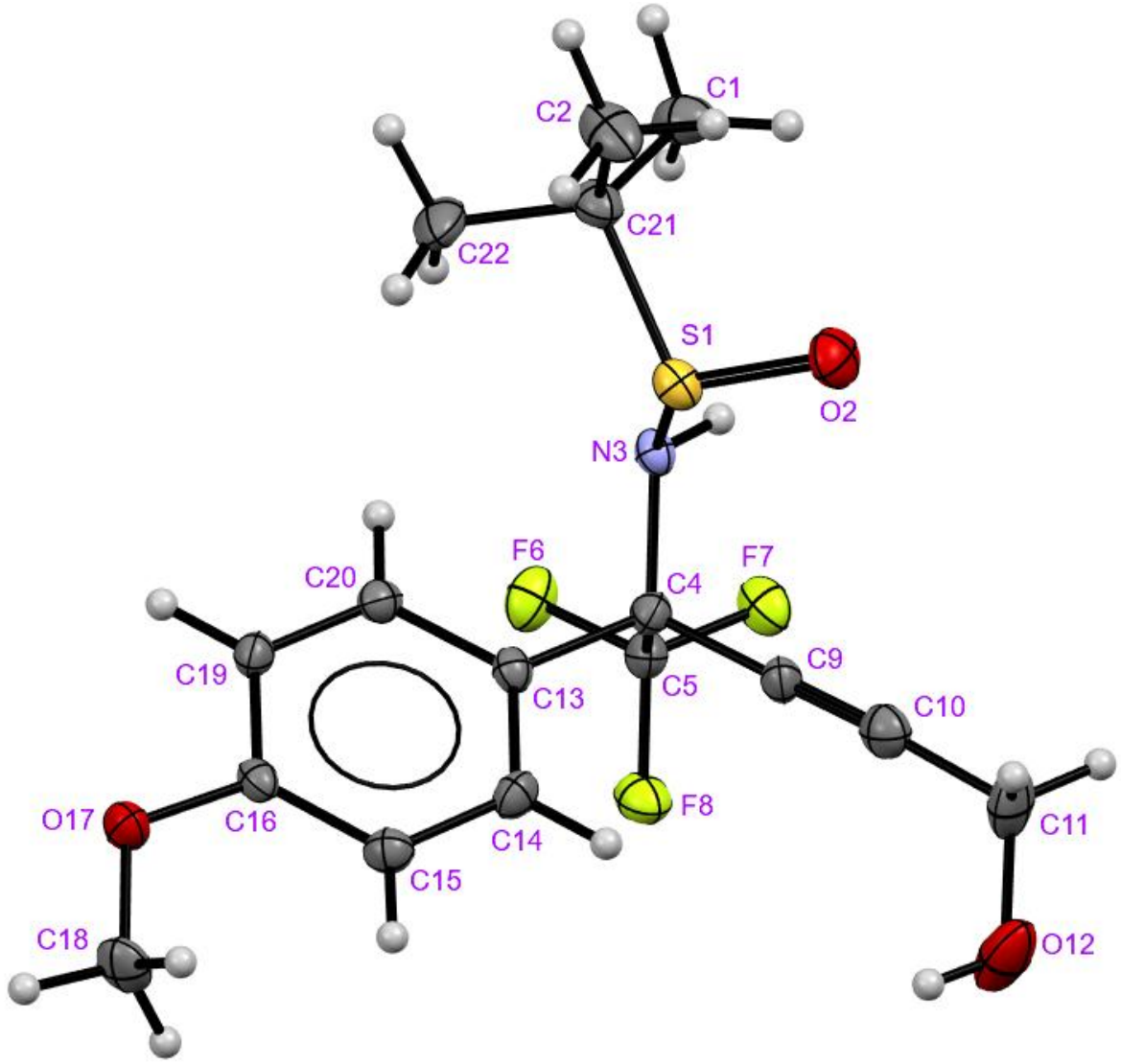


Figure 1: ORTEP representation of N-[4-hydroxy-1-(4-methoxyphenyl)-1-(trifluoromethyl)but-2-ynyl]-2-methyl-propane-2-sulfinamide with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms of arbitrary size.

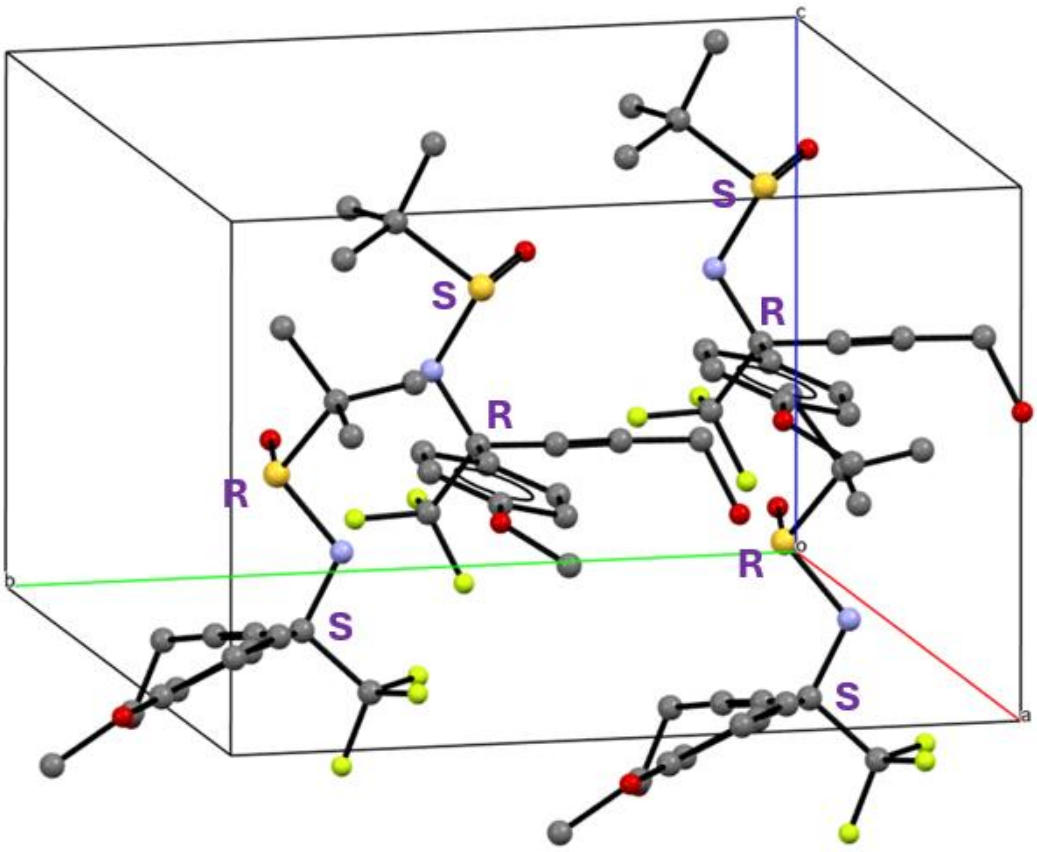


Figure 2: Crystal unit cell of N-[4-hydroxy-1-(4-methoxyphenyl)-1-(trifluoromethyl)but-2-ynyl]-2-methyl-propane-2-sulfinamide with stereocentres labelled in purple. Hydrogen atoms omitted for clarity.

Table 1. Crystal data and structure refinement for N-[4-hydroxy-1-(4-methoxyphenyl)-1-(trifluoromethyl)but-2-ynyl]-2-methyl-propane-2-sulfinamide

Crystal data	
Chemical formula	$C_{16}H_{20}F_3NO_3S$
M_r	363.39
Crystal system, space group	Monoclinic, *Cc*
Temperature (K)	100
a, *b*, *c* (Å)	14.2995 (2), 13.67036 (19), 9.04929 (14)
β (°)	92.2492 (14)
V (Å^3)	1767.58 (5)
Z	4
Radiation type	Cu *K*α
μ (mm^{-1})	2.04
Crystal size (mm)	0.40 × 0.40 × 0.20
Data collection	
Diffractometer	Oxford Diffraction XCALIBUR
Absorption correction	Multi-scan *CrysAlis PRO*, (Agilent, 2011)
T_{min}, T_{max}	0.44, 0.67
No. of measured, independent and observed [$I > 2.0\sigma(I)$] reflections	3642, 1908, 1885
R_{int}	0.020

θ_{max} (°)	58.9
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.556
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.022, 0.053, 0.95
No. of reflections	1900
No. of parameters	227
No. of restraints	8
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.16, −0.14
Absolute structure	Flack (1983), 655 Friedel-pairs
Absolute structure parameter	0.061 (15)

Computer programs: Xcalibur, (Oxford Diffraction, 2002), *CrysAlis PRO*, (Agilent, 2011), *SUPERFLIP* (Palatinus & Chapuis, 2007), *CRYSTALS* (Betteridge *et al.*, 2003), *CAMERON* (Watkin *et al.*, 1996).

