Modular Sulfon diimine Synthesis using a Stable Sulfinylamine Reagent

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1. Experimental

1.1 General Considerations

Reactions were performed under inert nitrogen atmosphere with anhydrous solvent unless otherwise stated. All glassware was oven dried at 200 °C and allowed to cool to room temperature under positive pressure of nitrogen. Reactions were monitored by TLC until deemed complete using aluminum backed silica plates. Plates were visualised under ultraviolet light (254 nm) and/or by staining with KMnO₄ solution. Cooling of reaction mixtures to 0 °C was achieved using an ice-water bath. Cooling of reaction mixtures between -20 °C and -78 °C was achieved using a dry ice-acetone bath.

Reagents were purchased from Sigma-Aldrich Chemical Co. Ltd., Alfa Aesar, Acros Organics Ltd., Fluorochem Ltd. or Strem Chemicals Inc. and were used as supplied. Grignard and organolithium reagents were titrated against salicylaldehyde phenylhydrazone.¹ Flash column chromatography was carried out using matrix 60 silica gel (particle size 0.040-0.063 nm). ‘Petrol’ refers to the fraction of light petroleum ether boiling in the range 40-60 °C.

¹H-NMR spectra were obtained on a Bruker AVIII400 (400 MHz) spectrometer using the residual solvent as an internal standard. ¹³C-NMR spectra were obtained on a Bruker AVIII400 (100 MHz) using the residual solvent as an internal standard. ¹⁹F-NMR spectra were obtained on a Bruker AVIII400 (376 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) with the multiplicities of the spectra reported as following: s, singlet; d, doublet; t, triplet; q, quartet; pent., quintet; m, multiplet; app., apparent; br., broad. Coupling constants (J) were given in Hertz (Hz).

Low resolution ESI mass spectra were recorded on a Waters LCT Premier spectrometer. High resolution mass spectrometry measurements were recorded on a Bruker Daltronics MicroTOF (ESI) spectrometer by the internal service at Chemistry Research Laboratory, University of Oxford. Samples for mass spectra were prepared as 1 mg/mL solution in MeOH (LRMS, HRMS-ESI).

Infrared spectra were recorded as thin films on a Bruker Tensor 27 FT-IR spectrometer. Melting points were determined using a Stuart Scientific Melting Point Apparatus SMP1.
1.2 Synthetic Procedures and Characterisation Data

1.2.1 Preparation of N-Sulfinyl-tert-octylamine

\[
\begin{align*}
\text{Me}_3\text{C} & \text{NH}_2 \quad \text{SOCl}_2, \text{Et}_3\text{N} \quad \text{Me}_3\text{C} & \text{N}_2\text{SO} \\
\text{Me}_3\text{C} & \text{Me} & \text{Me} & \text{Me} & \text{Me} & \text{Me} & \text{Me} & \text{Me} & \text{Me} \\
\text{Me}_3\text{C} & \text{Me} & \text{Me} & \text{Me} \\
\end{align*}
\]

*tert*-Octylamine (5.11 g, 39.6 mmol, 1.0 equiv.) was dissolved in anhydrous diethyl ether (100 mL) in a 250 mL 3-necked round bottom flask. Anhydrous triethylamine (11.6 mL, 83.2 mmol, 2.1 equiv.) was added and the reaction was cooled to 0 °C. Freshly distilled thionyl chloride (3.00 mL, 41.3 mmol, 1.05 equiv.) was added dropwise. The reaction was stirred at 0 °C for 2 h. Filtration through Celite ® (washed with diethyl ether) and removal of solvent under reduced pressure at room temperature afforded *N*-sulfinyl-*tert*-octylamine 1 as a yellow oil (6.71 g, 97%).

**Notes**

1. *N*-Sulfinyl-*tert*-octylamine should be stored in the freezer (-20 °C) and can be used without loss of performance for at least 2 months.
2. **CAUTION**: Hydrolysis of sulfinylamines results in the formation of toxic sulfur dioxide gas. Evolution of SO₂ from *N*-sulfinyl-*tert*-octylamine has not been observed in the normal course of use, but avoidance of contact with water or prolonged storage at room temperature is advised.
3. *tert*-Octylamine was purchased from Sigma-Aldrich or Fluorochem (both £27 for 100 g) and used without further purification.
4. After evaporation of diethyl ether following filtration, it is advised not to redisolve the product in solvent. Doing so may result in decomposition and the formation of a solid impurity.
5. The product can be further purified by vacuum distillation at 65 °C/5 mbar, but is not necessary. High temperature during distillation may cause decomposition of the product.

\(^1\text{H NMR}\) (400 MHz, CDCl₃): \(\delta\) (ppm) = 1.72 (s, 2H), 1.59 (s, 6H), 1.01 (s, 9H).

\(^{13}\text{C NMR}\) (100 MHz, CDCl₃): \(\delta\) (ppm) = 67.6, 55.5, 32.1, 31.5, 31.2.

\(\text{IR (ATR)}\): \(\tilde{\nu}\) (cm\(^{-1}\)) = 2980, 2888, 1382, 1252, 1152, 1073, 954.

\(\text{HRMS (EI}^+)\) calcd. for C₈H₈NOS\(^+\) [M+H]\(^+\): 176.1104; found: 176.1106.
1.2.2 General Procedure A for Diaryl Sulfilimine Synthesis

\[
\begin{align*}
\text{F-} \text{MgBr} & \xrightarrow{\text{O}_3\text{SSN-}t\text{-Oct}} \text{N-Sulfinyl-}t\text{-octylamine} \\
\text{THF, -78 °C} & \xrightarrow{TMS-OTf} \text{N-Sulfinyl-tert-octylamine} \quad 2a \\
\text{Me-} \text{MgBr} & \xrightarrow{\text{THF, -30 °C}} \text{N-Sulfinyl-tert-octylamine} \quad 3a
\end{align*}
\]

*N-Sulfinyl-tert-octylamine* 1 (158 mg, 0.90 mmol, 1.05 equiv.) was dissolved in anhydrous THF (2 mL) in an oven-dried 25 mL round bottom flask. Then the mixture was cooled to -78 °C before TMSOTf (195 mg, 0.86 mmol, 1.0 equiv.) was added, and 4-fluorophenylmagnesium bromide (0.97 mL, 0.89 M in THF, 0.86 mmol, 1.0 equiv.) was added dropwise after 1 min. The reaction was stirred at -78 °C for 2 min and then the temperature was increased to -30 °C (*see note*). 4-Methylphenylmagnesium bromide (1.40 mL, 0.91 M in THF, 1.27 mmol, 1.5 equiv.) was then added quickly. The mixture was stirred at -30 °C for 10 min. Then the reaction was quenched with sat. aq. tetrasodium EDTA solution. Ethyl acetate (60 mL) was added and the organic phase was separated. The aqueous phase was further extracted with ethyl acetate (2 × 30 mL). The combined organic extracts were dried over anhydrous Na₂SO₄, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (petrol/ethyl acetate with 1% Et₃N, 4:1 to 1:1 to 0:1) to afford *sulfilimine* 3a as a light yellow oil (252 mg, 85%).

**Note:** The reaction can be warmed from -78 °C to -30 °C through an addition of acetone to the dry ice-acetone bath over 5 min, or a quick replacement of the dry ice-acetone bath with an acetone bath at -30 °C.

1-(4-Fluorophenyl)-1-(p-tolyl)-N-(2,4,4-trimethylpentan-2-yl)-λ⁴-sulfanimine (3a)

\[
\begin{align*}
\text{F} & \quad \text{N} \quad t\text{-Oct} \\
\text{Me} & \quad \text{S} \quad t\text{-Oct}
\end{align*}
\]

**¹H NMR** (400 MHz, CDCl₃): \(\delta\) (ppm) = 7.61-7.56 (m, 2H), 7.47 (d, \(J = 8.2\) Hz, 2H), 7.18 (d, \(J = 8.2\) Hz, 2H), 7.08-7.02 (m, 2H), 2.33 (s, 3H), 1.63 (s, 2H), 1.31 (s, 6H), 0.95 (s, 9H).

**¹³C NMR** (100 MHz, CDCl₃): \(\delta\) (ppm) = 163.6 (d, \(¹J_{CF} = 250.2\) Hz), 141.8, 140.9 (d, \(¹J_{CF} = 2.6\) Hz), 140.4, 129.8, 128.8 (d, \(³J_{CF} = 8.7\) Hz), 126.7, 116.1 (d, \(²J_{CF} = 22.2\) Hz), 58.5, 58.4, 32.73, 32.70, 32.1, 31.8, 21.4.
19F NMR (376 MHz, CDCl3): δ (ppm) = -111.1 (tt, \(J = 9.0, 5.3\) Hz).

IR (ATR): \(\tilde{\nu}\) (cm\(^{-1}\)) = 2950, 1587, 1487, 1224, 1075, 1007, 833.

HRMS (ESI\(^+\)) calcd. for C\(_{21}\)H\(_{29}\)FNS\(^+\) [M+H\(^+\)]: 346.1999; found: 346.1997.

1-(4-Chlorophenyl)-1-(4-fluorophenyl)-N-(2,4,4-trimethylpentan-2-yl)-\(\lambda^4\)-sulfanimine (3g)

![Chemical structure](image)

Prepared according to General Procedure A using N-sulfinyl-\(t\)-octylamine 1 (164 mg, 0.934 mmol, 1.0 equiv.), TMSOTf (201 mg, 0.904 mmol, 1.0 equiv.), 4-chlorophenylmagnesium bromide (1.03 mL, 0.88 M in 2-methyltetrahydrofuran, 0.906 mmol, 1.0 equiv.) and 4-fluorophenylmagnesium bromide (1.42 mL, 0.96 M in THF, 1.36 mmol, 1.5 equiv.). Purification by flash column chromatography (petrol/ethyl acetate with 1% Et\(_3\)N, 7:1 to 1:1 to 0:1) afforded sulfilimine 3g as a light yellow oil (262 mg, 79%).

1H NMR (400 MHz, CDCl3): δ (ppm) = 7.63-7.57 (m, 2H), 7.55 (d, \(J = 8.6\) Hz, 2H), 7.35 (d, \(J = 8.6\) Hz, 2H), 7.10-7.03 (m, 2H), 1.61 (s, 2H), 1.29 (s, 6H), 0.94 (s, 9H).

13C NMR (100 MHz, (CD\(_3\))\(_2\)CO): δ (ppm) = 164.8 (d, \(J_{CF} = 248.5\) Hz), 146.1, 142.7 (d, \(J_{CF} = 2.9\) Hz), 136.7, 130.3, 129.4 (d, \(J_{CF} = 8.9\) Hz), 128.6, 117.2 (d, \(J_{CF} = 22.9\) Hz), 59.2, 59.0, 33.84, 33.79, 32.82, 32.75.

19F NMR (376 MHz, CDCl3): δ (ppm) = -110.1 (tt, \(J = 8.4, 5.2\) Hz).

IR (ATR): \(\tilde{\nu}\) (cm\(^{-1}\)) = 1653, 1589, 1472, 1390, 1228, 1128, 1088, 1006, 963, 812, 736.

HRMS (ESI\(^+\)) calcd. for C\(_{20}\)H\(_{26}\)F\(^{35}\)Cl NS\(^+\) [M+H\(^+\)]: 366.1453; found: 366.1446.

1-(4-Chlorophenyl)-1-(naphthalen-2-yl)-N-(2,4,4-trimethylpentan-2-yl)-\(\lambda^4\)-sulfanimine (3h)

![Chemical structure](image)
Prepared according to **General Procedure A** using \(N\)-sulfinyl-\(\textit{tert}\)-octylamine 1 (366 mg, 2.09 mmol, 1.05 equiv.), TMSOTf (445 mg, 2.00 mmol, 1.0 equiv.), 2-naphthylmagnesium bromide (3.80 mL, 0.52 M in THF, 1.98 mmol, 1.0 equiv.) and 4-chlorophenylmagnesium bromide (3.60 mL, 0.83 M in 2-methyltetrahydrofuran, 2.99 mmol, 1.5 equiv.). Purification by flash column chromatography (petrol/ethyl acetate with 1% \(\text{Et}_3\text{N}\), 7:1 to 5:1 to 0:1) afforded sulfilimine 3h as a light yellow oil (696 mg, 89%).

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 8.30-8.27 (m, 1H), 7.94-7.89 (m, 1H), 7.84-7.78 (m, 2H), 7.60 (d, \(J = 8.5\) Hz, 2H), 7.55-7.49 (m, 3H), 7.35 (d, \(J = 8.5\) Hz, 2H), 1.71 (s, 2H), 1.38 (s, 6H), 0.99 (s, 9H).

\(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 143.6, 141.7, 136.1, 134.0, 132.9, 129.4, 129.2, 128.7, 128.1, 127.9, 127.5, 127.1, 126.7, 123.0, 58.7, 58.3, 32.84, 32.82, 32.1, 31.8.

IR (ATR): \(\tilde{\nu}\) (cm\(^{-1}\)) = 1474, 1389, 1210, 1132, 1092, 1011, 857, 812, 763, 750.

HRMS (ESI\(^+\)) calcd. for \(\text{C}_{24}\text{H}_{29}\text{N}_3\text{Cl}_5\text{S}\) [M+H]\(^+\): 398.1704; found: 398.1701.

1-(4-Chlorophenyl)-1-phenyl-\(\textit{N}\)-(2,4,4-trimethylpentan-2-yl)-\(\lambda^4\)-sulfanimine (3j)

![Structural diagram](image)

Prepared according to **General Procedure A** using \(N\)-sulfinyl-\(\textit{tert}\)-octylamine 1 (337 mg, 1.93 mmol, 1.05 equiv.), TMSOTf (417 mg, 1.88 mmol, 1.0 equiv.), 4-chlorophenylmagnesium bromide (2.13 mL, 0.88 M in 2-methyltetrahydrofuran, 1.87 mmol, 1.0 equiv.) and phenyllithium (2.20 mL, 1.24 M in dibutyl ether, 2.73 mmol, 1.5 equiv.). Purification by flash column chromatography (petrol/ethyl acetate with 1% \(\text{Et}_3\text{N}\), 3:1 to 1:1 to 0:1) afforded sulfilimine 3j as a light yellow oil (590 mg, 91%).