Table 2. Selected geometric parameters for N-[4-hydroxy-1-(4-methoxyphenyl)-1-(trifluoromethyl)but-2-ynyl]-2-methyl-propane-2-sulfinamide (Å, º)

S1—O2	1.4889 (17)	C11—O12	1.417 (4)
S1—N3	1.6925 (19)	C13—C14	1.389 (3)
S1—C21	1.838 (3)	C13—C20	1.395 (3)
N3—C4	1.483 (3)	C14—C15	1.394 (3)
C4—C5	1.541 (3)	C15—C16	1.390 (3)
C4—C9	1.469 (3)	C16—O17	1.375 (2)
C4—C13	1.538 (3)	C16—C19	1.387 (3)
C5—F6	1.340 (3)	O17—C18	1.435 (3)
C5—F7	1.347 (3)	C19—C20	1.382 (3)
C5—F8	1.334 (3)	C21—C22	1.516 (4)
C9—C10	1.187 (3)	C21—C1	1.532 (3)
C10—C11	1.479 (3)	C21—C2	1.524 (3)
O2—S1—N3	109.99 (9)	C10—C11—O12	111.3 (2)
O2—S1—C21	105.41 (10)	C4—C13—C14	121.1 (2)
N3—S1—C21	99.17 (10)	C4—C13—C20	120.21 (19)
S1—N3—C4	113.25 (13)	C14—C13—C20	118.6 (2)
N3—C4—C5	105.90 (17)	C13—C14—C15	121.1 (2)
N3—C4—C9	112.74 (19)	C14—C15—C16	119.34 (19)
C5—C4—C9	107.15 (19)	C15—C16—O17	124.3 (2)
N3—C4—C13	110.62 (19)	C15—C16—C19	120.08 (19)
C5—C4—C13	108.84 (18)	O17—C16—C19	115.60 (19)
C9—C4—C13	111.30 (18)	C16—O17—C18	116.69 (17)
C4—C5—F6	112.69 (18)	C16—C19—C20	120.1 (2)
C4—C5—F7	111.38 (18)	C13—C20—C19	120.8 (2)
F6—C5—F7	106.33 (18)	S1—C21—C22	108.13 (18)
C4—C5—F8	111.53 (18)	S1—C21—C1	110.06 (17)
F6—C5—F8	107.64 (19)	C22—C21—C1	112.3 (2)
F7—C5—F8	106.95 (18)	S1—C21—C2	103.82 (18)
C4—C9—C10	177.1 (2)	C22—C21—C2	111.3 (2)
C9—C10—C11	177.1 (3)	C1—C21—C2	110.8 (2)

Structure of 1-tert-butyl-3-(4-chlorophenyl)-3-(trifluoromethyl)isothiazole 1-oxide

A single crystal was selected for X-ray data analysis. The crystal sample mounted had dimensions of 0.3 mm x 0.02 mm x 0.005 mm and was a colourless needle. Data collection was performed on an Oxford Diffraction Xcalibur diffractometer at 100 K. The unit cell was determined to be monoclinic (space group $P2_1/c$), and the structure contained one molecule in the crystal asymmetric unit (Figure 3). The relative stereochemistry of the molecules in the crystal unit cell is depicted in Figure 4. Crystallographic data is summarized in Table 3 and selected geometric parameters are listed in Table 4. Coordinates and structure factors have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2556114).

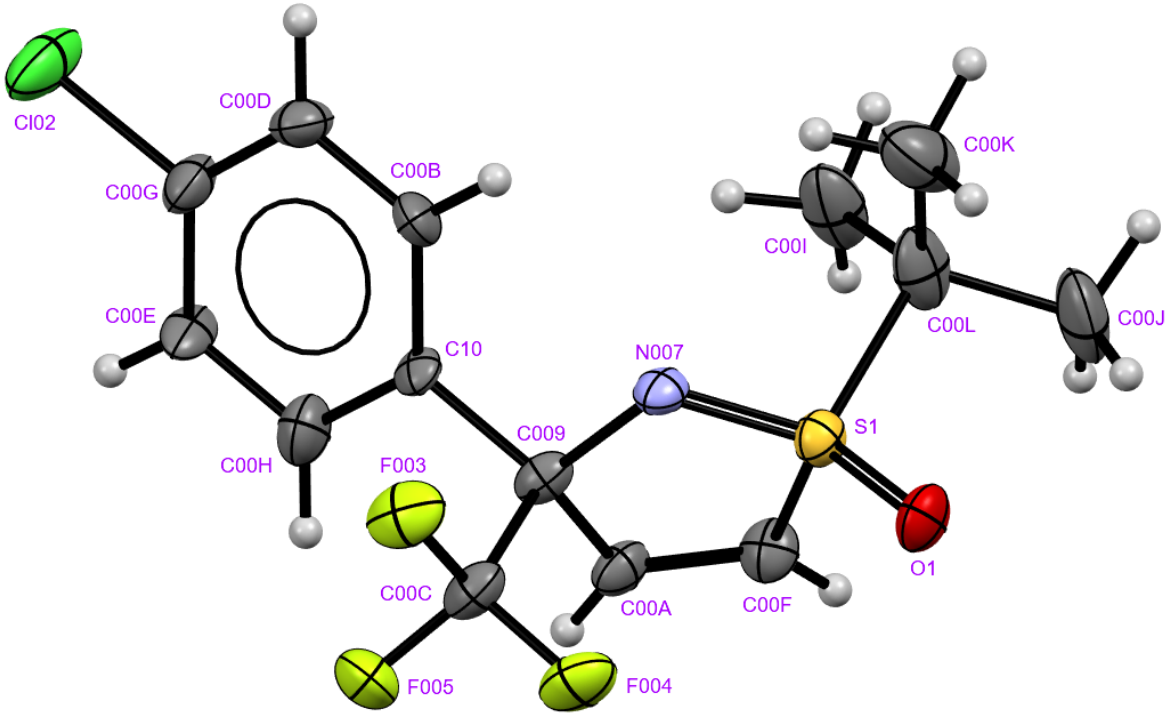


Figure 3: ORTEP representation of 1-tert-butyl-3-(4-chlorophenyl)-3-(trifluoromethyl)isothiazole 1-oxide with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms of arbitrary size.

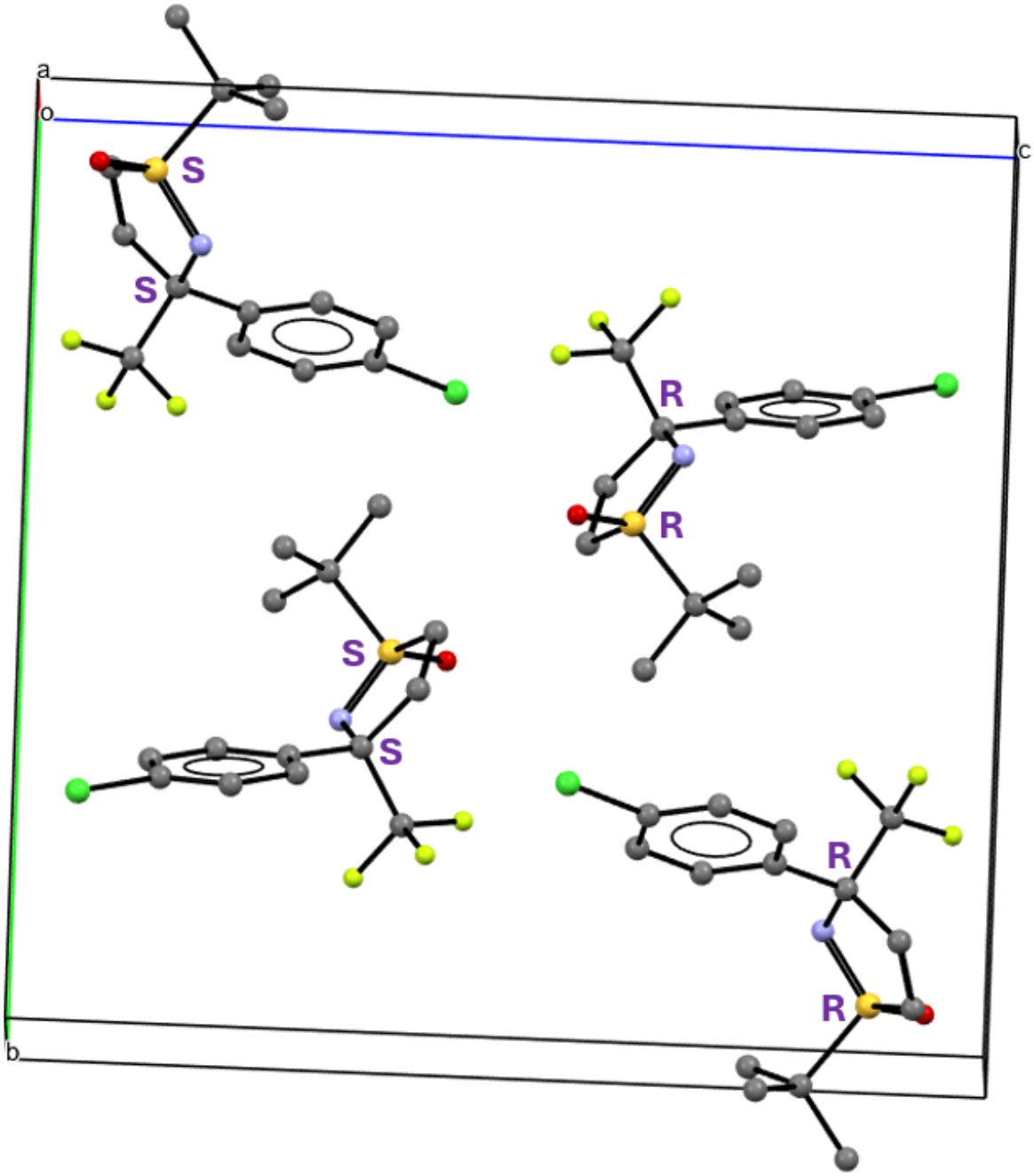


Figure 4: Crystal unit cell of 1-tert-butyl-3-(4-chlorophenyl)-3-(trifluoromethyl)isothiazole 1-oxide with stereocentres labelled in purple. Hydrogen atoms omitted for clarity.

Table 3. Crystal data and structure refinement for 1-tert-butyl-3-(4-chlorophenyl)-3-(trifluoromethyl)isothiazole 1-oxide

Crystal data	
Chemical formula	$C_{14}H_{15}ClF_3NOS$
M_r	337.78
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, *b*, *c* (Å)	6.4603 (3), 16.4143 (10), 16.9884 (9)
β (°)	93.220 (6)
V (Å^3)	1798.63 (17)
Z	4

Radiation type	Cu *Kα*
μ (mm^{-1})	3.21
Crystal size (mm)	0.3 × 0.02 × 0.01
Data collection	
Diffractometer	Oxford Diffraction XCALIBUR
Absorption correction	Multi-scan *CrysAlis PRO*, (Agilent, 2011)
T_{min}, T_{max}	0.670, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4619, 2458, 2131
R_{int}	0.046
θ_{max} (°)	58.9
$(\sin \theta/\lambda)_{max}$ ($Å^{-1}$)	0.556
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.144, 0.510, 2.49
No. of reflections	2458
No. of parameters	194
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	2.09, −0.83

Computer programs: Xcalibur, (Oxford Diffraction, 2002), *CrysAlis PRO*, (Agilent, 2011), *SHELXT* 2018/2 (Sheldrick, 2015), *SHELXL* 2018/3 (Sheldrick, 2015), Olex2.1.5 (Dolomanov *et. al*., 2009).

Table 4. Selected geometric parameters for 1-tert-butyl-3-(4-chlorophenyl)-3-(trifluoromethyl)isothiazole 1-oxide (Å, º)

S1—O1	1.460 (7)	C00D—C00G	1.380 (16)
S1—N007	1.528 (7)	C00E—H00E	0.9300
S1—C00F	1.753 (10)	C00E—C00G	1.345 (15)
S1—C00L	1.832 (11)	C00E—C00H	1.396 (14)
Cl02—C00G	1.751 (10)	C00F—H00F	0.9300
F003—C00C	1.351 (11)	C00H—H00H	0.9300
F004—C00C	1.326 (11)	C00I—H00C	0.9600
F005—C00C	1.335 (13)	C00I—H00G	0.9600
N007—C009	1.453 (12)	C00I—H00I	0.9600
C10—C009	1.543 (11)	C00I—C00L	1.540 (13)
C10—C00B	1.373 (13)	C00J—H00J	0.9600
C10—C00H	1.402 (15)	C00J—H00K	0.9600
C009—C00A	1.525 (12)	C00J—H00L	0.9600
C009—C00C	1.538 (13)	C00J—C00L	1.523 (15)
C00A—H00A	0.9300	C00K—H00M	0.9600
C00A—C00F	1.318 (14)	C00K—H00N	0.9600
C00B—H00B	0.9300	C00K—H00O	0.9600
C00B—C00D	1.397 (13)	C00K—C00L	1.502 (19)
C00D—H00D	0.9300		
O1—S1—N007	120.4 (4)	S1—C00F—H00F	126.5
O1—S1—C00F	112.3 (4)	C00A—C00F—S1	107.0 (7)
O1—S1—C00L	106.5 (4)	C00A—C00F—H00F	126.5
N007—S1—C00F	99.1 (4)	C00D—C00G—Cl02	118.9 (8)
N007—S1—C00L	108.6 (5)	C00E—C00G—Cl02	119.7 (8)
C00F—S1—C00L	109.6 (5)	C00E—C00G—C00D	121.5 (9)
C009—N007—S1	111.4 (6)	C10—C00H—H00H	120.7
C00B—C10—C009	120.5 (8)	C00E—C00H—C10	118.6 (11)

C00B—C10—C00H	119.6 (8)	C00E—C00H—H00H	120.7
C00H—C10—C009	119.9 (8)	H00C—C00I—H00G	109.5
N007—C009—C10	111.0 (7)	H00C—C00I—H00I	109.5
N007—C009—C00A	107.6 (7)	H00G—C00I—H00I	109.5
N007—C009—C00C	107.7 (7)	C00L—C00I—H00C	109.5
C00A—C009—C10	112.0 (7)	C00L—C00I—H00G	109.5
C00A—C009—C00C	108.8 (8)	C00L—C00I—H00I	109.5
C00C—C009—C10	109.5 (7)	H00J—C00J—H00K	109.5
C009—C00A—H00A	123.2	H00J—C00J—H00L	109.5
C00F—C00A—C009	113.7 (9)	H00K—C00J—H00L	109.5
C00F—C00A—H00A	123.2	C00L—C00J—H00J	109.5
C10—C00B—H00B	119.6	C00L—C00J—H00K	109.5
C10—C00B—C00D	120.9 (9)	C00L—C00J—H00L	109.5
C00D—C00B—H00B	119.6	H00M—C00K—H00N	109.5
F003—C00C—C009	110.7 (8)	H00M—C00K—H00O	109.5
F004—C00C—F003	107.4 (8)	H00N—C00K—H00O	109.5
F004—C00C—F005	107.2 (8)	C00L—C00K—H00M	109.5
F004—C00C—C009	112.4 (7)	C00L—C00K—H00N	109.5
F005—C00C—F003	105.7 (8)	C00L—C00K—H00O	109.5
F005—C00C—C009	113.0 (8)	C00I—C00L—S1	106.7 (7)
C00B—C00D—H00D	120.8	C00J—C00L—S1	107.7 (8)
C00G—C00D—C00B	118.5 (10)	C00J—C00L—C00I	111.6 (9)
C00G—C00D—H00D	120.8	C00K—C00L—S1	106.7 (7)
C00G—C00E—H00E	119.5	C00K—C00L—C00I	111.6 (10)
C00G—C00E—C00H	120.9 (10)	C00K—C00L—C00J	112.2 (10)
C00H—C00E—H00E	119.5		

Structure of [1-tert-butyl-3-(4-methoxyphenyl)-1-oxo-3-(trifluoromethyl)isothiazol-5-yl]methanol

A single crystal was selected for X-ray data analysis. The crystal sample mounted had dimensions of 0.1 mm x 0.05 mm x 0.02 mm and was a colourless prism. Data collection was performed on an Oxford Diffraction Xcalibur diffractometer at 100 K. The unit cell was determined to be monoclinic (space group $P2_1/c$), and the structure contained one molecule in the crystal asymmetric unit (Figure 5). The relative stereochemistry of the molecules in the crystal unit cell is depicted in Figure 6. Crystallographic data is summarized in Table 5 and selected geometric parameters are listed in Table 6. Coordinates and structure factors have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2556116).

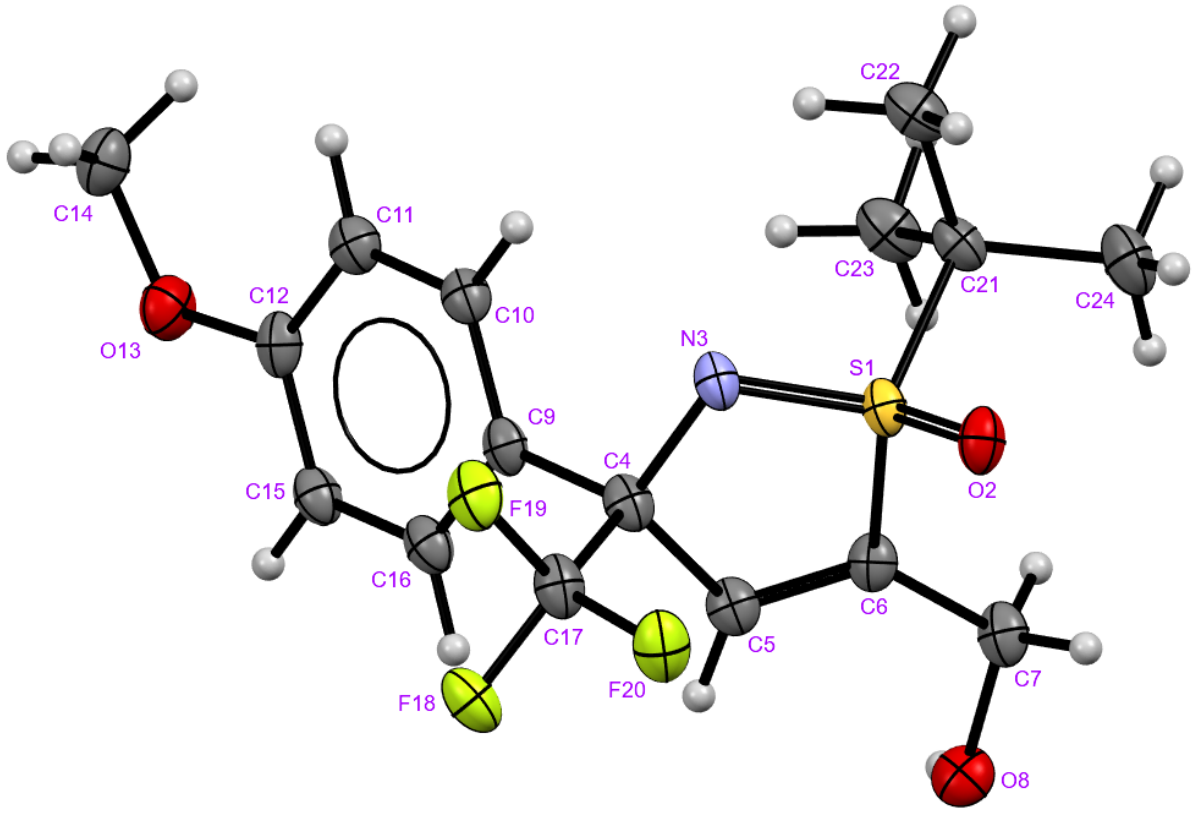


Figure 5: ORTEP representation of [1-tert-butyl-3-(4-methoxyphenyl)-1-oxo-3-(trifluoromethyl)isothiazol-5-yl]methanol with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms of arbitrary size.