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 7.61-7.57 (m, 2H), 7.55 (d, \(J = 8.6\) Hz, 2H), 7.38-7.30 (m, 5H), 1.62 (s, 2H), 1.30 (s, 6H), 0.94 (s, 9H).

\(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 144.1, 143.2, 136.1, 130.2, 129.2, 129.1, 128.0, 126.6, 58.6, 58.1, 32.6, 32.5, 31.9, 31.7.
IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 1472, 1276, 1261, 1209, 1087, 1009, 817, 750, 702.

HRMS (ESI$^+$) calcd. for C$_{20}$H$_{27}$N$_3$ClS$^+$ [M+H]$^+$: 348.1547; found: 348.1544.

1-(4-Chlorophenyl)-1-(6-methoxypyridin-3-yl)-N-(2,4,4-trimethylpentan-2-yl)-$\lambda^4$-sulfanimine (3k)

Preparation of organolithium reagent

5-Bromo-2-methoxypyridine (458 mg, 2.44 mmol, 1.2 equiv.) and THF (5 mL) were added to an oven-dried reaction tube and were cooled to -78 °C. $n$-Butyllithium (1.09 mL, 2.24 M in hexanes, 2.44 mmol, 1.2 equiv.) was added dropwise and the mixture was stirred at the same temperature for 40 min.

Preparation of diaryl sulfilimine

N-Sulfinyl-tert-octylamine 1 (370 mg, 2.11 mmol, 1.05 equiv.) was dissolved in anhydrous THF (4.0 mL) in an oven-dried 25 mL round bottom flask. The mixture was cooled to -78 °C before the addition of TMSOTf (440 mg, 1.98 mmol, 1.0 equiv.). 4-Chlorophenylmagnesium bromide (2.25 mL, 0.88 M in 2-methyltetrahydrofuran, 1.98 mmol, 1.0 equiv.) was added dropwise after 1 min. The reaction was stirred at -78 °C for 2 min and then the temperature was increased to -30 °C. Then the organolithium reagent was by syringe. The mixture was stirred at -30 °C for 10 min, then warmed to room temperature and stirred for 1.5 h. The reaction was subsequently quenched with sat. aq. tetrasodium EDTA solution. Ethyl acetate (60 mL) was then added and the organic phase was separated. The aqueous phase was further extracted with ethyl acetate (2 × 30 mL). The combined extracts were dried over anhydrous Na$_2$SO$_4$, filtered and concentrated in vacuo. The crude product was purified by flash column chromatography (petrol/ethyl acetate with 1% Et$_3$N, 4:1 to 1:1 to 0:1) to afford sulfilimine 3k as a light yellow oil (570 mg, 76%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 8.26 (dd, $J = 2.5$, 0.7 Hz, 1H), 7.67 (dd, $J = 8.7$, 2.5 Hz, 1H), 7.52 (d, $J = 8.6$ Hz, 2H), 7.31 (d, $J = 8.6$ Hz, 2H), 6.68 (dd, $J = 8.7$, 0.7 Hz, 1H), 3.86 (s, 3H), 1.58 (d, $J = 14.4$ Hz, 1H), 1.54 (d, $J = 14.4$ Hz, 1H), 1.25 (s, 3H), 1.24 (s, 3H), 0.89 (s, 9H).
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 165.2, 145.9, 142.9, 137.0, 136.1, 133.9, 129.1, 127.5, 112.4, 58.5, 58.1, 53.9, 32.7, 32.5, 31.9, 31.7.

IR (ATR): \(\tilde{\nu}\) (cm\(^{-1}\)) = 1587, 1473, 1362, 1276, 1261, 1010, 750.

HRMS (ESI\(^+\)) calcd. for C\(_{20}\)H\(_{28}\)O\(^{35}\)ClN\(_2\)S\(^2\) \([\text{M+H}]^+\): 379.1605; found: 379.1602.

1-(4-Chlorophenyl)-1-(thiophen-2-yl)-N-(2,4,4-trimethylpentan-2-yl)-\(\lambda^4\)-sulfanimine (3l)

\[
\begin{array}{c}
\text{Cl} \\
\text{S} \\
\text{N} \\
\text{Oct}
\end{array}
\]

Prepared according to General Procedure A using N-sulfinyl-\(\text{ tert}\)-octylamine 1 (372 mg, 2.12 mmol, 1.05 equiv.), TMSOTf (458 mg, 2.06 mmol, 1.0 equiv.), 4-chlorophenylmagnesium bromide (2.34 mL, 0.88 M in 2-methyltetrahydrofuran, 2.06 mmol, 1.0 equiv.) and 2-thienylmagnesium bromide (3.50 mL, 0.85 M in THF, 2.96 mmol, 1.5 equiv.). Purification by flash column chromatography (petrol/ethyl acetate with 1% Et\(_3\)N, 7:1 to 2:1 to 0:1) afforded sulfilimine 3l as a light yellow oil (627 mg, 86%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 7.66 (d, \(J = 8.6\) Hz, 2H), 7.43 (dd, \(J = 5.0, 1.3\) Hz, 1H), 7.37 (d, \(J = 8.6\) Hz, 2H), 7.27-7.21 (m, 1H), 6.97 (dd, \(J = 5.0, 3.7\) Hz, 1H), 1.63 (d, \(J = 14.5\) Hz, 1H), 1.60 (d, \(J = 14.5\) Hz, 1H), 1.32 (s, 3H), 1.31 (s, 3H), 0.95 (s, 9H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 149.4, 143.0, 136.4, 130.6, 129.1, 128.8, 127.4, 127.2, 58.8, 57.9, 32.5, 32.4, 31.9, 31.7.

IR (ATR): \(\tilde{\nu}\) (cm\(^{-1}\)) = 1471, 1276, 1261, 1209, 1087, 1008, 816, 766, 706.

HRMS (ESI\(^+\)) calcd. for C\(_{18}\)H\(_{23}\)N\(^{35}\)ClS\(_2\) \([\text{M+H}]^+\): 354.1112; found: 354.1111.
1-(Benzofuran-2-yl)-1-(4-chlorophenyl)-N-(2,4,4-trimethylpentan-2-yl)-λ⁴-sulfanimine (3m)

**Preparation of organolithium reagent**

Benzofuran (317 mg, 2.69 mmol, 1.5 equiv.) and THF (5.0 mL) were added to an oven-dried reaction tube. The reaction was cooled to 0 °C. n-Butyllithium (1.20 mL, 2.24 M in hexanes, 2.69 mmol, 1.5 equiv.) was added dropwise and the mixture stirred at the room temperature for 1 h.

**Preparation of diaryl sulfilimine**

N-Sulfinyl-tert-octylamine 1 (312 mg, 1.78 mmol, 1.05 equiv.) was dissolved in anhydrous THF (3.6 mL) in an oven-dried 25 mL round bottom flask. Then the reaction was cooled to -78 °C before TMSOTf (386 mg, 1.74 mmol, 1.0 equiv.) was added, 4-chlorophenylmagnesium bromide (1.97 mL, 0.88 M in 2-methyltetrahydrofuran, 1.73 mmol, 1.0 equiv.) was added dropwise after 1 min. The reaction was stirred at -78 °C for 2 min and then the temperature was increased to -30 °C. Then the lithium reagent was added by syringe. The mixture was stirred at -30 °C for 10 min and then warmed to room temperature and stirred for 1.5 h. Then the reaction was quenched with saturated aqueous tetrasodium EDTA solution and poured into a 250 mL separating funnel. Ethyl acetate (60 mL) was then added and the organic phase was separated. The aqueous phase was further extracted with ethyl acetate (2 × 30 mL). The combined extracts were dried over anhydrous Na₂SO₄, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (petrol/ethyl acetate with 1% Et₃N, 7:1 to 1:1 to 0:1) to afford sulfilimine 3m as a light yellow oil (584 mg, 87%).

**¹H NMR** (400 MHz, CDCl₃): δ (ppm) = 7.75 (d, J = 8.6 Hz, 2H), 7.57-7.52 (m, 1H), 7.45-7.39 (m, 3H), 7.32-7.27 (m, 1H), 7.22 (app. td, J = 7.5, 1.1 Hz, 1H), 7.04 (d, J = 1.1 Hz, 1H), 1.68 (s, 2H), 1.39 (s, 3H), 1.37 (s, 3H), 0.98 (s, 9H).

**¹³C NMR** (100 MHz, CDCl₃): δ (ppm) = 156.6, 156.4, 139.4, 136.8, 129.3, 127.6, 127.0, 126.1, 123.6, 122.0, 112.0, 109.8, 58.7, 57.8, 32.6, 32.4, 31.9, 31.8.

**IR** (ATR): ν (cm⁻¹) =1472, 1444, 1276, 1261, 1010, 816, 750.

**HRMS** (ESI⁺) calcd. for C₂₂H₂₇O³⁵ClNS⁺ [M+H]⁺: 388.1496; found: 388.1494.

S9
1-(4-Chlorophenyl)-1-(4-(5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)phenyl)-N-(2,4,4-trimethylpentan-2-yl)-λ₄-sulfanimine (3n)

**Preparation of organolithium reagent**

1-(4-Bromophenyl)-5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazole² (413 mg, 1.09 mmol, 1.3 equiv.) and THF (2.0 mL) were added to an oven-dried reaction tube and were cooled to -78 °C. n-Butyllithium (0.48 mL, 2.24 M in hexanes, 1.1 mmol, 1.3 equiv.) was added dropwise and the mixture was stirred at the same temperature for 40 min.

**Preparation of diaryl sulfinimine**

N-Sulfinyl-tert-octylamine 1 (155 mg, 0.89 mmol, 1.05 equiv.) was dissolved in anhydrous THF (4.0 mL) in an oven-dried 25 mL round bottom flask. The mixture was cooled to -78 °C before the addition of TMSOTf (190 mg, 0.86 mmol, 1.0 equiv.). 4-Chlorophenylmagnesium bromide (0.97 mL, 0.88 M in 2-methyltetrahydrofuran, 0.85 mmol, 1.0 equiv.) was added dropwise after 1 min. The reaction was stirred at -78 °C for 2 min and then the temperature was increased to -30 °C. Then the organolithium reagent was added by syringe. The mixture was stirred at -30 °C for 10 min, then warmed to room temperature and stirred for 1.5 h. The reaction was subsequently quenched with sat. aq. tetrasodium EDTA solution. Ethyl acetate (50 mL) was then added and the organic phase was separated. The aqueous phase was further extracted with ethyl acetate (2 × 30 mL). The combined extracts were dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. The crude product was purified by flash column chromatography (petrol/ethyl acetate with 1% Et₃N, 3:1 to 1:1 to 0:1) to afford sulfilimine 3n as a light yellow oil (413 mg, 85%).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.60 (d, J = 8.6 Hz, 2H), 7.56 (d, J = 8.6 Hz, 2H), 7.38 (d, J = 8.6 Hz, 2H), 7.36 (d, J = 8.6 Hz, 2H), 7.11 (d, J = 8.3 Hz, 2H), 7.06 (d, J = 8.3 Hz, 2H), 6.70 (s, 1H), 2.35 (s, 3H), 1.61 (s, 2H), 1.32 (s, 6H), 0.94 (s, 9H).
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 145.1, 143.7 (q, \(^2J_{\text{CF}} = 38.7\) Hz), 142.5, 140.8, 139.6, 136.7, 129.7, 129.5, 128.7, 128.1, 127.6, 125.92, 125.87, 125.5, 121.2 (q, \(^1J_{\text{CF}} = 268.8\) Hz), 105.9, 58.9, 58.1, 32.7, 32.5, 32.0, 31.8, 21.4.

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) (ppm) = -62.3.

IR (ATR): \(\tilde{\nu}\) (cm\(^{-1}\)) = 1472, 1276, 1261, 1235, 1161, 1133, 1094, 975, 750.

HRMS (ESI\(^+\)) calcd. for C\(_{31}\)H\(_{34}\)\(^{35}\)ClN\(_3\)F\(_3\)S\(^+\) [M+H]\(^+\): 572.2109; found: 572.2097.

I-(4-Methoxyphenyl)-1-(\(\rho\)-tolyl)-N-(2,4,4-trimethylpentan-2-yl)-\(\lambda^4\)-sulfanimine (3r)

\[
\begin{align*}
\text{MeO} & \quad \text{Me} \\
\text{N} & \quad \text{Oct}
\end{align*}
\]

Prepared according to **General Procedure A** using \(N\)-sulfinyl-\(t\)-octylamine I (208 mg, 1.19 mmol, 1.05 equiv.), TMSOTf (252 mg, 1.13 mmol, 1.0 equiv.), 4-methoxyphenylmagnesium bromide (2.30 mL, 0.48 M in THF, 1.10 mmol, 1.0 equiv.) and 4-methylphenylmagnesium bromide (1.80 mL, 0.94 M in THF, 1.69 mmol, 1.5 equiv.). Purification by flash column chromatography (petrol/ethyl acetate with 1% Et\(_3\)N, 3:1 to 1:1 to 0:1) afforded sulfilimine 3r as a light yellow oil (317 mg, 81%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 7.50 (d, \(J = 8.8\) Hz, 2H), 7.46 (d, \(J = 8.2\) Hz, 2H), 7.15 (d, \(J = 8.2\) Hz, 2H), 6.86 (d, \(J = 8.8\) Hz, 2H), 3.74 (s, 3H), 2.30 (s, 3H), 1.63 (s, 2H), 1.302 (s, 3H), 1.298 (s, 3H), 0.94 (s, 9H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 160.9, 142.0, 139.8, 136.4, 129.5, 128.4, 126.6, 114.3, 58.3, 58.2, 55.4, 32.62, 32.56, 32.0, 31.7, 21.2.

IR (ATR): \(\tilde{\nu}\) (cm\(^{-1}\)) = 1592, 1491, 1392, 1249, 1129, 1030, 828, 730.

HRMS (ESI\(^+\)) calcd. for C\(_{22}\)H\(_{32}\)NOS\(^+\) [M+H]\(^+\): 358.2199; found: 358.2200.
1-(4-Methoxyphenyl)-1-(m-tolyl)-N-(2,4,4-trimethylpentan-2-yl)-λ^4-sulfanimine (3s)

Prepared according to General Procedure A using N-sulfinyl-tert-octylamine 1 (305 mg, 1.74 mmol, 1.05 equiv.), TMSOTf (369 mg, 1.66 mmol, 1.0 equiv.), 4-methoxyphenylmagnesium bromide (3.45 mL, 0.48 M in THF, 1.66 mmol, 1.0 equiv.) and 3-methylphenylmagnesium chloride (3.10 mL, 0.80 M in THF, 2.48 mmol, 1.5 equiv.). Purification by flash column chromatography (petrol/ethyl acetate with 1% Et$_3$N, 3:1 to 1:1 to 0:1) afforded sulfilimine 3s as a light yellow oil (445 mg, 78%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 7.50 (d, $J = 8.8$ Hz, 2H), 7.43 (app. br. s, 1H), 7.35-7.30 (m, 1H), 7.21 (t, $J = 7.6$ Hz, 1H), 7.13-7.08 (m, 1H), 6.86 (d, $J = 8.8$ Hz, 2H), 3.74 (s, 3H), 2.30 (s, 3H), 1.63 (s, 2H), 1.31 (s, 3H), 1.30 (s, 3H), 0.93 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) = 160.9, 144.9, 138.8, 136.3, 130.5, 128.51, 128.46, 126.8, 123.7, 114.3, 58.3, 58.2, 55.3, 32.63, 32.56, 32.0, 31.7, 21.4.

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 1491, 1249, 827.

HRMS (ESI$^+$) calced. for C$_{22}$H$_{32}$NO$_5$ $^+$ [M+H]$^+$: 358.2199; found: 358.2190.

1-(4-Methoxyphenyl)-1-(o-tolyl)-N-(2,4,4-trimethylpentan-2-yl)-λ^4-sulfanimine (3t)

Prepared according to General Procedure A using N-sulfinyl-tert-octylamine 1 (266 mg, 1.52 mmol, 1.05 equiv.), TMSOTf (322 mg, 1.45 mmol, 1.0 equiv.), 4-methoxyphenylmagnesium bromide (3.00 mL, 0.48 M in THF, 1.44 mmol, 1.0 equiv.) and 2-methylphenylmagnesium chloride (3.00 mL, 0.73 M in THF, 2.19 mmol, 1.5 equiv.). Purification by flash column chromatography (petrol/ethyl acetate with 1% Et$_3$N, 3:1 to 1:1 to 0:1) afforded sulfilimine 3t as a light yellow oil (400 mg, 78%).
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 8.10 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.34-7.29 (m, 3H), 7.23 (td, $J = 7.4, 1.5$ Hz, 1H), 7.08-7.04 (m, 1H), 6.79 (d, $J = 8.9$ Hz, 2H), 3.68 (s, 3H), 2.27 (s, 3H), 1.63 (s, 2H), 1.28 (s, 6H), 0.93 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) = 160.6, 142.9, 135.3, 135.2, 130.2, 129.7, 128.7, 126.9, 126.8, 114.4, 58.4, 58.3, 55.2, 32.6, 32.3, 31.9, 31.6, 19.0.

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 1492, 1250, 827, 756.

HRMS (ESI$^+$) calcd. for C$_{22}$H$_{32}$NOS$^+$ [M+H]$^+$: 358.2199; found: 358.2196.

Prepared according to **General Procedure A** using N-sulfinyl-tert-octylamine 1 (358 mg, 2.04 mmol, 1.0 equiv.), TMSOTf (433 mg, 1.95 mmol, 1.0 equiv.), 4-methoxyphenylmagnesium bromide (4.05 mL, 0.48 M in THF, 1.94 mmol, 1.0 equiv.) and 2-naphthylmagnesium bromide (5.60 mL, 0.53 M in THF, 2.97 mmol, 1.5 equiv.). Purification by flash column chromatography (petrol/ethyl acetate with 1% Et$_3$N, 3:1 to 1:1 to 0:1) afforded **sulfilimine 3u** as a light yellow oil (598 mg, 78%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 8.33-8.30 (m, 1H), 7.93-7.87 (m, 1H), 7.81-7.74 (m, 2H), 7.57 (d, $J = 8.8$ Hz, 2H), 7.51-7.45 (m, 3H), 6.87 (d, $J = 8.8$ Hz, 2H), 3.72 (s, 3H), 1.73 (s, 2H), 1.40 (s, 3H), 1.39 (s, 3H), 0.99 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) = 161.0, 142.2, 136.0, 133.8, 132.9, 128.8, 128.6, 128.5, 127.8, 127.2, 126.8, 126.4, 123.1, 114.4, 58.5, 58.2, 55.3, 32.8, 32.6, 32.0, 31.7.

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 1591, 1492, 1382, 1249, 1129, 1029, 825, 730.

HRMS (ESI$^+$) calcd. for C$_{25}$H$_{32}$NOS$^+$ [M+H]$^+$: 394.2199; found: 394.2191.
1.2.3 General Procedure B for Diaryl Sulfondiimine Synthesis

To a 10 mL vial containing Rh$_2$(esp)$_2$ (9.0 mg, 0.012 mmol, 5.0 mol%), 4 Å MS (c. 0.2 g) and PhI=NNs (136 mg, 0.337 mmol, 1.5 equiv.) was added a solution of sulfilimine 3a (80 mg, 0.23 mmol, 1.0 equiv.) in anhydrous CH$_2$Cl$_2$ (1.1 mL). DBU (0.14 mL, 0.93 mmol, 4.0 equiv.) was then quickly added at room temperature and the reaction was sealed and stirred at 60 °C for 8 h. Two portions of PhI=NNs (2 × 137 mg, 0.678 mmol, 3.0 equiv.) were subsequently added at the 8$^{th}$ and 16$^{th}$ hour. The reaction mixture was then transferred to a 100 mL round bottom flask, to separate from the 4 Å MS, washing the vial several times with CH$_2$Cl$_2$. The solvent was then removed under reduced pressure. The crude product was purified by flash column chromatography (petrol/ethyl acetate 6:1 to 4:1) to afford *sulfondiimine* 4a as a light yellow solid (55 mg, 44%).

1.2.4 General Procedure C for Aryl-Alkyl and Dialkyl Sulfondiimine Synthesis

$N$-Sulfinyl-*tert*-octylamine 1 (240 mg, 1.37 mmol, 1.05 equiv.) was dissolved in anhydrous THF (2.7 mL) in an oven-dried 25 mL round bottom flask. The mixture was then cooled to -78 °C and TMSOTf (297 mg, 1.34 mmol, 1.0 equiv.) was added. Then 4-fluorophenylmagnesium bromide (1.47 mL, 0.91 M in THF, 1.34 mmol, 1.0 equiv.) was added dropwise after 1 min. The reaction was stirred at -78 °C for 2 min and then the temperature was increased to -30 °C (see note 1). Methylmagnesium bromide (0.67 mL, 3.0 M in diethyl ether, 2.0 mmol, 1.5 equiv.) was then added quickly. The mixture was stirred at -30 °C for 10 min. Then the reaction was quenched with sat. aq. tetrasodium EDTA solution (100 mL) and poured into a 250 mL separating funnel. Ethyl acetate (80 mL) was then added and the organic phase was separated. The aqueous phase was further extracted with ethyl acetate (2 × 40 mL). The combined extracts were dried over anhydrous Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The crude sulfilimine was dissolved in a mixture
of diethyl ether (15 mL) and petroleum ether (5 mL) and acidified by an 1 M aq. solution of 4-toluenesulfonic acid (35 mL). The organic layer was discarded. The aqueous phase was washed once with a mixture of diethyl ether (5 mL) and petroleum ether (15 mL). The aqueous phase was then extracted with CH₂Cl₂ (3 × 40 mL), combined CH₂Cl₂ extracts dried over Na₂SO₄, filtered and concentrated under reduced pressure to afford the 4-toluenesulfonic acid-sulfilimine salt 3ba (c. 85% yield). The sulfilimine salt 3ba was then dissolved in CH₂Cl₂ (50 mL) and treated with 1 M aq. NaOH (50 mL). The organic layer was separated and the aqueous phase was extracted with CH₂Cl₂ (2 × 50 mL). The combined organic extracts were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure to afford sulfilimine 3b as a light yellow oil (300 mg, 83%).

Notes:

1. The reaction can be warmed from -78 °C to -30 °C through an addition of acetone to the dry ice-acetone bath over 5 min, or a quick replacement of the dry ice-acetone bath with an acetone bath at -30 °C.
2. Solvents were removed in a rotary evaporator below 30 °C due to instability of the sulfilimine 3b at high temperatures.
3. After performing an acid-base workup as mentioned above, crude S-aryl-S-alkyl and S,S-dialkyl sulfilimines were used without further purification in the next step. For long-term storage, 4-toluenesulfonic acid salt would be preferred over the neutral sulfilimine due to enhanced stability.
4. EDTA solution is used to complex the magnesium salts present in the Grignard reagents, which otherwise emulsions may be formed and complicate the aqueous work-up if only water is used instead.
5. The S-aryl-S-alkyl and S,S-dialkyl sulfilimines are typically very polar and appear to be strongly basic, which often stay on the baseline of the TLC plate even when ethyl acetate is used as the eluent. When mixtures of ethyl acetate and methanol were used, the sulfilimine may travel further up the TLC plate but “streaking” is often observed. For sulfilimine 3b, 3:1 petrol/ethyl acetate can be used to observe the by-products (which are removed during the diethyl ether/petroleum ether washes).

A solution of sulfilimine 3b (300 mg, 1.11 mmol, 1.0 equiv.) in anhydrous CH₂Cl₂ (5.6 mL) was
added to a 25 mL vial containing Rh$_2$(esp)$_2$ (21 mg, 0.028 mmol, 2.5 mol%), 4 Å MS (c. 0.4 g) and PhI=NNs (583 mg, 1.44 mmol, 1.3 equiv.). DBU (0.34 mL, 2.2 mmol, 2.0 equiv.) was then added at room temperature quickly and the reaction was sealed and stirred at 40 °C for 24 h. The reaction mixture was then transferred to a 100 mL round bottom flask, to separate from the 4 Å MS, washing the vial several times with CH$_2$Cl$_2$. The solvent was then removed under reduced pressure. The crude product was purified by flash column chromatography (petrol/ethyl acetate, 4:1 to 2:1) to afford sulfondiimine 4b as a light yellow solid (444 mg, 71% yield over two steps).

**Notes:**

1. The reaction was run under air.
2. The reaction is run for 24 hours as standard as some S,S-diaryl substrates need extended reaction times, but it may be finished sooner for S-aryl-S-alkyl and S,S-dialkyl substrates.
3. The protected sulfondiimines are stable towards air and moisture and do not need any special care to be taken when handling them.

$N'$-((4-Fluorophenyl)(p-tolyl)((2,4,4-trimethylpentan-2-yl)imino)-$\lambda^6$-sulfaneylidene)-4-nitrobenzenesulfonamide (4a)

![Structure](image)

*mp* 169-171 °C (CH$_2$Cl$_2$)

Rf 0.50 (petrol/ethyl acetate, 3:1).

$^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) = 8.08 (d, $J = 8.9$ Hz, 2H), 7.82-7.76 (m, 2H), 7.72 (d, $J = 8.9$ Hz, 2H), 7.60 (d, $J = 8.5$ Hz, 2H), 7.14 (d, $J = 8.5$ Hz, 2H), 7.08-6.99 (m, 2H), 2.37 (s, 3H), 1.60 (d, $J = 14.6$ Hz, 1H), 1.56 (d, $J = 14.6$ Hz, 1H), 1.38 (s, 3H), 1.35 (s, 3H), 1.08 (s, 9H).

$^{13}$C NMR (100 MHz, (CD$_3$)$_2$CO): δ (ppm) = 166.0 (d, $^1J_{CF} = 253.5$ Hz), 150.9, 150.3, 145.0, 139.7, 139.3 (d, $^3J_{CF} = 3.1$ Hz), 132.2 (d, $^3J_{CF} = 9.5$ Hz), 130.8, 129.2, 128.6, 124.8, 117.2 (d, $^2J_{CF} = 23.1$ Hz), 61.0, 58.7, 32.7, 32.6, 32.54, 32.51, 21.5.

$^{19}$F NMR (376 MHz, CDCl$_3$): δ (ppm) = -105.2 (tt, $J = 8.0$, 4.9 Hz).

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 2980, 1528, 1488, 1349, 1301, 1222, 1152, 1074, 1029, 1005, 734, 612.