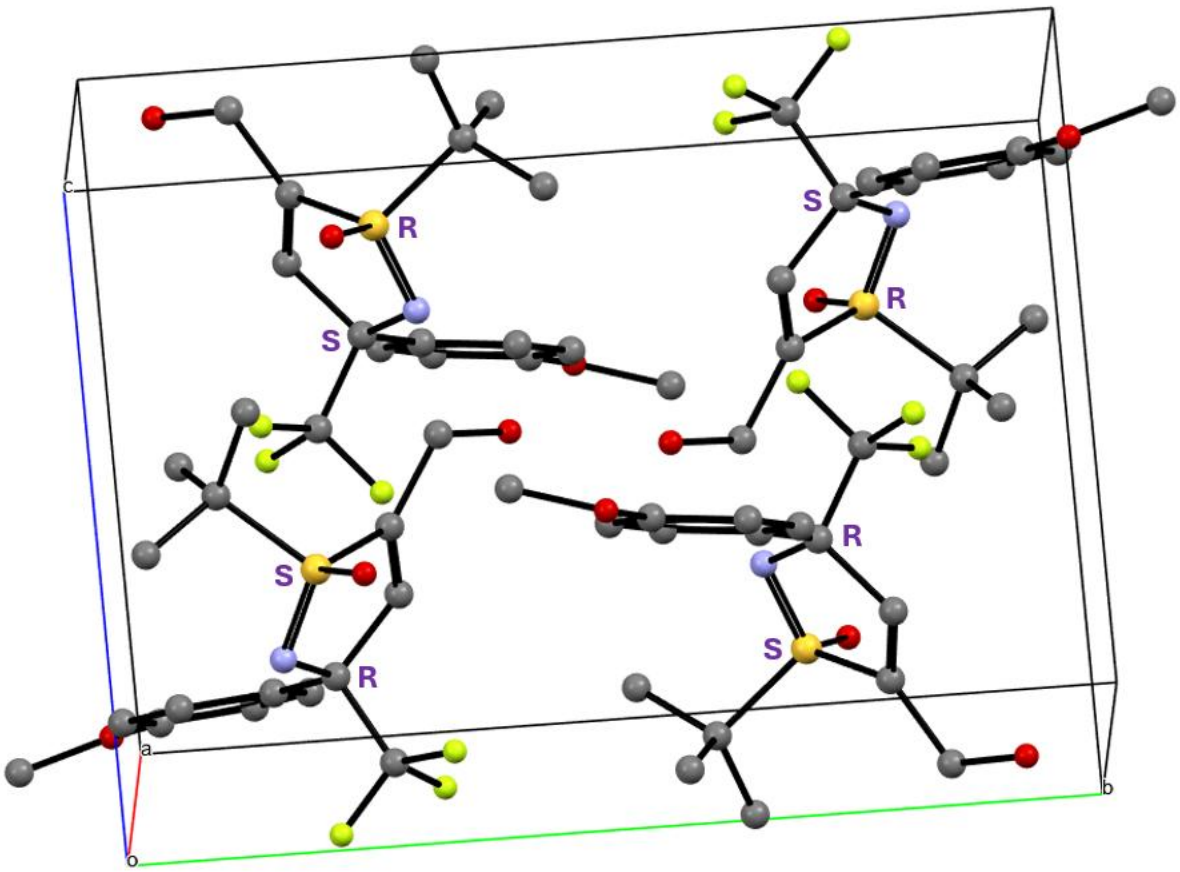


Figure 6: Crystal unit cell of [1-tert-butyl-3-(4-methoxyphenyl)-1-oxo-3-(trifluoromethyl)isothiazol-5-yl]methanol with stereocentres labelled in purple. Hydrogen atoms omitted for clarity.

Table 5. Crystal data and structure refinement for [1-tert-butyl-3-(4-methoxyphenyl)-1-oxo-3-(trifluoromethyl)isothiazol-5-yl]methanol

Crystal data	
Chemical formula	$C_{16}H_{20}F_3NO_3S$
M_r	363.39
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	10.8991 (8), 14.2014 (11), 12.0337 (8)
β (°)	116.805 (9)
V (Å^3)	1662.5 (2)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	2.17
Crystal size (mm)	0.10 × 0.05 × 0.02
Data collection	
Diffractometer	Oxford Diffraction XCALIBUR
Absorption correction	Multi-scan *CrysAlis PRO*, (Agilent, 2011)
T_{min}, T_{max}	0.90, 0.96
No. of measured, independent and observed [$I > 2.0\sigma(I)$] reflections	3962, 2666, 1947
R_{int}	0.021
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.576
Refinement	

$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.112, 0.97
No. of reflections	2107
No. of parameters	221
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.35, −0.56

Computer programs: Xcalibur, (Oxford Diffraction, 2002), *CrysAlis PRO*, (Agilent, 2011), *SUPERFLIP* (Palatinus & Chapuis, 2007), *CRYSTALS* (Betteridge *et al.*, 2003), *CAMERON* (Watkin *et al.*, 1996).

Table 6. Selected geometric parameters for [1-tert-butyl-3-(4-methoxyphenyl)-1-oxo-3-(trifluoromethyl)isothiazol-5-yl]methanol (Å, º)

S1—O2	1.4538 (19)	C10—C11	1.390 (4)
S1—N3	1.549 (2)	C11—C12	1.388 (4)
S1—C6	1.776 (3)	C12—O13	1.365 (3)
S1—C21	1.818 (3)	C12—C15	1.404 (4)
N3—C4	1.469 (4)	O13—C14	1.443 (4)
C4—C5	1.524 (4)	C15—C16	1.376 (4)
C4—C9	1.532 (4)	C17—F18	1.349 (3)
C4—C17	1.533 (4)	C17—F19	1.338 (3)
C5—C6	1.319 (4)	C17—F20	1.343 (3)
C6—C7	1.511 (4)	C21—C22	1.533 (4)
C7—O8	1.421 (3)	C21—C23	1.526 (4)
C9—C10	1.395 (4)	C21—C24	1.534 (4)
C9—C16	1.401 (4)		
O2—S1—N3	119.45 (11)	C9—C10—C11	121.2 (3)
O2—S1—C6	110.78 (12)	C10—C11—C12	119.7 (3)
N3—S1—C6	99.41 (13)	C11—C12—O13	125.1 (3)
O2—S1—C21	106.96 (13)	C11—C12—C15	119.7 (3)
N3—S1—C21	108.06 (14)	O13—C12—C15	115.3 (2)
C6—S1—C21	112.12 (12)	C12—O13—C14	116.9 (2)
S1—N3—C4	110.47 (18)	C12—C15—C16	120.0 (3)
N3—C4—C5	108.2 (2)	C9—C16—C15	121.1 (3)
N3—C4—C9	112.3 (2)	C4—C17—F18	112.8 (2)
C5—C4—C9	110.7 (2)	C4—C17—F19	111.0 (2)
N3—C4—C17	106.6 (2)	F18—C17—F19	106.9 (2)
C5—C4—C17	109.5 (2)	C4—C17—F20	112.7 (2)
C9—C4—C17	109.5 (2)	F18—C17—F20	106.0 (2)
C4—C5—C6	114.6 (3)	F19—C17—F20	107.1 (2)
S1—C6—C5	106.2 (2)	S1—C21—C22	105.69 (19)
S1—C6—C7	125.0 (2)	S1—C21—C23	108.8 (2)
C5—C6—C7	128.6 (3)	C22—C21—C23	111.4 (3)
C6—C7—O8	110.5 (2)	S1—C21—C24	108.3 (2)
C4—C9—C10	121.3 (2)	C22—C21—C24	110.8 (3)
C4—C9—C16	120.4 (2)	C23—C21—C24	111.5 (2)
C10—C9—C16	118.2 (3)		

Structure of **3-(4-Chloro-phenyl)-isothiazole**

A single crystal was selected for X-ray data analysis. The crystal sample mounted had dimensions of

1.0 mm x 0.05 mm x 0.05 mm and was an orange needle. Data collection was performed on an Oxford Diffraction Xcalibur diffractometer at 100 K. The unit cell was determined to be orthorhombic (space group $P2_12_12_1$), and the structure contained one molecule in the crystal asymmetric unit (Figure 7). Crystallographic data is summarized in Table 7 and selected geometric parameters are listed in Table 8. Coordinates and structure factors have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2556118).

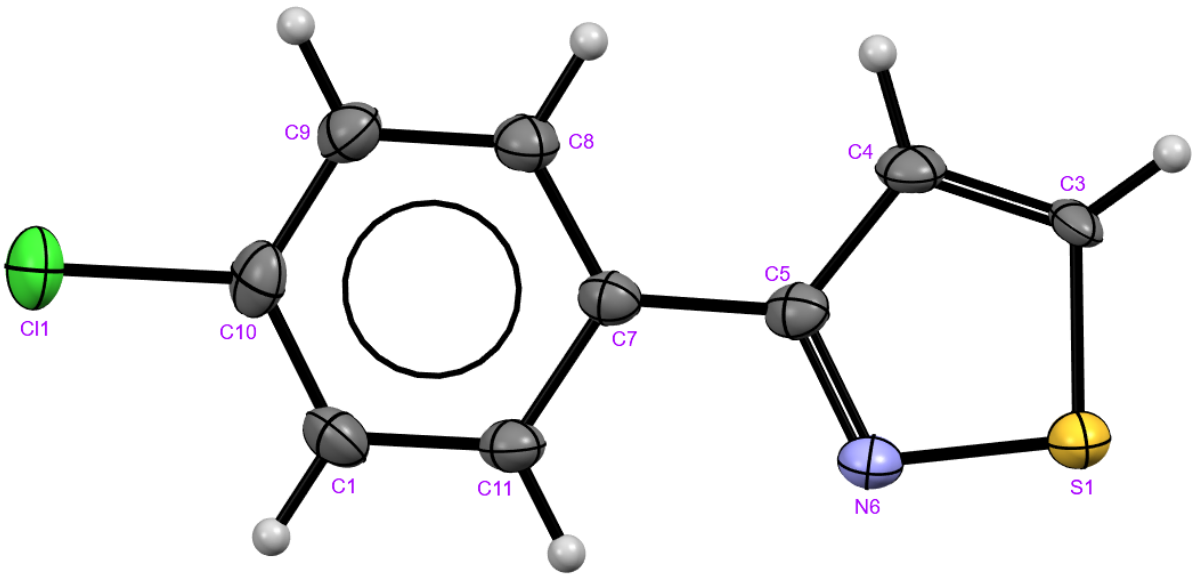


Figure 7: ORTEP representation of 3-(4-Chloro-phenyl)-isothiazole with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms of arbitrary size.

Table 7. Crystal data and structure refinement for 3-(4-Chloro-phenyl)-isothiazole

Crystal data	
Chemical formula	C_9H_6ClNS
M_r	195.66
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	100
a, *b*, *c* (Å)	3.95417 (17), 10.2658 (3), 20.6628 (6)
V (Å^3)	838.76 (5)
Z	4
Radiation type	Cu *K*α
μ (mm^{-1})	5.82
Crystal size (mm)	1.00 × 0.05 × 0.05
Data collection	
Diffractometer	Oxford Diffraction XCALIBUR
Absorption correction	Multi-scan *CrysAlis PRO*, (Agilent, 2011)
T_{min}, T_{max}	0.75, 0.75
No. of measured, independent and observed [$I > 2.0\sigma(I)$] reflections	3651, 1171, 1143
R_{int}	0.025
θ_{max} (°)	58.9
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.555
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.035, 0.074, 0.98

No. of reflections	1166
No. of parameters	111
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.26, −0.25
Absolute structure	Flack (1983), 411 Friedel-pairs
Absolute structure parameter	0.48 (4)

Computer programs: Xcalibur, (Oxford Diffraction, 2002), *CrysAlis PRO*, (Agilent, 2011), *SIR92* (Altomare *et al.*, 1994), *CRYSTALS* (Betteridge *et al.*, 2003), *CAMERON* (Watkin *et al.*, 1996).