HRMS (ESI$^+$) calcd. for C$_{27}$H$_{33}$FN$_3$O$_4$S$_2$$^+$ [M+H]$^+$: 546.1891; found: 546.1885.
**N-((4-Fluorophenyl)(methyl)((2,4,4-trimethylpentan-2-yl)imino)-\(\lambda^6\)-sulfaneylidene)-4-nitrobenzenesulfonamide (4b)**

\[
\text{mp } 153-155 \, ^\circ\text{C} \quad (\text{CH}_2\text{Cl}_2)
\]

\[R_f \quad 0.54 \quad \text{(petrol/ethyl acetate, 3:1).}\]

\[^1\text{H NMR} \quad (400 \text{ MHz, CDCl}_3): \, \delta \text{ (ppm) } = 8.27 \, (d, \, J = 8.9 \, \text{Hz}, \, 2\, \text{H}), \, 8.07 \, (d, \, J = 8.9 \, \text{Hz}, \, 2\, \text{H}), \, 7.99-7.94 \, (m, \, 2\, \text{H}), \, 7.21-7.15 \, (m, \, 2\, \text{H}), \, 3.46 \, (s, \, 3\, \text{H}), \, 1.47 \, (d, \, J = 14.4 \, \text{Hz}, \, 1\, \text{H}), \, 1.41 \, (d, \, J = 14.4 \, \text{Hz}, \, 1\, \text{H}), \, 1.29 \, (s, \, 3\, \text{H}), \, 1.14 \, (s, \, 3\, \text{H}), \, 1.00 \, (s, \, 9\, \text{H}).\]

\[^{13}\text{C NMR} \quad (100 \text{ MHz, (CD}_3)_2\text{CO}): \, \delta \text{ (ppm) } = 166.3 \, (d, \, ^1J_{CF} = 253.4 \, \text{Hz}), \, 151.4, \, 150.4, \, 139.6 \, (d, \, ^4J_{CF} = 3.1 \, \text{Hz}), \, 131.7 \, (d, \, ^3J_{CF} = 9.6 \, \text{Hz}), \, 128.6, \, 125.1, \, 117.4 \, (d, \, ^2J_{CF} = 23.0 \, \text{Hz}), \, 60.3, \, 58.5, \, 49.2, \, 32.6, \, 32.5, \, 32.4, \, 32.3.\]

\[^{19}\text{F NMR} \quad (376 \text{ MHz, CDCl}_3): \, \delta \text{ (ppm) } = -104.6 \, (tt, \, J = 8.0, \, 4.9 \, \text{Hz}).\]

\[\text{IR (ATR): } \tilde{\nu} \text{ (cm}^{-1}) = 2953, \, 1589, \, 1528, \, 1487, \, 1349, \, 1293, \, 1223, \, 1149, \, 1035, \, 840.\]

\[\text{HRMS (ESI}^+\text{) calcd. for } \text{C}_{21}\text{H}_{29}\text{FN}_{3}\text{O}_4\text{S}_2^+ [\text{M+H}]^+: \, 470.1578; \, \text{found: } 470.1577.\]

**N-((4-Methoxyphenyl)(methyl)((2,4,4-trimethylpentan-2-yl)imino)-\(\lambda^6\)-sulfaneylidene)-4-nitrobenzenesulfonamide (4c)**

Sulfilimine prepared according to **General Procedure C** using \(N\)-sulfinyl-\(\text{tert}\)-octylamine 1 (164 mg, 0.937 mmol, 1.05 equiv.), TMSOTf (202 mg, 0.909 mmol, 1.0 equiv.), 4-methoxyphenylmagnesium bromide (1.85 mL, 0.49 M in THF, 0.907 mmol, 1.0 equiv.) and methylmagnesium bromide (0.46 mL, 3.0 M in diethyl ether, 1.4 mmol, 1.5 equiv.). Following the general purification method, **sulfilimine 3c** was generated as light yellow oil with a crude yield of 84% (215 mg). Sulfoniimine prepared using Rh$_2$(esp)$_2$ (15 mg, 0.020 mmol, 2.5 mol%), PhI=NNs (400 mg, 0.990 mmol, 1.3 equiv.) and DBU (0.23 mL, 1.5 mmol, 2.0 equiv.). Purification by flash
column chromatography (petrol/ethyl acetate, 3:1 to 1:1) afforded sulfondiimine 4c as a light yellow solid (279 mg, 64% yield over two steps).

**mp** 117-119 °C (CH₂Cl₂)

**Rf** 0.5 (petrol/ethyl acetate, 1:1).

**¹H NMR** (400 MHz, CDCl₃): δ (ppm) = 8.25 (d, J = 8.9 Hz, 2H), 8.06 (d, J = 8.9 Hz, 2H), 7.84 (d, J = 9.0 Hz, 2H), 6.94 (d, J = 9.0 Hz, 2H), 3.84 (s, 3H), 3.42 (s, 3H), 1.47 (d, J = 14.4 Hz, 1H), 1.42 (d, J = 14.4 Hz, 1H), 1.30 (s, 3H), 1.16 (s, 3H), 1.00 (s, 9H).

**¹³C NMR** (100 MHz, CDCl₃): δ (ppm) = 163.4, 150.2, 149.3, 133.3, 129.6, 127.6, 124.0, 114.7, 59.8, 57.8, 55.8, 49.7, 32.0, 31.9, 31.83, 31.80.

**IR** (ATR): ν (cm⁻¹) = 2950, 1591, 1528, 1349, 1293, 1176, 1083, 1031, 855, 797.

**HRMS** (ESI⁺) calcd. for C₂₂H₃₁N₃NaO₅S₂⁺ [M+Na]⁺: 504.1597; found: 504.1596.

**N-((4-Chlorophenyl)(methyl)((2,4,4-trimethylpentan-2-yl)imino)-λ⁶-sulfaneylidene)-4-nitrobenzenesulfonamide (4d)**

Sulfilimine prepared according to **General Procedure C** using N-sulfinyl-tert-octylamine 1 (316 mg, 1.81 mmol, 1.05 equiv.), TMSOTf (381 mg, 1.71 mmol, 1.0 equiv.), 4-chlorophenylmagnesium bromide (1.95 mL, 0.88 M in 2-methyltetrahydrofuran, 1.72 mmol, 1.0 equiv.) and methylmagnesium bromide (0.85 mL, 3.0 M in diethyl ether, 2.6 mmol, 1.5 equiv.). Following the general purification method, **sulfilimine 3d** was generated as light yellow oil with a crude yield of 78% (380 mg). Sulfondiimine prepared using Rh₂(esp)₂ (24 mg, 0.032 mmol, 2.5 mol%), PhI=NNs (726 mg, 1.80 mmol, 1.3 equiv.) and DBU (0.40 mL, 2.7 mmol, 2.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 7:1 to 3:1) afforded **sulfondiimine 4d** as a white solid (546 mg, 66% yield over two steps).

**mp** 153-155 °C (CH₂Cl₂)

**Rf** 0. 6 (petrol / ethyl acetate = 2:1).
${^1}H$ NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 8.25 (d, $J = 8.9$ Hz, 2H), 8.05 (d, $J = 8.9$ Hz, 2H), 7.87 (d, $J = 8.7$ Hz, 2H), 7.45 (d, $J = 8.7$ Hz, 2H), 3.44 (s, 3H), 1.45 (d, $J = 14.4$ Hz, 1H), 1.40 (d, $J = 14.4$ Hz, 1H), 1.28 (s, 3H), 1.13 (s, 3H), 0.98 (s, 9H).

${^{13}}C$ NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) = 149.8, 149.3, 141.1, 139.8, 129.7, 129.0, 127.5, 124.0, 60.0, 57.6, 49.3, 31.89, 31.87, 31.73, 31.71.

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 1527, 1349, 1294, 1221, 1149, 1089, 1075, 1035, 1006, 968, 855, 735.

HRMS (ESI$^+$) calcd. for C$_{21}$H$_{28}$N$_3$Na$_3$ClO$_4$S$_2$ $^+[M+Na]^+$: 508.1102; found: 508.1104.

$N$-(Methyl(naphthalen-2-yl)((2,4,4-trimethylpentan-2-yl)imino)-$\lambda^6$-sulfaneylidene)-4-nitrobenzenesulfonamide (4e)

![Structure](image)

Sulfilimine prepared according to General Procedure C using $N$-sulfinyl-tert-octylamine 1 (249 mg, 1.42 mmol, 1.05 equiv.), TMSOTf (300 mg, 1.35 mmol, 1.0 equiv.), 2-naphthylmagnesium bromide (2.60 mL, 0.52 M in THF, 1.35 mmol, 1.0 equiv.) and methylmagnesium bromide (0.70 mL, 3.0 M in diethyl ether, 2.1 mmol, 1.5 equiv.). Following the general purification method, sulfilimine 3e was generated as light yellow oil with a crude yield of 78% (318 mg). Sulfon dichloride prepared using Rh$_2$(esp)$_2$ (20 mg, 0.026 mmol, 2.5 mol%), PhI=NNs (524 mg, 1.30 mmol, 1.3 equiv.) and DBU (0.30 mL, 2.0 mmol, 2.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 4:1 to 2:1) afforded sulfon dichloride 4e as a light yellow solid (356 mg, 53% yield over two steps).

$mp$ 154-156 °C (CH$_2$Cl$_2$)

$R_f$ 0.5 (petrol/ethyl acetate, 1.5:1).

${^1}H$ NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 8.47 (d, $J = 1.8$ Hz, 1H), 8.16 (d, $J = 8.9$ Hz, 2H), 8.04 (d, $J = 8.9$ Hz, 2H), 7.96-7.84 (m, 4H), 7.67-7.57 (m, 2H), 3.52 (s, 3H), 1.50 (s, 2H), 1.36 (s, 3H), 1.22 (s, 3H), 1.04 (s, 9H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) = 149.9, 149.1, 138.6, 134.8, 132.2, 129.7, 129.4, 129.3, 129.2, 127.91, 127.89, 127.6, 123.9, 122.1, 60.0, 57.7, 49.2, 32.0, 31.94, 31.90, 31.8.

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 1526, 1348, 1293, 1220, 1148, 1089, 1031, 1008, 969, 739.

HRMS (ESI$^+$) calcd. for C$_{25}$H$_{32}$N$_3$O$_4$S$_2$ $[\text{M+H}]^+$: 502.1829; found: 502.1827.

N-(Methyl(thiophen-2-yl)((2,4,4-trimethylpentan-2-yl)imino)-7$^6$-sulfaneylidene)-4-nitrobenzenesulfonamide (4f)

Sulfilimine prepared according to General Procedure C using N-sulfinyl-tert-octylamine 1 (295 mg, 1.69 mmol, 1.05 equiv.), TMSOTf (340 mg, 1.53 mmol, 1.0 equiv.), 2-thienylmagnesium bromide (1.80 mL, 0.85 M in THF, 1.53 mmol, 1.0 equiv.) and methylmagnesium bromide (0.77 mL, 3.0 M in diethyl ether, 2.3 mmol, 1.5 equiv.). Following the general purification method, sulfilimine 3f was generated as light yellow oil with a crude yield of 76% (300 mg). Sulfoniimine prepared using Rh$_2$(esp)$_2$ (22 mg, 0.029 mmol, 2.5 mol%), PhI=NNs (621 mg, 1.54 mmol, 1.3 equiv.) and DBU (0.34 mL, 2.3 mmol, 2.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 7:1 to 3:1) afforded sulfoniimine 4f as a white solid (414 mg, 60% yield over two steps).

$mp$ 132-134 °C (CH$_2$Cl$_2$)

R$_f$ 0.42 (petrol/ethyl acetate, 3:1).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 8.28 (d, $J$ = 8.9 Hz, 2H), 8.10 (d, $J$ = 8.9 Hz, 2H), 7.64 (dd, $J$ = 5.1, 1.3 Hz, 1H), 7.60 (dd, $J$ = 3.9, 1.3 Hz, 1H), 7.10 (dd, $J$ = 5.1, 3.9 Hz, 1H), 3.58 (s, 3H), 1.47 (d, $J$ = 14.4 Hz, 1H), 1.41 (d, $J$ = 14.4 Hz, 1H), 1.34 (s, 3H), 1.19 (s, 3H), 1.00 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) = 149.9, 149.4, 144.2, 134.5, 132.1, 128.6, 127.5, 124.1, 60.3, 57.6, 51.1, 31.9, 31.8, 31.6, 31.5.

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 1527, 1349, 1293, 1241, 1220, 1149, 1090, 1028, 1008, 854, 738.

HRMS (ESI$^+$) calcd. for C$_{19}$H$_{27}$N$_3$NaO$_4$S$_3$ $[\text{M+Na}]^+$: 480.1056; found: 480.1050.
N-((4-Chlorophenyl)(4-fluorophenyl)((2,4,4-trimethylpentan-2-yl)imino)-λ^6-sulfaneylidene)-4-nitrobenzenesulfonamide (4g)

Prepared according to General Procedure B using sulfilimine 3g (152 mg, 0.416 mmol, 1.0 equiv.), Rh_{2}(esp)_{2} (16 mg, 0.021 mmol, 5.0 mol%), PhI=NNs (3 × 262 mg, 1.95 mmol, 4.5 equiv.) and DBU (0.25 mL, 1.7 mmol, 4.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 12:1 to 4:1) afforded sulfondiimine 4g as a white solid (111 mg, 47% yield).

mp 191-192 °C (CH_{2}Cl_{2})

Rf 0.50 (petrol/ethyl acetate, 5:1).

^{1}H NMR (400 MHz, CDCl_{3}) = 8.14 (d, J = 8.9 Hz, 2H), 7.81-7.77 (m, 2H), 7.75 (d, J = 8.9 Hz, 2H), 7.69 (d, J = 8.8 Hz, 2H), 7.34 (d, J = 8.8 Hz, 2H), 7.14-6.99 (m, 2H), 1.57 (s, 2H), 1.35 (s, 3H), 1.34 (s, 3H), 1.07 (s, 9H).

^{13}C NMR (100 MHz, (CD_{3})_{2}CO): δ (ppm) = 166.2 (d, {^{1}J_{CF} = 253.6 Hz}), 150.6, 150.4, 141.8, 139.9, 138.7 (d, {^{2}J_{CF} = 3.1 Hz}), 132.3 (d, {^{4}J_{CF} = 9.6 Hz}), 131.0, 130.4, 128.6, 124.9, 117.4 (d, {^{2}J_{CF} = 23.1 Hz}), 61.2, 58.6, 32.6, 32.52, 32.48 (2 × C).

^{19}F NMR (376 MHz, CDCl_{3}): δ (ppm) = -104.3 (ddd, J = 13.0, 8.0, 4.9 Hz).

IR (ATR): ν (cm^{-1}) = 1528, 1349, 1299, 1276, 1261, 1219, 1152, 1089, 1072, 1028, 1002, 750.

HRMS (ESI^+) calcd. for C_{26}H_{29}N_{3}F_{3}ClNaO_{4}S_{2}^{+} [M+Na]^+: 588.1164; found: 588.1166.

N-((4-Chlorophenyl)(naphthalen-2-yl)((2,4,4-trimethylpentan-2-yl)imino)-λ^6-sulfaneylidene)-4-nitrobenzenesulfonamide (4h)

Prepared according to General Procedure B using sulfilimine 3h (253 mg, 0.637 mmol, 1.0 equiv.), Rh_{2}(esp)_{2} (24 mg, 0.032 mmol, 5.0 mol%), PhI=NNs (3 × 397 mg, 2.95 mmol, 4.5 equiv.) and DBU
(0.38 mL, 2.5 mmol, 4.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 7:1 to 4:1) afforded sulfoniimine 4h as a white solid (125 mg, 33%).

**mp** 191-193 °C (CH₂Cl₂)

**Rf** 0.50 (petrol/ethyl acetate, 5:1).

**¹H NMR** (400 MHz, CDCl₃) = 8.33 (d, J = 2.3 Hz, 1H), 7.91 (d, J = 8.9 Hz, 2H), 7.84 (app. d, J = 8.1 Hz, 1H), 7.81-7.73 (m, 4H), 7.69-7.54 (m, 5H), 7.35 (d, J = 8.9 Hz, 2H), 1.66 (d, J = 14.5 Hz, 1H), 1.60 (d, J = 14.5 Hz, 1H), 1.44 (s, 3H), 1.39 (s, 3H), 1.12 (s, 9H).

**¹³C NMR** (100 MHz, CDCl₃): δ (ppm) = 149.2, 148.9, 140.6, 139.5, 137.4, 134.7, 132.0, 129.9, 129.8, 129.6, 129.4, 129.30, 129.27, 128.0, 127.9, 127.6, 123.5, 122.7, 60.9, 58.0, 32.2, 32.10, 32.05, 32.0.

**IR** (ATR): ν (cm⁻¹) = 1527, 1348, 1300, 1276, 1216, 1152, 1088, 1026, 1003, 909, 750.

**HRMS** (ESI⁺) calcd. for C₃₀H₃₃N₃ClO₄S₂⁺ [M+H⁺]: 598.1596; found: 598.1592.

**N-(Cyclopropyl(4-fluorophenyl)((2,4,4-trimethylpentan-2-yl)imino)-1,6-sulfaneylidene)-4-nitrobenzenesulfonamide (4i)**

Sulfilimine prepared according to **General Procedure C** using N-sulfinyl-tert-octylamine 1 (276 mg, 1.57 mmol, 1.05 equiv.), TMSOTf (334 mg, 1.50 mmol, 1.0 equiv.), cyclopropylmagnesium bromide (1.71 mL, 0.88 M in 2-methyltetrahydrofuran, 1.50 mmol, 1.0 equiv.) and 4-fluorophenylmagnesium bromide (2.30 mL, 0.96 M in THF, 2.21 mmol, 1.5 equiv.). Following the general purification method, **sulfilimine 3i** was generated as light yellow oil with a crude yield of 65% (289 mg). Sulfoniimine prepared using Rh₂(esp)₂ (19 mg, 0.025 mmol, 2.5 mol%), PhI=NNs (531 mg, 1.31 mmol, 1.3 equiv.) and DBU (0.30 mL, 2.0 mmol, 2.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 5:1 to 3:1) afforded **sulfoniimine 4i** as a light yellow solid (297 mg, 40% yield over two steps).

**mp** 87-89 °C (CH₂Cl₂)

**Rf** 0.62 (petrol/ethyl acetate, 2:1).
**1H NMR** (400 MHz, CDCl$_3$): $\delta$ (ppm) = 8.26 (d, $J = 8.9$ Hz, 2H), 8.06 (d, $J = 8.9$ Hz, 2H), 7.98-7.91 (m, 2H), 7.19-7.11 (m, 2H), 2.32 (tt, $J = 7.6$, 4.6 Hz, 1H), 1.71 (ddt, $J = 10.5$, 6.3, 4.6 Hz, 1H), 1.53-1.39 (m, 3H), 1.36 (s, 3H), 1.14 (s, 3H), 1.12-1.02 (m, 2H), 0.97 (s, 9H).

**13C NMR** (100 MHz, (CD$_3$)$_2$CO): $\delta$ (ppm) = 166.2 (d, $^1J_{CF} = 252.8$ Hz), 151.9, 150.3, 140.3 (d, $^4J_{CF} = 2.8$ Hz), 132.1 (d, $^3J_{CF} = 9.5$ Hz), 128.6, 125.0, 117.2 (d, $^2J_{CF} = 22.5$ Hz), 60.1, 58.8, 38.7, 32.8, 32.7, 32.5, 32.4, 9.5, 8.7.

**19F NMR** (376 MHz, CDCl$_3$): $\delta$ (ppm) = -105.2 (tt, $J = 8.0$, 5.1 Hz).

**IR** (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 1527, 1349, 1296, 1276, 1260, 1149, 1090, 1075, 1030, 1007, 765, 749.

**HRMS** (ESI$^+$) calcd. for C$_{23}$H$_{30}$N$_5$FNaO$_4$S$_2$ $[M+Na]^+$: 518.1554; found: 518.1560.

**N-((4-Chlorophenyl)(phenyl)(2,4,4-trimethylpentan-2-yl)imino)-6-sulfaneylidene)-4-nitrobenzenesulfonamide (4j)**

![Structural formula of compound 4j](image)

Prepared according to General Procedure B using sulfilimine 3j (251 mg, 0.723 mmol, 1.0 equiv.), Rh$_2$(esp)$_2$ (27 mg, 0.036 mmol, 5.0 mol%), PhI=NNs (3 × 438 mg, 3.25 mmol, 4.5 equiv.) and DBU (0.44 mL, 2.9 mmol, 4.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 7:1 to 3:1) afforded sulfoniimine 4j as a light yellow solid (138 mg, 35%).

**mp** 145-147 °C (CH$_2$Cl$_2$)

**Rf** 0.50 (petrol/ethyl acetate = 5:1).

**1H NMR** (400 MHz, CDCl$_3$): $\delta$ (ppm) = 8.08 (d, $J = 8.9$ Hz, 2H), 7.75-7.68 (m, 6H), 7.52-7.46 (m, 1H), 7.39-7.31 (m, 4H), 1.61 (d, $J = 14.6$ Hz, 1H), 1.57 (d, $J = 14.6$ Hz, 1H), 1.38 (s, 3H), 1.35 (s, 3H), 1.08 (s, 9H).

**13C NMR** (100 MHz, CDCl$_3$): $\delta$ (ppm) = 149.4, 149.1, 141.4, 140.7, 139.5, 132.9, 129.7, 129.3, 129.2, 128.2, 127.6, 123.7, 60.7, 57.9, 32.04, 32.0, 31.97 (2 × C).

**IR** (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 1527, 1348, 1300, 1276, 1261, 1217, 1151, 1088, 1071, 1030, 1006, 995, 749.

**HRMS** (ESI$^+$) calcd. for C$_{26}$H$_{31}$N$_3$ClO$_4$S$_2$ $[M+H]^+$: 548.1439; found: 548.1441.
N-((4-Chlorophenyl)(6-methoxypyridin-3-yl)((2,4,4-trimethylpentan-2-yl)imino)-$\lambda^6$-sulfaneylidene)-4-nitrobenzenesulfonamide (4k)

Prepared according to General Procedure B using sulfilimine 3k (230 mg, 0.608 mmol, 1.0 equiv.), Rh$_2$(esp)$_2$ (23 mg, 0.030 mmol, 5.0 mol%), PhI=NNs (3 × 370 mg, 2.75 mmol, 4.5 equiv.) and DBU (0.37 mL, 2.5 mmol, 4.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 7:1 to 3:1) afforded sulfondiimine 4k as a white solid (199 mg, 57%).

$\text{mp}$ 197-198 °C (CH$_2$Cl$_2$)

Rf 0.41 (petrol/ethyl acetate, 5:1).

$^1$H NMR (400 MHz, CDCl$_3$) : $\delta$ (ppm) = 8.46 (d, $J = 2.4$ Hz, 1H), 8.13 (d, $J = 8.8$ Hz, 2H), 7.81 (dd, $J = 8.9$, 2.4 Hz, 1H), 7.76 (d, $J = 8.8$ Hz, 2H), 7.72 (d, $J = 8.8$ Hz, 2H), 7.35 (d, $J = 8.8$ Hz, 2H), 6.68 (d, $J = 8.9$ Hz, 1H), 3.92 (s, 3H), 1.57 (s, 2H), 1.37 (s, 3H), 1.35 (s, 3H), 1.06 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$) : $\delta$ (ppm) = 166.4, 149.3, 149.2, 148.6, 140.6, 139.6, 137.9, 130.3, 129.46, 129.45, 127.6, 123.8, 111.5, 60.8, 57.9, 54.5, 32.03, 31.99, 31.95, 31.93.

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 1586, 1529, 1477, 1371, 1349, 1308, 1276, 1261, 1217, 1153, 1087, 1027, 1000, 908, 750.

HRMS (ESI$^+$) calcd. for C$_{26}$H$_{32}$N$_4$ClO$_3$S$_2$ $[\text{M+H}]^+$: 579.1497; found: 579.1485.

N-((4-Chlorophenyl)(thiophen-2-yl)((2,4,4-trimethylpentan-2-yl)imino)-$\lambda^6$-sulfaneylidene)-4-nitrobenzenesulfonamide (4l)

Prepared according to General Procedure B using sulfilimine 3l (203 mg, 0.575 mmol, 1.0 equiv.), Rh$_2$(esp)$_2$ (21 mg, 0.028 mmol, 5.0 mol%), PhI=NNs (3 × 356 mg, 2.64 mmol, 4.5 equiv.) and DBU (0.35 mL, 2.3 mmol, 4.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 7:1 to 3:1) afforded sulfoniimine 4l as a light yellow solid (128 mg, 40%).
mp 131-133 °C (CH$_2$Cl$_2$)

R$_f$ 0.33 (petrol/ethyl acetate, 5:1).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 8.15 (d, $J$ = 8.8 Hz, 2H), 7.78 (d, $J$ = 8.8 Hz, 2H), 7.70 (d, $J$ = 8.9 Hz, 2H), 7.65 (dd, $J$ = 1.3 Hz, 2H), 7.33-7.26 (m, 3H), 7.01 (dd, $J$ = 5.1, 3.9 Hz, 1H), 1.64 (d, $J$ = 14.5 Hz, 1H), 1.58 (d, $J$ = 14.5 Hz, 1H), 1.49 (s, 3H), 1.38 (s, 3H), 1.08 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) = 150.6, 150.4, 144.6, 142.1, 139.7, 136.6, 134.7, 130.4, 130.2, 130.0, 128.5, 124.9, 61.4, 58.6, 32.63, 32.56, 32.5, 32.1.

(ART): $\tilde{\nu}$ (cm$^{-1}$) = 1527, 1348, 1300, 1276, 1260, 1216, 1153, 1089, 1026, 1004, 749.

HRMS (ESI) calcd. for C$_{28}$H$_{31}$N$_3$ClNaO$_3$S$_3$ [M$+$Na]$^+$: 576.0823; found: 576.0823.

$N$-(Benzofuran-2-yl(4-chlorophenyl)((2,4,4-trimethylpentan-2-yl)imino)-$\lambda^6$-sulfaneylidene)-4-nitrobenzenesulfonamide (4m)

Prepared according to General Procedure B using sulfilimine 3m (240 mg, 0.620 mmol, 1.0 equiv.), Rh$_2$(esp)$_2$ (24 mg, 0.032 mmol, 5.0 mol%), PhI=NNs (3 × 385 mg, 2.86 mmol, 4.5 equiv.) and DBU (0.38 mL, 2.6 mmol, 4.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 7:1 to 3:1) afforded sulfoniimine 4m as a light yellow solid (145 mg, 40%).

mp 201-202 °C (CH$_2$Cl$_2$)

R$_f$ 0.44 (petrol/ethyl acetate, 5:1).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 8.08 (d, $J$ = 8.9 Hz, 2H), 7.82 (d, $J$ = 8.9 Hz, 2H), 7.79 (d, $J$ = 8.9 Hz, 2H), 7.71-7.66 (m, 2H), 7.43-7.26 (m, 5H), 1.63 (d, $J$ = 14.6 Hz, 1H), 1.58 (d, $J$ = 14.6 Hz, 1H), 1.47 (s, 3H), 1.38 (s, 3H), 1.09 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) = 156.3, 149.6, 149.2, 149.0, 140.0, 137.4, 129.6, 129.5, 128.2, 127.7, 126.1, 124.7, 123.6, 123.2, 115.6, 112.2, 60.9, 57.5, 32.2, 31.92, 31.87, 31.1.