Table 8. Selected geometric parameters for 3-(4-Chloro-phenyl)-isothiazole (Å, º)

S1—C3	1.698 (3)	C7—C11	1.403 (4)
S1—N6	1.649 (3)	C8—C9	1.390 (5)
C3—C4	1.368 (5)	C9—C10	1.369 (5)
C4—C5	1.430 (5)	C10—Cl1	1.758 (3)
C5—N6	1.317 (4)	C10—C1	1.387 (5)
C5—C7	1.476 (4)	C11—C1	1.385 (5)
C7—C8	1.388 (4)		
C3—S1—N6	95.42 (15)	C8—C7—C11	118.2 (3)
S1—C3—C4	108.8 (2)	C7—C8—C9	121.3 (3)
C3—C4—C5	110.8 (3)	C8—C9—C10	118.9 (3)
C4—C5—N6	115.2 (3)	C9—C10—Cl1	119.5 (3)
C4—C5—C7	125.0 (3)	C9—C10—C1	121.8 (3)
N6—C5—C7	119.9 (3)	Cl1—C10—C1	118.7 (3)
C5—N6—S1	109.9 (2)	C7—C11—C1	121.0 (3)
C5—C7—C8	121.8 (3)	C10—C1—C11	118.7 (3)
C5—C7—C11	120.0 (3)		

Structure of 3-(4-chlorophenyl)-2,3-dihydroisothiazole 1-oxide

A single crystal was selected for X-ray data analysis. The crystal sample mounted had dimensions of 1.0 mm x 0.05 mm x 0.05 mm and was a colourless needle. Data collection was performed on an Oxford Diffraction Xcalibur diffractometer at 100 K. The unit cell was determined to be monoclinic (space group $P2_1$), and the structure contained one molecule in the crystal asymmetric unit (Figure 8). The absolute stereochemistry of the molecules in the crystal unit cell is depicted in Figure 9. Crystallographic data is summarized in Table 9 and selected geometric parameters are listed in Table 10. Coordinates and structure factors have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2556119).

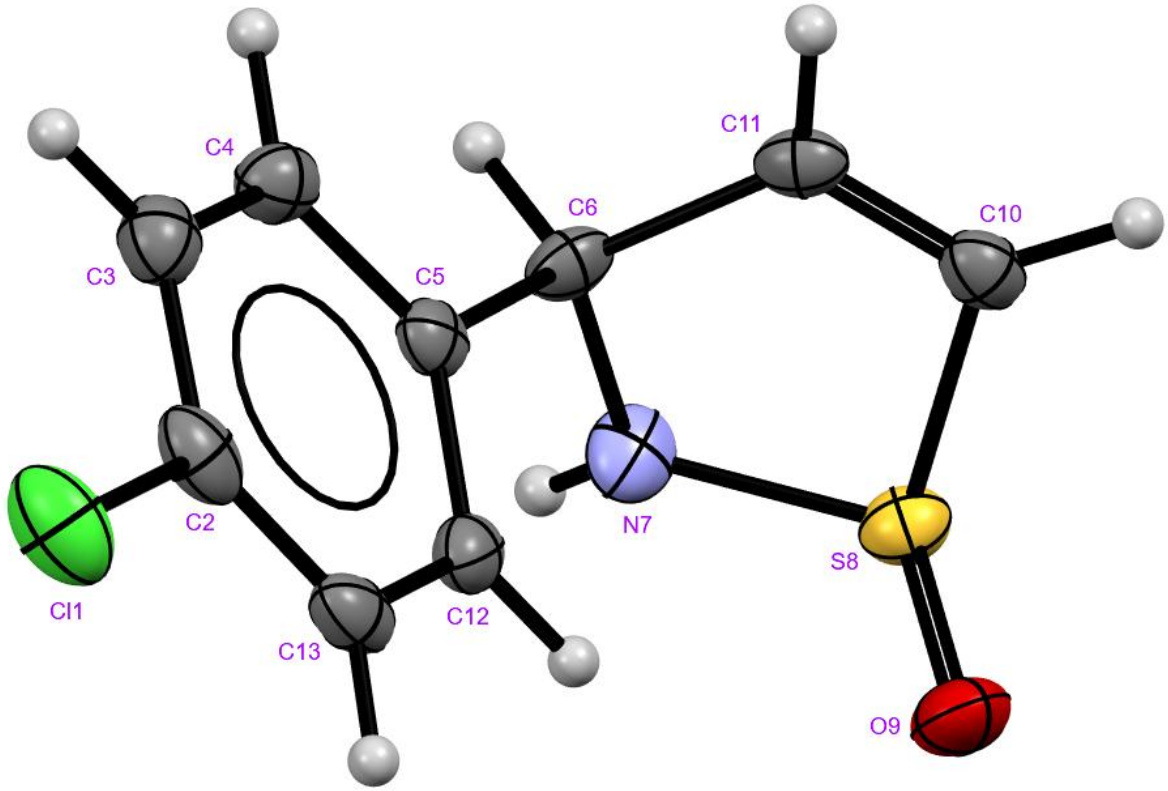


Figure 8: ORTEP representation of 3-(4-chlorophenyl)-2,3-dihydroisothiazole 1-oxide with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms of arbitrary size.

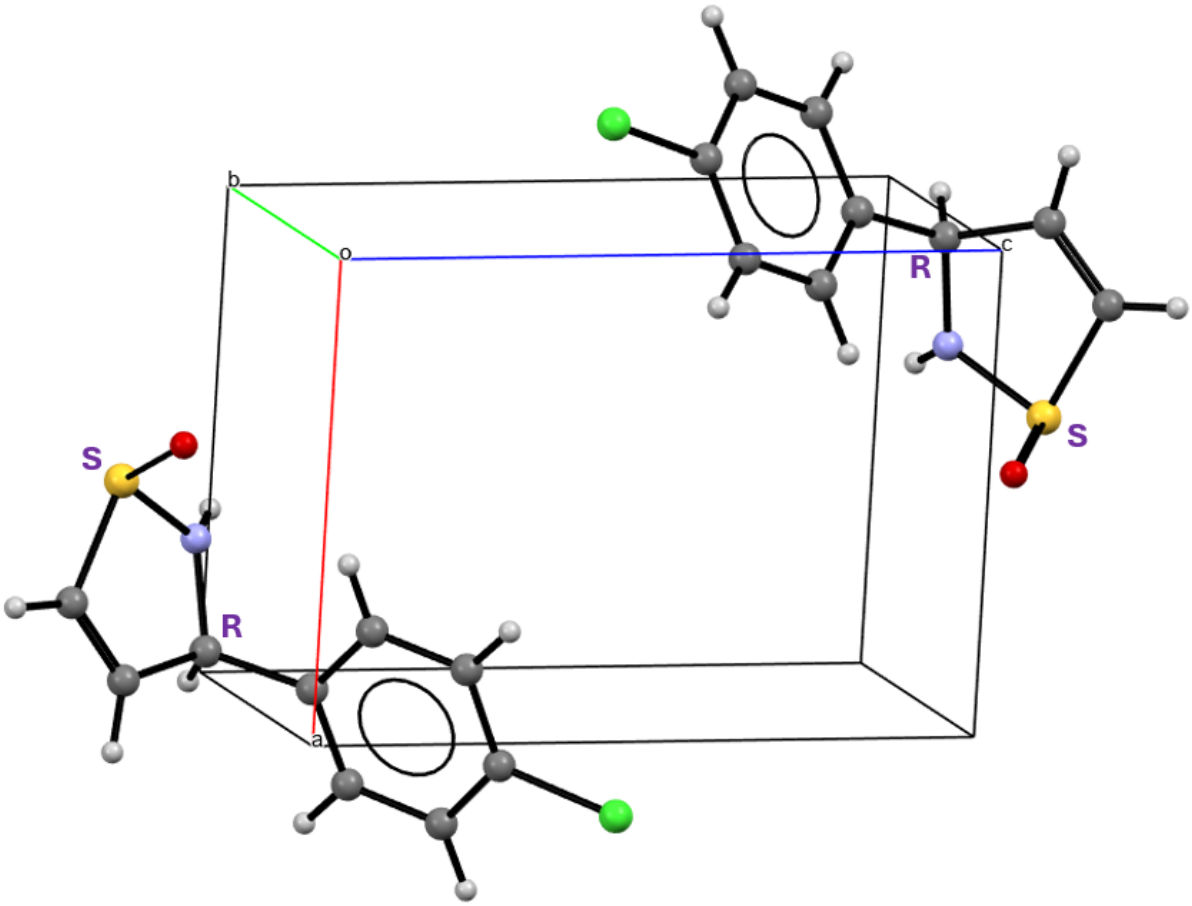


Figure 9: Crystal unit cell of 3-(4-chlorophenyl)-2,3-dihydroisothiazole 1-oxide with stereocentres labelled in purple.

Table 9. Crystal data and structure refinement for 3-(4-chlorophenyl)-2,3-dihydroisothiazole 1-oxide

Crystal data	
Chemical formula	C_9H_8ClNOS
M_r	213.69
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	100
a, *b*, *c* (Å)	6.32860 (12), 8.64578 (18), 8.65317 (18)
β (°)	93.0532 (19)
V (Å^3)	472.79 (2)
Z	2
Radiation type	Cu *K*α
μ (mm^{-1})	5.29
Crystal size (mm)	0.05 × 0.02 × 0.02
Data collection	
Diffractometer	Oxford Diffraction XCALIBUR
Absorption correction	Multi-scan *CrysAlis PRO*, (Agilent, 2011)
T_{min}, T_{max}	0.90, 0.90
No. of measured, independent and observed [$I > 2.0\sigma(I)$] reflections	2179, 1253, 1238
R_{int}	0.014
θ_{max} (°)	58.9

$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.555
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.021, 0.050, 0.97
No. of reflections	1246
No. of parameters	123
No. of restraints	5
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.16, −0.14
Absolute structure	Flack (1983), 528 Friedel-pairs
Absolute structure parameter	0.002 (16)

Computer programs: Xcalibur, (Oxford Diffraction, 2002), *CrysAlis PRO*, (Agilent, 2011), *SUPERFLIP* (Palatinus & Chapuis, 2007), *CRYSTALS* (Betteridge *et al.*, 2003), *CAMERON* (Watkin *et al.*, 1996).