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 1525, 1349, 1301, 1261, 1223, 1152, 1077, 1030, 1006, 833, 746.
**HRMS** (ESI⁺) calcd. for C_{28}H_{31}N_{3}^{35}ClO_{3}S_{2}^{+} [M+H]⁺: 588.1388; found: 588.1387.

\[ N-\text{(4-Chlorophenyl)-(4-(5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)phenyl)}(\text{2,4,4-trimethylpentan-2-yl)imino})-\lambda^{6}-\text{sulfaneylidene)-4-nitrobenzenesulfonamide (4n)} \]

Prepared according to **General Procedure B** using sulfilimine 3n (170 mg, 0.298 mmol, 1.0 equiv.), Rh_{2}(esp)_{2} (12 mg, 0.016 mmol, 5.0 mol%), PhI=NNs (3 × 181 mg, 1.34 mmol, 4.5 equiv.) and DBU (0.18 mL, 1.2 mmol, 4.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 7:1 to 3:1) afforded sulfondiimine 4n as a light blue oil (93 mg, 40%).

Rf 0.56 (petrol/ethyl acetate, 5:1).

\[ ^{1}H \text{ NMR (400 MHz, CDCl}_{3}\text{): } \delta \text{ (ppm) } = 8.11 \text{ (d, } J = 8.9 \text{ Hz, 2H}), 7.78 \text{ (d, } J = 8.8 \text{ Hz, 2H}), 7.75 \text{ (d, } J = 8.9 \text{ Hz, 2H}), 7.66 \text{ (d, } J = 8.9 \text{ Hz, 2H}), 7.39 \text{ (d, } J = 8.8 \text{ Hz, 2H}), 7.34 \text{ (d, } J = 8.9 \text{ Hz, 2H}), 7.17 \text{ (d, } J = 7.9 \text{ Hz, 2H}), 7.09 \text{ (d, } J = 7.9 \text{ Hz, 2H}), 6.73 \text{ (s, 1H)}, 2.38 \text{ (s, 3H)}, 1.61 \text{ (d, } J = 14.5 \text{ Hz, 1H}), 1.56 \text{ (d, } J = 14.6 \text{ Hz, 1H}), 1.38 \text{ (s, 3H)}, 1.34 \text{ (s, 3H)}, 1.07 \text{ (s, 9H)}. \]

\[ ^{13}C \text{ NMR (100 MHz, (CD}_{3}\text{)CO): } \delta \text{ (ppm) } = 150.6, 150.4, 146.7, 144.4 \text{ (q, }^{2}J_{\text{CF}} = 38.2 \text{ Hz}), 143.9, 142.9, 141.3, 140.7, 140.0, 131.0, 130.53, 130.49, 130.4, 130.0, 128.6, 127.2, 126.9, 124.9, 122.5 \text{ (q, }^{1}J_{\text{CF}} = 266.5 \text{ Hz}), 107.0, 61.4, 58.6, 32.63, 32.59, 32.5, 32.4, 21.5. \]

\[ ^{19}F \text{ NMR (376 MHz, CDCl}_{3}\text{): } \delta \text{ (ppm) } = -62.5 \]

\[ \text{IR (ATR): } \tilde{\nu} \text{ (cm}^{-1}) = 1529, 1471, 1349, 1276, 1261, 1235, 1153, 1090, 1030, 1003, 827, 750. \]

**HRMS** (ESI⁺) calcd. for C_{37}H_{38}N_{3}F_{3}^{35}ClO_{4}S_{2}^{+} [M+H]⁺: 772.2000; found: 772.1997.

\[ N-\text{(Butyl(2-methylallyl))((2,4,4-trimethylpentan-2-yl)imino)}-\lambda^{6}-\text{sulfaneylidene)-4-nitrobenzenesulfonamide (4o)} \]
Sulfilimine prepared according to **General Procedure C** using *N*-sulfinyl-*tert*-octylamine 1 (399 mg, 2.28 mmol, 1.05 equiv.), TMSOTf (486 mg, 2.19 mmol, 1.0 equiv.), *n*-butylmagnesium chloride (1.11 mL, 1.96 M in THF, 2.18 mmol, 1.0 equiv.) and 2-methyl-1-propenylmagnesium bromide (6.70 mL, 0.49 M in THF, 3.28 mmol, 1.5 equiv.). Following the general purification method, *sulfilimine 3o* was generated as light yellow oil with a crude yield of 77% (454 mg). Sulfondiimine prepared using Rh$_2$(esp)$_2$ (31 mg, 0.041 mmol, 2.5 mol%), PhI=NNs (861 mg, 2.13 mmol, 1.3 equiv.) and DBU (0.50 mL, 3.4 mmol, 2.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 5:1 to 2:1) afforded *sulfondiimine 4o* as a yellow solid (163 mg, 16% yield over two steps).

**mp** 113-115 °C (CH$_2$Cl$_2$)

**Rf** 0.65 (petrol/ethyl acetate, 3:1).

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 8.25 (d, $J = 8.9$ Hz, 2H), 8.04 (d, $J = 8.9$ Hz, 2H), 4.92-4.86 (m, 2H), 4.16 (d, $J = 19.3$ Hz, 1H), 3.34 (d, $J = 19.3$ Hz, 1H), 2.91-2.81 (m, 1H), 2.79-2.70 (m, 1H), 2.00 (d, $J = 14.6$ Hz, 1H), 1.72 (s, 3H), 1.62 (d, $J = 14.6$ Hz, 1H), 1.47 (s, 3H), 1.30 (s, 3H), 1.27-1.15 (m, 4H), 0.97 (s, 9H), 0.73-0.68 (m, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) = 150.8, 149.1, 144.1, 127.3, 123.9, 111.9, 66.6, 52.6, 51.8, 45.4, 31.8, 31.5, 28.5, 27.6, 25.7, 21.2, 20.7, 13.5.

**IR** (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 1527, 1348, 1276, 1261, 1146, 1091, 979, 910, 854, 750.

**HRMS** (ESI$^+$) calcd. for C$_{22}$H$_{38}$N$_3$O$_4$S$_2$ $^+$ [M+H]$^+$: 472.2298; found: 472.2293.

*N-(Butyl(methyl)((2,4,4-trimethylpentan-2-yl)imino)-$\lambda^6$-sulfaneylidene)-4-nitrobenzenesulfonamide (4p)*

![Chemical Structure](image)

Sulfilimine prepared according to **General Procedure C** using *N*-sulfinyl-*tert*-octylamine 1 (307 mg, 1.75 mmol, 1.05 equiv.), TMSOTf (371 mg, 1.67 mmol, 1.0 equiv.), *n*-butylmagnesium chloride (0.85 mL, 1.96 M in THF, 1.7 mmol, 1.0 equiv.) and methylmagnesium bromide (0.84 mL, 3.0 M in diethyl ether, 2.5 mmol, 1.5 equiv.). Following the general purification method, *sulfilimine 3p* was generated as light yellow oil with a crude yield of 77% (298 mg). Sulfondiimine prepared
using Rh₂(esp)₂ (22 mg, 0.029 mmol, 2.5 mol%), PhI=NNs (690 mg, 1.71 mmol, 1.3 equiv.) and DBU (0.40 mL, 2.7 mmol, 2.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 4:1 to 2:1) afforded sulfondiimine 4p as a light yellow solid (187 mg, 26% yield over two steps).

*m* 80-82 °C (CH₂Cl₂)

*RF* 0.35 (petrol/ethyl acetate, 2:1).

**¹H NMR** (400 MHz, CDCl₃): δ (ppm) = 8.26 (d, *J* = 8.9 Hz, 2H), 8.05 (d, *J* = 8.9 Hz, 2H), 3.43-3.37 (m, 2H), 3.17 (s, 3H), 1.81-1.71 (m, 2H), 1.45-1.37 (m, 2H), 1.37 (d, *J* = 14.4 Hz, 1H), 1.27 (s, 3H), 1.23 (s, 3H), 0.93-0.87 (m, 12H).

**¹³C NMR** (100 MHz, CDCl₃): δ (ppm) = 150.2, 149.3, 127.5, 123.9, 60.0, 59.3, 57.6, 44.6, 32.3, 32.0, 31.8, 31.7, 25.6, 21.4, 13.6.

**IR** (ATR): ν (cm⁻¹) = 1528, 1349, 1276, 1146, 1089, 1029, 989, 750.

**HRMS (ESI⁺)** calcd. for C₁₉H₃₅N₃NaO₄S₂⁺ [M+Na]⁺: 454.1805; found: 454.1798.

*N-(Cyclopropyl(2-methylallyl))(2,4,4-trimethylpentan-2-yl)imino)-λ⁶-sulfaneylidene)-4-nitrobenzenesulfonamide (4q)*

Sulfilimine prepared according to **General Procedure C** using *N*-sulfinyl-tert-octylamine 1 (355 mg, 2.03 mmol, 1.05 equiv.), TMSOTf (444 mg, 2.00 mmol, 1.0 equiv.), cyclopropylmagnesium bromide (2.38 mL, 0.84 M in 2-methyltetrahydrofuran, 2.00 mmol, 1.0 equiv.) and 2-methyl-1-propenylmagnesium bromide (6.00 mL, 0.50 M in THF, 3.00 mmol, 1.5 equiv.). Following the general purification method, *sulfilimine 3q* was generated as light yellow oil with a crude yield of 89% (455 mg). Sulfondiimine prepared using Rh₂(esp)₂ (33 mg, 0.044 mmol, 2.5 mol%), PhI=NNs (930 mg, 2.30 mmol, 1.3 equiv.) and DBU (0.53 mL, 3.6 mmol, 2.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 4:1 to 2:1) afforded sulfondiimine 4q as a light brown solid (315 mg, 35% yield over two steps).

*m* 119-121 °C (CH₂Cl₂)
\[ R_f 0.54 \text{ (petrol/ethyl acetate, 3:1).} \]

\[ ^1H\text{NMR (400 MHz, CDCl}_3\text{): } \delta \text{ (ppm) = } 8.24 \text{ (d, } J = 8.9 \text{ Hz, 2H), 7.99 \text{ (d, } J = 8.9 \text{ Hz, 2H), 4.93 \text{ (s, 1H), 4.86 \text{ (s, 1H), 4.08 \text{ (d, } J = 19.3 \text{ Hz, 1H), 3.37 \text{ (d, } J = 19.3 \text{ Hz, 1H), 2.20 \text{ (tt, } J = 7.7, 4.8 \text{ Hz, 1H), 1.97 \text{ (d, } J = 14.6 \text{ Hz, 1H), 1.69 \text{ (s, 3H), 1.63 \text{ (d, } J = 14.6 \text{ Hz, 1H), 1.49 \text{ (s, 3H), 1.29 \text{ (s, 3H), 1.23-1.16 \text{ (m, 1H), 0.96 \text{ (s, 9H), 0.76-0.61 \text{ (m, 2H), 0.27-0.21 \text{ (m, 1H).} \]

\[ ^{13}\text{C NMR (100 MHz, CDCl}_3\text{): } \delta \text{ (ppm) = } 150.8, 149.0, 143.3, 127.2, 123.9, 111.2, 66.4, 51.8, 46.1, 31.7, 31.5, 29.6, 28.5, 27.5, 20.6, 3.9, 2.4. \]

\[ \text{IR (ATR): } \tilde{\nu} \text{ (cm}^{-1}\text{) = 1526, 1348, 1289, 1145, 1090, 1016, 973, 854, 768, 733.} \]

\[ \text{HRMS (ESI}\text{) calcd. for C}_{21}\text{H}_{34}\text{N}_{3}\text{O}_{4}\text{S}_{2}^{+} \text{[M+H]}^{+}: 456.1985; \text{found: 456.1979.} \]

1.2.5 General Procedure D for Diaryl Sulfoximine Synthesis

Sulfilimine 3a (471 mg, 1.37 mmol, 1.0 equiv.) was dissolved in anhydrous MeCN (7.0 mL) in an oven-dried 50 mL round bottom flask. Then the reaction was heated to 40 °C before TPAP (24 mg, 0.068 mmol, 5.0 mol%) was added, then NMO (1.01 g, 8.63 mmol, 6.0 equiv.) was added. The reaction was stirred at 40 °C for 24 h until completion of the reaction (TLC). The reaction was quenched with water and extracted with ethyl acetate (3 × 50 mL). The combined organic extracts were washed with brine, dried over anhydrous Na$_2$SO$_4$, and concentrated. The crude product was purified by flash column chromatography (petrol/ethyl acetate, 20:1 to 10:1) to afford sulfoximine 5d as a colourless oil (490 mg, 99%).

1.2.6 General Procedure E for Aryl-Alkyl and Dialkyl Sulfoximine Synthesis
N-Sulfinyl-tert-octylamine 1 (248 mg, 1.42 mmol, 1.05 equiv.) was dissolved in anhydrous THF (3.0 mL) in an oven-dried 25 mL round bottom flask. Then the mixture was cooled to -78 °C and TMSOTf (310 mg, 1.37 mmol, 1.0 equiv.) was added. 4-Fluorophenylmagnesium bromide (1.57 mL, 0.87 M in THF, 1.37 mmol, 1.0 equiv.) was added dropwise after 1 min. The mixture was stirred at -78 °C for 2 min and then the temperature was increased to -30 °C. Methylmagnesium bromide (0.70 mL, 3.0 M in diethyl ether, 2.1 mmol, 1.5 equiv.) was then added quickly. The mixture was stirred at -30 °C for 10 min. Then the reaction was quenched with sat. aq. tetrasodium EDTA solution and poured into a 250 mL separating funnel. Ethyl acetate (80 mL) was then added and the organic phase was separated. The aqueous phase was further extracted with ethyl acetate (2 × 40 mL). The combined extracts were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crude sulfilimine was dissolved in a mixture of diethyl ether (15 mL) and petroleum ether (5 mL) and acidified by a 1 M aq. solution of 4-toluenesulfonic acid (35 mL) and the organic layer was then discarded. The aqueous phase was washed once with a mixture of diethyl ether (5 mL) and petroleum ether (15 mL). The aqueous phase was then extracted with CH₂Cl₂ (3 × 40 mL), dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo to afford the 4-toluenesulfonic acid-sulfilimine salt 3ba (c. 85% yield). The sulfilimine salt was then dissolved in CH₂Cl₂ (50 mL) and treated with 1M aq. NaOH solution (50 mL). The organic layer was separated and the aqueous phase was extracted with CH₂Cl₂ (2 × 50 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated under reduced pressure to afford sulfilimine 3b as a light yellow oil (301 mg, 82%).