Table 10. Selected geometric parameters for 3-(4-chlorophenyl)-2,3-dihydroisothiazole 1-oxide (Å, º)

Cl1—C2	1.747 (2)	C6—N7	1.463 (3)
C2—C3	1.387 (4)	C6—C11	1.508 (3)
C2—C13	1.381 (4)	N7—S8	1.638 (2)
C3—C4	1.385 (4)	S8—O9	1.4948 (18)
C4—C5	1.388 (3)	S8—C10	1.777 (2)
C5—C6	1.522 (3)	C10—C11	1.313 (3)
C5—C12	1.390 (3)	C12—C13	1.393 (4)
Cl1—C2—C3	119.1 (2)	N7—C6—C11	103.3 (2)
Cl1—C2—C13	119.04 (19)	C6—N7—S8	117.57 (17)
C3—C2—C13	121.9 (2)	N7—S8—O9	110.61 (11)
C2—C3—C4	118.6 (2)	N7—S8—C10	90.10 (11)
C3—C4—C5	120.7 (2)	O9—S8—C10	103.74 (11)
C4—C5—C6	119.2 (2)	S8—C10—C11	112.35 (19)
C4—C5—C12	119.7 (2)	C6—C11—C10	115.4 (2)
C6—C5—C12	121.0 (2)	C5—C12—C13	120.3 (2)
C5—C6—N7	114.5 (2)	C12—C13—C2	118.8 (2)
C5—C6—C11	111.23 (19)		

Structure of N-(1-(2,4-dichlorophenyl)-4,4-dimethylpent-2-yn-1-yl)-2-methylpropane-2-sulfinamide

A single crystal grown from heptane was selected for X-ray data analysis. The crystal sample mounted had dimensions of 0.2 mm x 0.1 mm x 0.05 mm and was a colourless prism. Data collection was performed on an Oxford Diffraction Xcalibur diffractometer at 100 K. The unit cell was determined to be triclinic (space group *P*-1), and the structure contained one molecule in the crystal asymmetric unit (Figure 12). The relative stereochemistry of the molecules in the crystal unit cell is depicted in Figure 13. Crystallographic data is summarized in Table 13 and selected geometric parameters are listed in

Table 14. Coordinates and structure factors have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2556121).

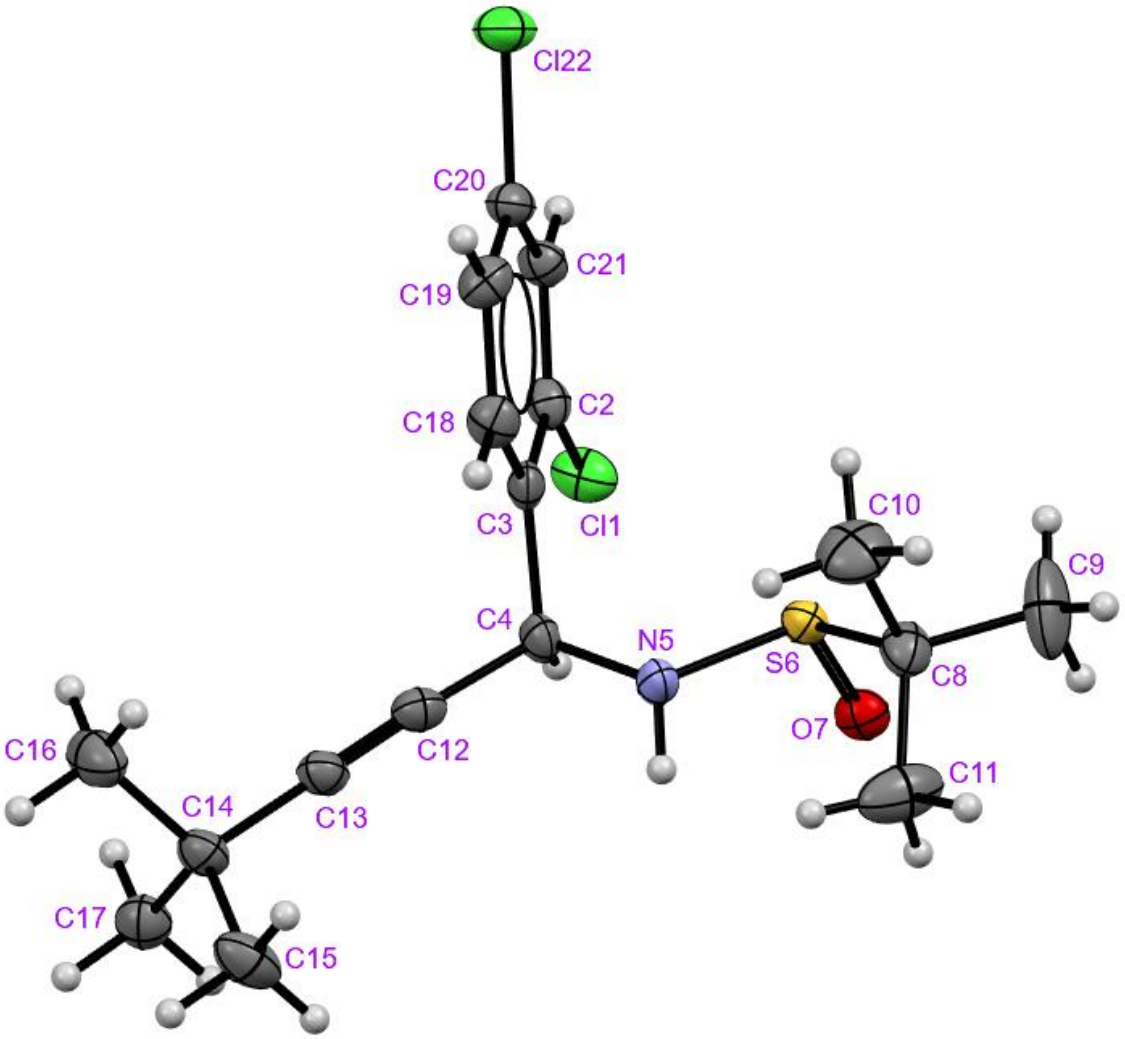


Figure 12: ORTEP representation of N-(1-(2,4-dichlorophenyl)-4,4-dimethylpent-2-yn-1-yl)-2-methylpropane-2-sulfinamide with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms of arbitrary size.

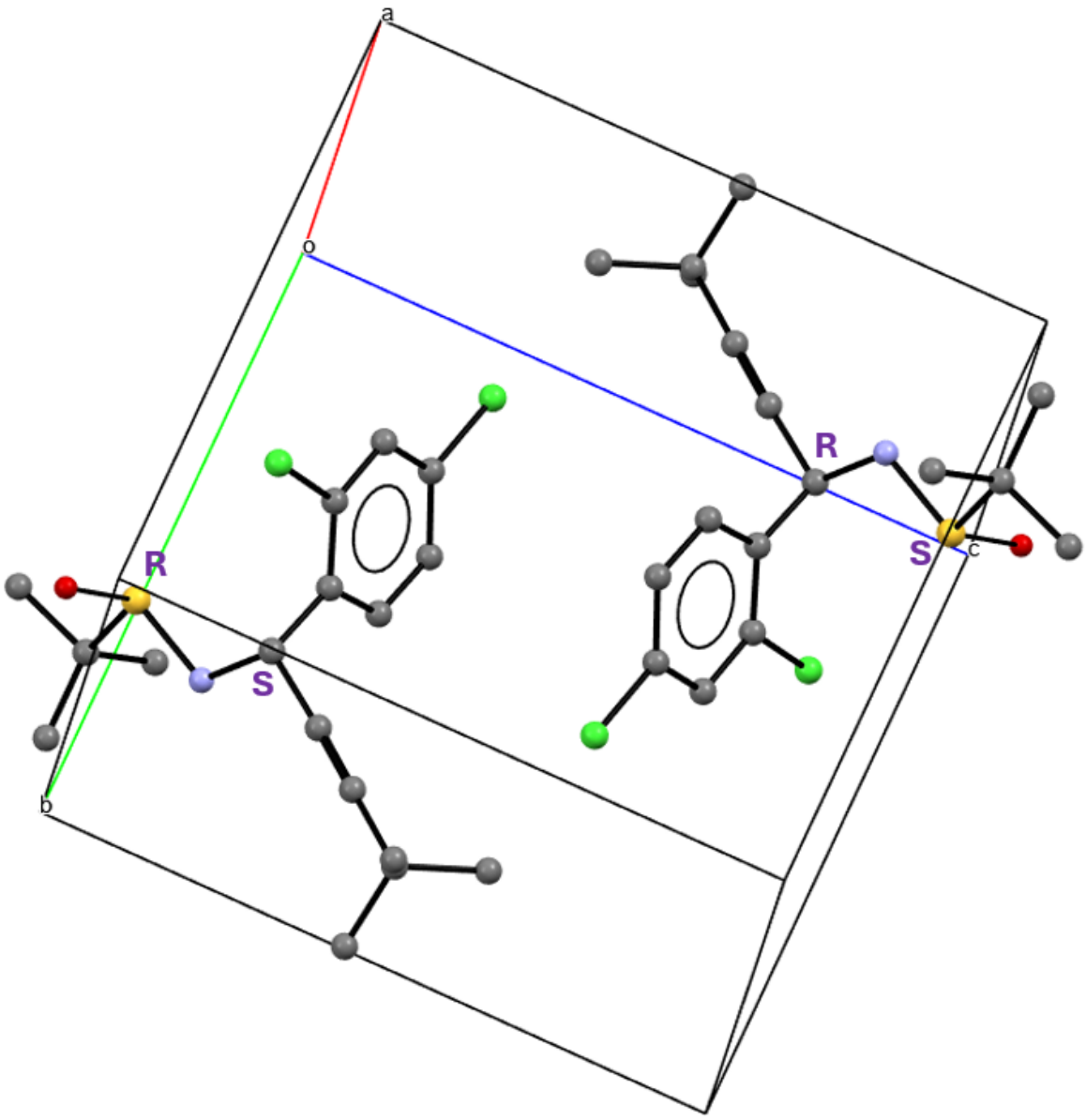


Figure 13: Crystal unit cell of N-(1-(2,4-dichlorophenyl)-4,4-dimethylpent-2-yn-1-yl)-2-methylpropane-2-sulfinamidewith stereocentres labelled in purple. Hydrogen atoms omitted for clarity.