(Please see notes on General Procedure C for further guidance.)

Sulfilimine 3b (301 mg, 1.12 mmol, 1.0 equiv.) was dissolved in anhydrous MeCN (6.0 mL) in an oven-dried 50 mL round bottom flask. Then the mixture was heated to 40 °C before TPAP (20 mg, 0.057 mmol, 5.0 mol%) was added, then NMO (787 mg, 6.73 mmol, 6.0 equiv.) was added. The reaction was stirred at 40 °C for 24 h until completion of the reaction (TLC). The reaction was quenched with water and extracted with ethyl acetate (3 × 50 mL). The combined extracts were washed with brine, dried over anhydrous Na₂SO₄, and concentrated. The crude product was purified by flash column chromatography (petrol/ethyl acetate, 5:1 to 3:1) to afford sulfoximine 5a as a colourless oil (315 mg, 99%).
(4-Fluorophenyl)(methyl)((2,4,4-trimethylpentan-2-yl)imino)-λ₆-sulfanone (5a)

![Chemical Structure](image)

Rf 0.33 (petrol/ethyl acetate, 4:1).

$^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.97-7.89 (m, 2H), 7.18-7.11 (m, 2H), 2.97 (s, 3H), 1.51 (d, $J = 14.3$ Hz, 1H), 1.44 (d, $J = 14.3$ Hz, 1H), 1.26 (s, 3H), 1.11 (s, 3H), 1.03 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ (ppm) = 164.9 (d, $^1J_{CF} = 253.0$ Hz), 141.8 (d, $^4J_{CF} = 3.2$ Hz), 130.4 (d, $^3J_{CF} = 9.2$ Hz), 116.1 (d, $^2J_{CF} = 22.2$ Hz), 58.8, 58.3, 48.7, 32.9, 32.7, 32.0, 31.9.

$^{19}$F NMR (376 MHz, CDCl$_3$): δ (ppm) = -107.5 (tt, $J = 8.5, 5.2$ Hz).

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 2956, 2903, 1589, 1491, 1363, 1226, 1150, 1090, 1077, 970, 838

HRMS (ESI$^+$) calcd. for C$_{15}$H$_{25}$FNOS$^+$ [M+H]$^+$: 286.1635; found: 286.1637.

(4-Methoxyphenyl)(methyl)((2,4,4-trimethylpentan-2-yl)imino)-λ₆-sulfanone (5b)

![Chemical Structure](image)

Sulfilimine prepared according to General Procedure E using N-sulfinyl-tert-octylamine 1 (135 mg, 0.770 mmol, 1.05 equiv.), TMSOTf (163 mg, 0.730 mmol, 1.0 equiv.), 4-methoxyphenylmagnesium bromide (1.5 mL, 0.49 M in THF, 0.74 mmol, 1.0 equiv.) and methylmagnesium bromide (0.37 mL, 3.0 M in diethyl ether, 1.1 mmol, 1.5 equiv.). Following the general purification method, sulfilimine 3c was generated as light yellow oil with a crude yield of 83% (170 mg). Sulfoximine prepared using TPAP (11 mg, 0.031 mmol, 5.0 mol%), NMO (0.42 g, 3.6 mmol, 6.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 4:1 to 2:1) afforded sulfoximine 5b as a colourless oil (164 mg, 75% yield over two steps).

Rf 0.45 (petrol/ethyl acetate, 2:1).

$^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.85 (d, $J = 8.9$ Hz, 2H), 6.96 (d, $J = 8.9$ Hz, 2H), 3.85 (s, 3H), 2.96 (s, 3H), 1.52 (d, $J = 14.3$ Hz, 1H), 1.46 (d, $J = 14.3$ Hz, 1H), 1.26 (s, 3H), 1.13 (s, 3H), 1.04 (s, 9H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) = 162.5, 137.4, 129.8, 114.1, 58.7, 58.4, 55.6, 48.9, 32.9, 32.7, 32.1, 31.9.

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 2980, 2902, 1594, 1495, 1252, 1151, 1132, 1079, 969, 833.

HRMS (ESI$^+$) calcd. for C$_{16}$H$_{28}$NO$_2$S$^+$ [M+H]$^+$: 298.1835; found: 298.1836.

Cyclopropyl(4-fluorophenyl)((2,4,4-trimethylpentan-2-yl)imino)-$\lambda^6$-sulfanone (5c)

Sulfilimine prepared according to General Procedure E using N-sulfinyl-tert-octylamine 1 (231 mg, 1.32 mmol, 1.05 equiv.), TMSOTf (290 mg, 1.31 mmol, 1.0 equiv.), cyclopropylmagnesium bromide (1.55 mL, 0.84 M in 2-methyltetrahydrofuran, 1.30 mmol, 1.0 equiv.) and 4-fluorophenylmagnesium bromide (2.00 mL, 0.96 M in THF, 1.92 mmol, 1.5 equiv.). Following the general purification method, sulfilimine 3i was generated as light yellow oil with a crude yield of 78% (300 mg). Sulfoximine prepared using TPAP (18 mg, 0.050 mmol, 5.0 mol%), NMO (0.70 g, 6.0 mmol, 6.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 5:1 to 3:1) afforded sulfoximine 5c as a white solid (195 mg, 48% yield over two steps).

$m_p$ 77-79 °C (CH$_2$Cl$_2$)

$R_f$ 0.5 (petrol/ethyl acetate, 3:1).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 7.91-7.86 (m, 2H), 7.17-7.11 (m, 2H), 2.39 (tt, $J = 7.8, 4.8$ Hz, 1H), 1.51 (d, $J = 14.4$ Hz, 1H), 1.46 (d, $J = 14.4$ Hz, 1H), 1.43-1.34 (m, 1H), 1.28 (s, 3H), 1.14 (s, 3H), 1.07-0.94 (m, 11H), 0.80-0.70 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) = 164.7 (d, $^1J_{CF} = 252.7$ Hz), 142.0 (d, $^4J_{CF} = 3.3$ Hz), 130.5 (d, $^3J_{CF} = 8.8$ Hz), 115.9 (d, $^2J_{CF} = 22.2$ Hz), 58.5, 58.4, 36.3, 33.2, 33.0, 32.1, 32.0, 6.8, 5.5.

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ (ppm) = -108.1 (tt, $J = 8.5, 5.2$ Hz).

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 1588, 1490, 1276, 1261, 1226, 1149, 1114, 1077, 887, 836.

HRMS (ESI$^+$) calcd. for C$_{17}$H$_{27}$ONFS$^+$ [M+H]$^+$: 312.1792; found: 312.1792.
(4-Fluorophenyl)(p-tolyl)(2,4,4-trimethylpentan-2-yl)imino-λ⁶-sulfanone (5d)

\[
\begin{array}{c}
\text{O} \\
\text{S-N-t-Oct} \\
\text{F} \\
\text{Me}
\end{array}
\]

\[\text{R} = 0.65 \text{ (petrol / ethyl acetate = 9:1).}\]

\[^1\text{H NMR} \; (400 \text{ MHz, CDCl}_3): \; \delta \text{ (ppm) = 7.97-7.90 (m, 2H), 7.80 (d, } J = 8.3 \text{ Hz, 2H), 7.21 (d, } J = 8.3 \text{ Hz, 2H), 7.09-7.02 (m, 2H), 2.36 (s, 3H), 1.58 (s, 2H), 1.28 (s, 6H), 1.08 (s, 9H).}\]

\[^{13}\text{C NMR} \; (100 \text{ MHz, CDCl}_3): \; \delta \text{ (ppm) = 164.5 (d, } ^1J_{\text{CF}} = 252.7 \text{ Hz), 142.8, 142.3, 142.1 (d, } ^4J_{\text{CF}} = 3.1 \text{ Hz), 130.5 (d, } ^3J_{\text{CF}} = 9.5 \text{ Hz), 129.6, 128.0, 115.8 (d, } ^2J_{\text{CF}} = 22.3 \text{ Hz), 59.0, 58.8, 33.1, 33.0, 32.11, 32.07, 21.5.}\]

\[^19\text{F NMR} \; (376 \text{ MHz, CDCl}_3): \; \delta \text{ (ppm) = -108.3 (tt, } J = 8.4, 5.2 \text{ Hz).}\]

\[\text{IR (ATR): } \tilde{\nu} \text{ (cm}^{-1}) = 2953, 2903, 1589, 1488, 1363, 1259, 1218, 1150, 1090, 836, 813, 714, 672.\]

\[\text{HRMS \; (ESI\textsuperscript{+}) calcd. for C}_{21}\text{H}_{29}\text{FNOS} \; [\text{M+H}]^+: \; 362.1948; \text{ found: 362.1946.}\]

(4-Chlorophenyl)(4-fluorophenyl)(2,4,4-trimethylpentan-2-yl)imino-λ⁶-sulfanone (5e)

\[
\begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{S-N-t-Oct} \\
\text{F}
\end{array}
\]

Prepared according to **General Procedure D** except reaction was carried out at 50 °C instead of 40 °C, using sulfilimine 3g (140 mg, 0.384 mmol, 1.0 equiv.), TPAP (6.8 mg, 0.019 mmol, 5.0 mol%), NMO (270 mg, 2.31 mmol, 6.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 15:1) afforded sulfoximine 5e as a colourless oil (113 mg, 78%).

\[\text{R} = 0.45 \text{ (petrol/ethyl acetate, 7:1).}\]

\[^1\text{H NMR} \; (400 \text{ MHz, CDCl}_3): \; \delta \text{ (ppm) = 7.96-7.90 (m, 2H), 7.85 (d, } J = 8.7 \text{ Hz, 2H), 7.38 (d, } J = 8.7 \text{ Hz, 2H), 7.13-7.05 (m, 2H), 1.58 (s, 2H), 1.28 (s, 3H), 1.27 (s, 3H), 1.07 (s, 9H).}\]

\[^{13}\text{C NMR} \; (100 \text{ MHz, CDCl}_3): \; \delta \text{ (ppm) = 164.7 (d, } ^1J_{\text{CF}} = 253.6 \text{ Hz), 144.3, 141.3 (d, } ^4J_{\text{CF}} = 3.2 \text{ Hz), 138.2, 130.6 (d, } ^3J_{\text{CF}} = 9.3 \text{ Hz), 129.4, 129.2, 116.1 (d, } ^2J_{\text{CF}} = 22.3 \text{ Hz), 59.2, 58.7, 33.1, 33.0, 32.10, 32.05.}\]

\[^19\text{F NMR} \; (376 \text{ MHz, CDCl}_3): \; \delta \text{ (ppm) = -107.4 (tt, } J = 8.2, 5.2 \text{ Hz).}\]
IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 1653, 1589, 1472, 1390, 1228, 1128, 1088, 1006, 963, 813, 736.

HRMS (ESI$^+$) calcd. for C$_{20}$H$_{26}$F$_{35}$ClNOS$^+$ [M+H]$^+$: 382.1402; found: 382.1395.

(4-Chlorophenyl)(phenyl)((2,4,4-trimethylpentan-2-yl)imino)-$\lambda^6$-sulfanone (5f)

\[
\begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{S} \\
\text{N-t-Oct} \\
\text{Cl}
\end{array}
\]

Prepared according to General Procedure D except reaction was carried out at 50 °C instead of 40 °C, using sulfilimine 3j (210 mg, 0.605 mmol, 1.0 equiv.), TPAP (11 mg, 0.031 mmol, 5.0 mol%), NMO (428 mg, 3.66 mmol, 6.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 10:1 to 6:1) afforded sulfoximine 5f as a colourless oil (184 mg, 84%).

$R_f$ 0.50 (petrol/ethyl acetate, 15:1).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 7.95-7.91 (m, 2H), 7.88 (d, $J = 8.7$ Hz, 2H), 7.46-7.39 (m, 3H), 7.37 (d, $J = 8.7$ Hz, 2H), 1.59 (s, 2H), 1.283 (s, 3H), 1.278 (s, 3H), 1.08 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) = 145.3, 144.4, 138.0, 131.7, 129.5, 129.0, 128.9, 127.9, 59.1, 58.6, 33.1, 33.0, 32.1, 32.0.

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 1473, 1276, 1261, 1213, 1153, 1087, 1066, 1013, 827, 749, 701.

HRMS (ESI$^+$) calcd. for C$_{20}$H$_{27}$O$_3$ClNOS$^+$ [M+H]$^+$: 364.1496; found: 364.1500.

(4-Methoxyphenyl)(p-tolyl)((2,4,4-trimethylpentan-2-yl)imino)-$\lambda^6$-sulfanone (5g)

\[
\begin{array}{c}
\text{MeO} \\
\text{O} \\
\text{S} \\
\text{N-t-Oct} \\
\text{Me}
\end{array}
\]

Prepared according to General Procedure D using sulfilimine 3r (155 mg, 0.434 mmol, 1.0 equiv.), TPAP (8.1 mg, 0.023 mmol, 5.0 mol%), NMO (310 mg, 2.65 mmol, 6.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 7:1) afforded sulfoximine 5g as a colourless oil (142 mg, 88%).