Table 13. Crystal data and structure refinement for N-(1-(2,4-dichlorophenyl)-4,4-dimethylpent-2-yn-1-yl)-2-methylpropane-2-sulfinamide

Crystal data	
Chemical formula	$C_{17}H_{23}Cl_2NOS$
M_r	360.35
Crystal system, space group	Triclinic, *P*1
Temperature (K)	100
a, *b*, *c* (Å)	9.3914 (7), 9.6216 (6), 12.0784 (13)
α, β, γ (°)	92.219 (7), 110.518 (9), 109.493 (6)
V (Å^3)	948.48 (16)
Z	2
Radiation type	Cu *K*α
μ (mm^{-1})	4.11

Crystal size (mm)	0.20 × 0.10 × 0.05
Data collection	
Diffractometer	Oxford Diffraction XCALIBUR
Absorption correction	Multi-scan *CrysAlis PRO*, (Agilent, 2011)
T_{min}, T_{max}	0.66, 0.81
No. of measured, independent and observed [$I > 2.0\sigma(I)$] reflections	4980, 2598, 2375
R_{int}	0.028
θ_{max} (°)	58.9
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.556
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.049, 0.103, 1.02
No. of reflections	2582
No. of parameters	204
No. of restraints	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.50, −0.47

Computer programs: Xcalibur, (Oxford Diffraction, 2002), *CrysAlis PRO*, (Agilent, 2011), *SUPERFLIP* (Palatinus & Chapuis, 2007), *CRYSTALS* (Betteridge *et al.*, 2003), *CAMERON* (Watkin *et al.*, 1996).

Table 14. Selected geometric parameters for N-(1-(2,4-dichlorophenyl)-4,4-dimethylpent-2-yn-1-yl)-2-methylpropane-2-sulfinamide (Å, º)

Cl1—C2	1.742 (3)	C8—C10	1.519 (5)
C2—C3	1.393 (4)	C8—C11	1.506 (5)
C2—C21	1.388 (4)	C12—C13	1.184 (5)
C3—C4	1.517 (4)	C13—C14	1.479 (5)
C3—C18	1.396 (5)	C14—C15	1.534 (5)
C4—N5	1.497 (4)	C14—C16	1.544 (5)
C4—C12	1.473 (4)	C14—C17	1.533 (5)
N5—S6	1.670 (3)	C18—C19	1.386 (5)
S6—O7	1.495 (2)	C19—C20	1.386 (5)
S6—C8	1.841 (3)	C20—C21	1.384 (5)
C8—C9	1.528 (5)	C20—Cl22	1.740 (3)
Cl1—C2—C3	120.3 (2)	C9—C8—C11	112.1 (3)
Cl1—C2—C21	117.0 (2)	C10—C8—C11	111.6 (3)
C3—C2—C21	122.7 (3)	C4—C12—C13	175.9 (4)
C2—C3—C4	122.5 (3)	C12—C13—C14	179.3 (3)
C2—C3—C18	117.0 (3)	C13—C14—C15	108.3 (3)
C4—C3—C18	120.5 (3)	C13—C14—C16	109.3 (3)
C3—C4—N5	109.7 (2)	C15—C14—C16	110.3 (3)
C3—C4—C12	113.1 (3)	C13—C14—C17	109.7 (3)
N5—C4—C12	108.3 (2)	C15—C14—C17	109.6 (3)
C4—N5—S6	113.0 (2)	C16—C14—C17	109.6 (3)
N5—S6—O7	110.59 (13)	C3—C18—C19	121.9 (3)
N5—S6—C8	98.67 (15)	C18—C19—C20	118.9 (3)
O7—S6—C8	106.09 (14)	C19—C20—C21	121.5 (3)
S6—C8—C9	102.8 (2)	C19—C20—Cl22	119.3 (3)
S6—C8—C10	107.5 (3)	C21—C20—Cl22	119.2 (2)
C9—C8—C10	110.4 (3)	C2—C21—C20	118.0 (3)

S6—C8—C11	111.9 (2)		

Structure of N-(1-(4-chlorophenyl)-4,4-dimethylpent-2-yn-1-yl)-2-methylpropane-2-sulfinamide

A single crystal grown from heptane was selected for X-ray data analysis. The crystal sample mounted had dimensions of 0.2 mm x 0.02 mm x 0.02 mm and was a colourless prism. Data collection was performed on an Oxford Diffraction Xcalibur diffractometer at 100 K. The unit cell was determined to be triclinic (space group *P*-1), and the structure contained one molecule in the crystal asymmetric unit with rotational disorder of the t-butyl which could be modelled (Figure 14). The relative stereochemistry of the molecules in the crystal unit cell is depicted in Figure 15. Crystallographic data is summarized in Table 15 and selected geometric parameters are listed in Table 16. Coordinates and structure factors have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2556122).

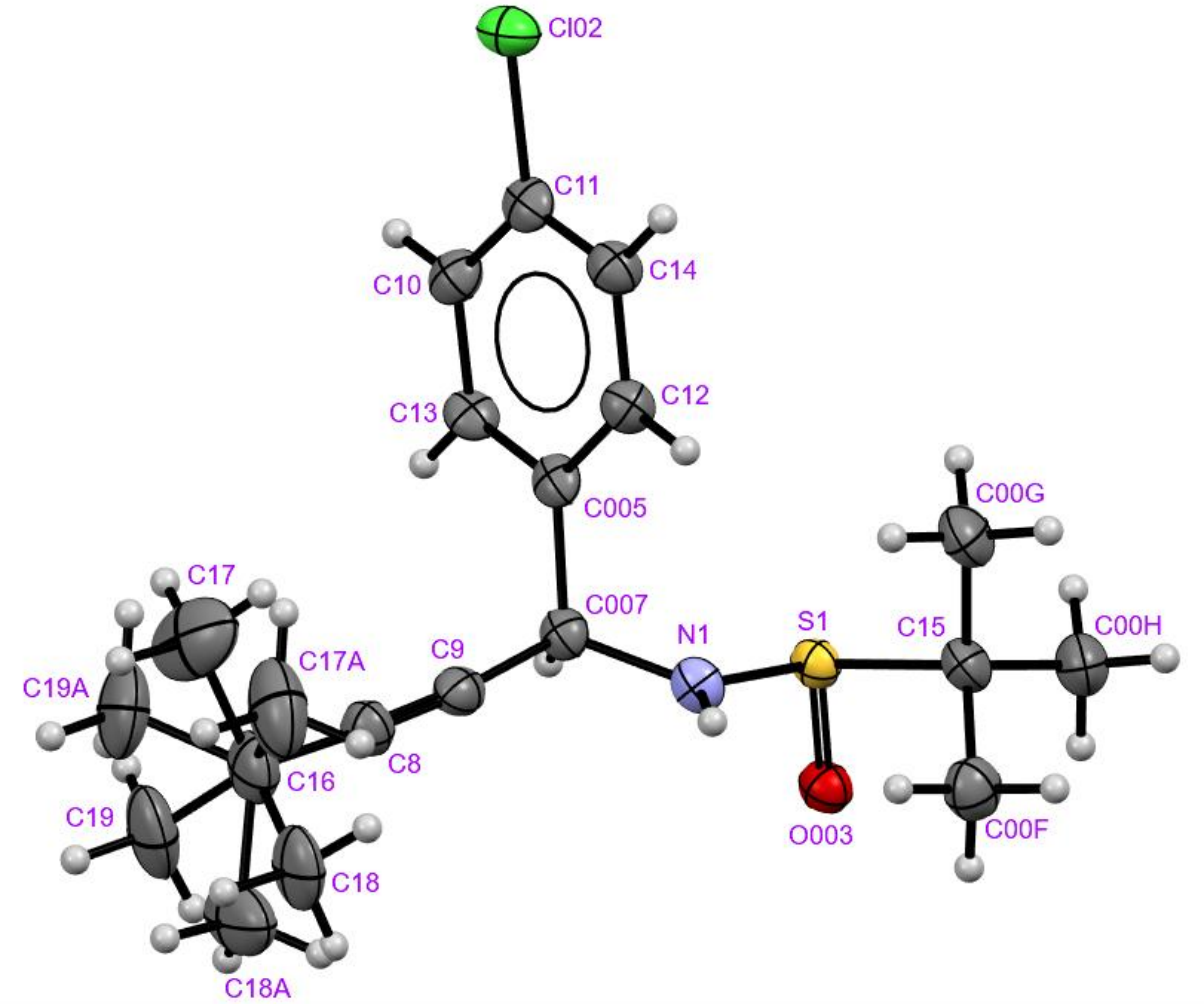


Figure 14: ORTEP representation of N-(1-(4-chlorophenyl)-4,4-dimethylpent-2-yn-1-yl)-2-methylpropane-2-sulfinamide with thermal ellipsoids shown at the 50% probability level. Rotational disorder of the t-butyl group was modelled. Hydrogen atoms of arbitrary size.

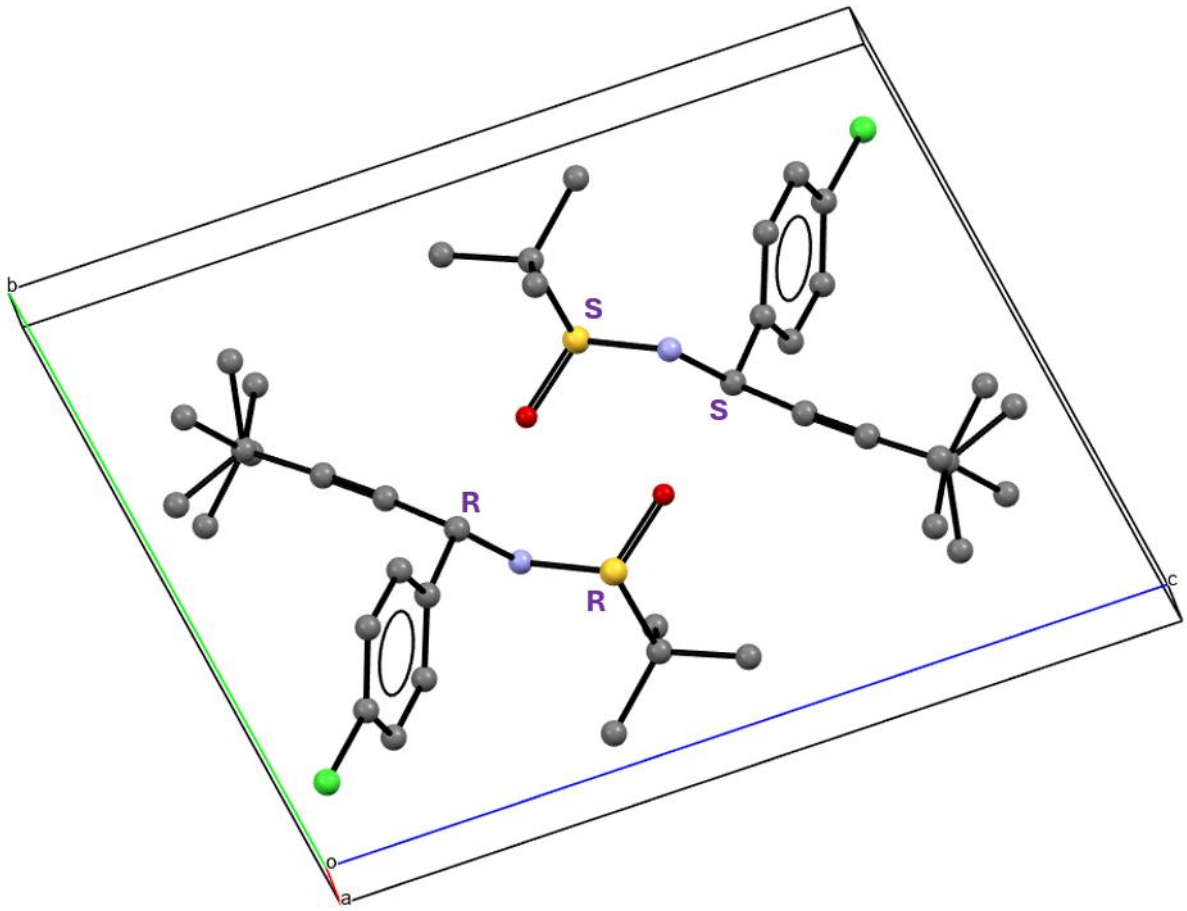


Figure 15: Crystal unit cell of N-(1-(4-chlorophenyl)-4,4-dimethylpent-2-yn-1-yl)-2-methylpropane-2-sulfinamide with stereocentres labelled in purple. Hydrogen atoms omitted for clarity.

Table 15. Crystal data and structure refinement for N-(1-(4-chlorophenyl)-4,4-dimethylpent-2-yn-1-yl)-2-methylpropane-2-sulfinamide

Crystal data	
Chemical formula	$C_{17}H_{24}ClNOS$
M_r	325.88
Crystal system, space group	Triclinic, *P*1

Temperature (K)	100
a, *b*, *c* (Å)	6.2050 (7), 10.7122 (14), 14.6914 (18)
α, β, γ (°)	98.572 (11), 102.117 (10), 102.092 (10)
V (Å^3)	914.4 (2)
Z	2
Radiation type	Cu *K*α
μ (mm^{-1})	2.89
Crystal size (mm)	0.20 × 0.02 × 0.02
Data collection	
Diffractometer	Oxford Diffraction XCALIBUR
Absorption correction	Multi-scan *CrysAlis PRO*, (Agilent, 2011)
T_{min}, T_{max}	0.585, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3662, 2447, 2007
R_{int}	0.026
θ_{max} (°)	58.9
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.556
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.098, 0.315, 1.36
No. of reflections	2447
No. of parameters	221
No. of restraints	156
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.47, −0.53

Computer programs: Xcalibur, (Oxford Diffraction, 2002), *CrysAlis PRO*, (Agilent, 2011), *SHELXT* 2018/2 (Sheldrick, 2015), *SHELXL* 2018/3 (Sheldrick, 2015), Olex2.1.5 (Dolomanov *et. al*., 2009).

Table 16. Selected geometric parameters for N-(1-(4-chlorophenyl)-4,4-dimethylpent-2-yn-1-yl)-2-methylpropane-2-sulfinamide (Å, º)

S1—O003	1.503 (4)	C00G—H00F	0.9600
S1—N1	1.673 (5)	C00H—H00G	0.9600
S1—C15	1.846 (6)	C00H—H00H	0.9600
Cl02—C11	1.743 (6)	C00H—H00I	0.9600
N1—H1	0.8600	C16—C17	1.519 (8)
N1—C007	1.492 (8)	C16—C19	1.522 (7)
C005—C13	1.377 (8)	C16—C18	1.518 (7)
C005—C007	1.531 (8)	C16—C18A	1.521 (8)

C005—C12	1.398 (8)	C16—C19A	1.520 (8)
C13—H13	0.9300	C16—C17A	1.523 (8)
C13—C10	1.389 (8)	C17—H17A	0.9600
C007—H007	0.9800	C17—H17B	0.9600
C007—C9	1.471 (8)	C17—H17C	0.9600
C11—C14	1.388 (9)	C19—H19A	0.9600
C11—C10	1.383 (8)	C19—H19B	0.9600
C14—H14	0.9300	C19—H19C	0.9600
C14—C12	1.390 (8)	C18—H18A	0.9600
C15—C00F	1.512 (8)	C18—H18B	0.9600
C15—C00G	1.537 (9)	C18—H18C	0.9600
C15—C00H	1.516 (9)	C18A—H18D	0.9600
C9—C8	1.204 (8)	C18A—H18E	0.9600
C10—H10	0.9300	C18A—H18F	0.9600
C12—H12	0.9300	C19A—H19D	0.9600
C8—C16	1.483 (9)	C19A—H19E	0.9600
C00F—H00A	0.9600	C19A—H19F	0.9600
C00F—H00B	0.9600	C17A—H17D	0.9600
C00F—H00C	0.9600	C17A—H17E	0.9600
C00G—H00D	0.9600	C17A—H17F	0.9600
C00G—H00E	0.9600		
O003—S1—N1	109.8 (2)	C15—C00H—H00I	109.5
O003—S1—C15	105.7 (3)	H00G—C00H—H00H	109.5
N1—S1—C15	99.7 (3)	H00G—C00H—H00I	109.5
S1—N1—H1	123.8	H00H—C00H—H00I	109.5
C007—N1—S1	112.4 (4)	C8—C16—C17	107.3 (7)
C007—N1—H1	123.8	C8—C16—C19	105.1 (7)
C13—C005—C007	118.6 (5)	C8—C16—C18	110.2 (6)
C13—C005—C12	119.2 (5)	C8—C16—C18A	112.8 (8)
C12—C005—C007	122.2 (5)	C8—C16—C19A	110.7 (8)
C005—C13—H13	119.7	C8—C16—C17A	107.8 (8)
C005—C13—C10	120.6 (5)	C17—C16—C19	109.6 (10)
C10—C13—H13	119.7	C18—C16—C17	113.9 (9)
N1—C007—C005	112.0 (4)	C18—C16—C19	110.3 (9)
N1—C007—H007	108.8	C18A—C16—C17A	107.4 (11)
C005—C007—H007	108.8	C19A—C16—C18A	109.7 (10)
C9—C007—N1	109.6 (5)	C19A—C16—C17A	108.3 (10)
C9—C007—C005	108.9 (5)	C16—C17—H17A	109.5
C9—C007—H007	108.8	C16—C17—H17B	109.5
C14—C11—Cl02	119.3 (4)	C16—C17—H17C	109.5
C10—C11—Cl02	119.5 (5)	H17A—C17—H17B	109.5
C10—C11—C14	121.3 (5)	H17A—C17—H17C	109.5
C11—C14—H14	120.8	H17B—C17—H17C	109.5
C11—C14—C12	118.3 (5)	C16—C19—H19A	109.5
C12—C14—H14	120.8	C16—C19—H19B	109.5
C00F—C15—S1	112.1 (4)	C16—C19—H19C	109.5
C00F—C15—C00G	111.5 (6)	H19A—C19—H19B	109.5
C00F—C15—C00H	110.2 (5)	H19A—C19—H19C	109.5
C00G—C15—S1	108.1 (4)	H19B—C19—H19C	109.5
C00H—C15—S1	104.1 (4)	C16—C18—H18A	109.5
C00H—C15—C00G	110.6 (5)	C16—C18—H18B	109.5
C8—C9—C007	174.8 (6)	C16—C18—H18C	109.5
C13—C10—H10	120.3	H18A—C18—H18B	109.5
C11—C10—C13	119.5 (6)	H18A—C18—H18C	109.5
C11—C10—H10	120.3	H18B—C18—H18C	109.5

C005—C12—H12	119.4	C16—C18A—H18D	109.5
C14—C12—C005	121.1 (6)	C16—C18A—H18E	109.5
C14—C12—H12	119.4	C16—C18A—H18F	109.5
C9—C8—C16	177.3 (6)	H18D—C18A—H18E	109.5
C15—C00F—H00A	109.5	H18D—C18A—H18F	109.5
C15—C00F—H00B	109.5	H18E—C18A—H18F	109.5
C15—C00F—H00C	109.5	C16—C19A—H19D	109.5
H00A—C00F—H00B	109.5	C16—C19A—H19E	109.5
H00A—C00F—H00C	109.5	C16—C19A—H19F	109.5
H00B—C00F—H00C	109.5	H19D—C19A—H19E	109.5
C15—C00G—H00D	109.5	H19D—C19A—H19F	109.5
C15—C00G—H00E	109.5	H19E—C19A—H19F	109.5
C15—C00G—H00F	109.5	C16—C17A—H17D	109.5
H00D—C00G—H00E	109.5	C16—C17A—H17E	109.5
H00D—C00G—H00F	109.5	C16—C17A—H17F	109.5
H00E—C00G—H00F	109.5	H17D—C17A—H17E	109.5
C15—C00H—H00G	109.5	H17D—C17A—H17F	109.5
C15—C00H—H00H	109.5	H17E—C17A—H17F	109.5

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