$R_f$ 0.40 (petrol/ethyl acetate, 5:1).
\[^1\text{H} \text{NMR}\] (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 7.86 (d, \(J = 8.9\) Hz, 2H), 7.80 (d, \(J = 8.3\) Hz, 2H), 7.18 (d, \(J = 8.0\) Hz, 2H), 6.87 (d, \(J = 8.9\) Hz, 2H), 3.78 (s, 3H), 2.33 (s, 3H), 1.58 (s, 2H), 1.28 (s, 3H), 1.27 (s, 3H), 1.09 (s, 9H).

\[^{13}\text{C} \text{NMR}\] (100 MHz, (CD\(_3\))\(_2\)CO): \(\delta\) (ppm) = 163.3, 145.0, 142.9, 138.9, 130.8, 130.4, 128.7, 115.0, 59.6, 59.1, 56.2, 33.8, 33.7, 32.8, 32.7, 21.6.

\(\text{IR (ATR): } \tilde{\nu} (\text{cm}^{-1}) = 1594, 1492, 1387, 1251, 1151, 1091, 1027, 951, 801, 716, 673.\)

\(\text{HRMS (ESI\(^+\)) calcd. for } C_{22}H_{32}NO_2S^+ [M+H]^+: 374.2148; \text{ found: 374.2146.}\)

(4-Methoxyphenyl)(m-toly)((2,4,4-trimethylpentan-2-yl)imino)-\(\lambda^6\)-sulfanone (5h)

Prepared according to \textbf{General Procedure D} except reaction was carried out at 50 °C instead of 40 °C, using sulfilimine 3s (135 mg, 0.378 mmol, 1.0 equiv.), TPAP (6.9 mg, 0.019 mmol, 5.0 mol%), NMO (263 mg, 2.25 mmol, 6.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 12:1) afforded \textit{sulfoximine 5h} as a colorless oil (128 mg, 91%).

\(R_f\) 0.46 (petrol/ethyl acetate, 9:1).

\[^1\text{H} \text{NMR}\] (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 7.87 (d, \(J = 8.9\) Hz, 2H), 7.76-7.69 (m, 2H), 7.29-7.24 (m, 1H), 7.22-7.18 (m, 1H), 6.88 (d, \(J = 8.9\) Hz, 2H), 3.78 (s, 3H), 2.35 (s, 3H), 1.59 (s, 2H), 1.282 (s, 3H), 1.277 (s, 3H), 1.09 (s, 9H).

\[^{13}\text{C} \text{NMR}\] (100 MHz, (CD\(_3\))\(_2\)CO): \(\delta\) (ppm) = 163.4, 147.7, 139.8, 138.7, 133.0, 130.9, 129.7, 128.9, 125.9, 115.0, 59.6, 59.1, 56.2, 33.8, 33.7, 32.8, 32.7, 21.6.

\(\text{IR (ATR): } \tilde{\nu} (\text{cm}^{-1}) = 1594, 1493, 1386, 1252, 1151, 1090, 955, 832, 694.\)

\(\text{HRMS (ESI\(^+\)) calcd. for } C_{22}H_{32}NO_2S^+ [M+H]^+: 374.2148; \text{ found: 374.2140.}\)

(4-Methoxyphenyl)(o-toly)((2,4,4-trimethylpentan-2-yl)imino)-\(\lambda^6\)-sulfanone (5i)
Prepared according to General Procedure D using sulfilimine 3t (60 mg, 0.17 mmol, 1.0 equiv.), TPAP (9.2 mg, 0.026 mmol, 15 mol%), NMO (117 mg, 1.00 mmol, 6.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 12:1) afforded sulfoximine 5i as a colourless oil (45 mg, 72%).

Rf 0.50 (petrol/ethyl acetate, 9:1).

\[ ^1H\text{NMR} (400\text{ MHz, CDCl}_3): \delta (\text{ppm}) = 8.36 (\text{dd, } J = 7.6, 1.9 \text{ Hz, 1H}), 7.80 (\text{d, } J = 9.0 \text{ Hz, 2H}), 7.37-7.28 (\text{m, 2H}), 7.12-7.08 (\text{m, 1H}), 6.88 (\text{d, } J = 9.0 \text{ Hz, 2H}), 3.81 (\text{s, 3H}), 2.33 (\text{s, 3H}), 1.59 (\text{s, 2H}), 1.27 (\text{s, 3H}), 1.21 (\text{s, 3H}), 1.08 (\text{s, 9H}). \]

\[ ^{13}C\text{NMR} (100\text{ MHz, CDCl}_3): \delta (\text{ppm}) = 162.0, 143.9, 137.5, 136.6, 132.6, 131.7, 130.2, 130.1, 126.1, 113.7, 59.0, 58.7, 55.6, 32.7, 32.5, 32.14, 32.07, 20.2. \]

\[ \text{IR (ATR): } \tilde{\nu} (\text{cm}^{-1}) = 1594, 1494, 1251, 1151, 1083, 833, 803, 759, 717. \]

HRMS (ESI⁺) calcd. for C₂₂H₃₂NO₂S⁺ [M+H⁺]: 374.2148; found: 374.2138.

(4-Methoxyphenyl)(napthalen-2-yl)((2,4,4-trimethylpentan-2-yl)imino)-\(\lambda^6\)-sulfanone (5j)

Prepared according to General Procedure D using sulfilimine 3u (153 mg, 0.389 mmol, 1.0 equiv.), TPAP (6.9 mg, 0.019 mmol, 5.0 mol%), NMO (277 mg, 2.37 mmol, 6.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 9:1) afforded sulfoximine 5j as a white solid (146 mg, 92%).

mp 106-108 °C (CH₂Cl₂)

Rf 0.45 (petrol/ethyl acetate, 5:1).

\[ ^1H\text{NMR} (400\text{ MHz, CDCl}_3): \delta (\text{ppm}) = 8.61-8.55 (\text{m, 1H}), 7.98-7.91 (\text{m, 3H}), 7.87 (\text{dd, } J = 8.7, 1.8 \text{ Hz, 1H}), 7.85-7.79 (\text{m, 2H}), 7.58-7.51 (\text{m, 2H}), 6.89 (\text{d, } J = 9.0 \text{ Hz, 2H}), 3.78 (\text{s, 3H}), 1.66 (\text{d, } J = 14.4 \text{ Hz, 1H}), 1.62 (\text{d, } J = 14.4 \text{ Hz, 1H}), 1.35 (\text{s, 3H}), 1.30 (\text{s, 3H}), 1.14 (\text{s, 9H}). \]

\[ ^{13}C\text{NMR} (100\text{ MHz, CDCl}_3): \delta (\text{ppm}) = 162.2, 143.5, 137.1, 134.3, 132.6, 130.1, 129.3, 128.8, 128.4, 128.2, 127.8, 127.1, 124.0, 114.0, 58.9, 58.8, 55.6, 33.3, 33.0, 32.12, 32.10. \]
IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 1593, 1493, 1386, 1254, 1152, 1083, 955, 832, 748.

HRMS (ESI$^+$) calcd. for C$_{25}$H$_{32}$NO$_2$S$^+$/[M+H]$^+$: 410.2148; found: 410.2141.

(4-Chlorophenyl)(6-methoxypyridin-3-yl)((2,4,4-trimethylpentan-2-yl)imino)-$\lambda^6$-sulfanone (5k)

Prepared according to General Procedure D using sulfilimine 3k (96.6 mg, 0.256 mmol, 1.0 equiv.), TPAP (4.5 mg, 0.013 mmol, 5.0 mol%), NMO (180 mg, 1.54 mmol, 6.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 10:1) afforded sulfoximine 5k as a colourless oil (88 mg, 88%).

R$_f$ 0.50 (petrol/ethyl acetate, 5:1).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 8.72 (dd, $J$ = 2.5, 0.7 Hz, 1H), 7.95 (dd, $J$ = 8.8, 2.5 Hz, 1H), 7.85 (d, $J$ = 8.7 Hz, 2H), 7.38 (d, $J$ = 8.7 Hz, 2H), 6.72 (dd, $J$ = 8.8, 0.7 Hz, 1H), 3.94 (s, 3H), 1.57 (s, 2H), 1.28 (s, 3H), 1.25 (s, 3H), 1.06 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) = 165.9, 148.2, 144.4, 138.2, 138.1, 134.4, 129.3, 129.2, 111.2, 59.2, 58.6, 54.3, 33.2, 33.1, 32.1, 32.0.

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 1587, 1476, 1366, 1276, 1261, 1121, 1154, 1118, 1087, 1013, 823.

HRMS (ESI$^+$) calcd. for C$_{20}$H$_{28}$S$_2$ClO$_2$N$_2$S$^+$/[M+H]$^+$: 395.1555; found: 395.1553.

(4-Chlorophenyl)(thiophen-2-yl)((2,4,4-trimethylpentan-2-yl)imino)-$\lambda^6$-sulfanone (5l)

Prepared according to General Procedure D except reaction was carried out at 50 °C instead of 40 °C, using sulfilimine 3l (223 mg, 0.632 mmol, 1.0 equiv.), TPAP (12 mg, 0.034 mmol, 5.0 mol%), NMO (447 mg, 3.82 mmol, 6.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 11:1 to 6:1) afforded sulfoximine 5l as a colourless oil (201 mg, 87%).

R$_f$ 0.50 (petrol/ethyl acetate, 15:1).
**H NMR** (400 MHz, CDCl$_3$): $\delta$ (ppm) = 7.95 (d, $J = 8.7$ Hz, 2H), 7.50 (dd, $J = 5.0$, 1.3 Hz, 1H), 7.43 (dd, $J = 3.7$, 1.3 Hz, 1H), 7.39 (d, $J = 8.7$ Hz, 2H), 6.98 (dd, $J = 5.0$, 3.7 Hz, 1H), 1.58 (s, 2H), 1.33 (s, 3H), 1.329 (s, 3H), 1.08 (s, 9H).

**C NMR** (100 MHz, CDCl$_3$): $\delta$ (ppm) = 148.5, 144.6, 138.1, 132.5, 131.9, 129.1, 129.0, 127.8, 59.4, 58.5, 33.1, 32.7, 32.1, 32.0.

**IR** (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 1473, 1276, 1261, 1212, 1154, 1088, 1012, 997, 826, 750.

**HRMS (ESI$^+$) calcd. for C$_{18}$H$_{25}$O$_3$ClNS$_2$$^+ [M+H]^+$: 370.1061; found: 370.1059.

**Butyl(2-methylallyl)((2,4,4-trimethylpentan-2-yl)imino)-6-sulfanone (5m)**

Sulfilimine prepared according to **General Procedure E** using N-sulfinyl-tert-octylamine 1 (512 mg, 2.92 mmol, 1.05 equiv.), TMSOTf (605 mg, 2.72 mmol, 1.0 equiv.), n-butylmagnesium chloride (1.39 mL, 1.96 M in THF, 2.72 mmol, 1.0 equiv.) and 2-methyl-1-propenylmagnesium bromide (8.00 mL, 0.49 M in THF, 3.92 mmol, 1.5 equiv.). Following the general purification method, sulfilimine 3o was generated as light yellow oil with a crude yield of 81% (600 mg).

Sulfoximine prepared using TPAP (39 mg, 0.11 mmol, 5.0 mol%), NMO (1.54 g, 13.2 mmol, 6.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 3:1 to 1:1) afforded sulfoximine 5m as a light yellow oil (187 mg, 24% yield over two steps).

**Rf** 0.61 (petrol/ethyl acetate, 1:1).

**H NMR** (400 MHz, CDCl$_3$): $\delta$ (ppm) = 4.93 (s, 1H), 4.84 (s, 1H), 3.98 (d, $J = 19.6$ Hz, 1H), 3.03 (d, $J = 19.6$ Hz, 1H), 2.55-2.38 (m, 2H), 1.76 (d, $J = 14.7$ Hz, 1H), 1.70 (s, 3H), 1.68 (d, $J = 14.7$ Hz, 1H), 1.62-1.47 (m, 2H), 1.43-1.31 (m, 5H), 1.22 (s, 3H), 0.95 (s, 9H), 0.87 (t, $J = 7.3$ Hz, 3H).

**C NMR** (100 MHz, CDCl$_3$): $\delta$ (ppm) = 145.6, 110.7, 63.6, 54.5, 53.1, 42.0, 31.9, 31.4, 29.3, 27.5, 25.9, 22.0, 20.7, 13.8.

**IR** (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 1469, 1368, 1276, 1261, 1138, 1071, 1045, 895, 839, 763.

**HRMS (ESI$^+$) calcd. for C$_{16}$H$_{34}$NOS$^+$ [M+H]$^+$: 288.2356; found: 288.2354.
Cyclopropyl(2-methylallyl)((2,4,4-trimethylpentan-2-yl)imino)-\(\lambda^6\)-sulfanone (5n)

Sulfilimine prepared according to General Procedure E using N-sulfinyl-tert-octylamine 1 (340 mg, 1.94 mmol, 1.05 equiv.), TMSOTf (416 mg, 1.87 mmol, 1.0 equiv.), cyclopropylmagnesium bromide (2.23 mL, 0.84 M in 2-methyltetrahydrofuran, 1.87 mmol, 1.0 equiv.) and 2-methyl-1-propenylmagnesium bromide (5.60 mL, 0.49 M in THF, 2.74 mmol, 1.5 equiv.). Following the general purification method, sulfilimine 3q was generated as light yellow oil with a crude yield of 81% (387 mg). Sulfoximine prepared using TPAP (27 mg, 0.076 mmol, 5.0 mol%), NMO (1.07 g, 9.15 mmol, 6.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 4:1 to 2:1) afforded sulfoxime 5n as a colourless oil (236 mg, 47% yield over two steps).

\(R\): 0.65 (petrol/ethyl acetate, 3:1).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 4.96 (s, 1H), 4.78 (s, 1H), 3.88 (d, \(J = 19.8\) Hz, 1H), 3.05 (d, \(J = 19.8\) Hz, 1H), 1.88 (tt, \(J = 8.0, 5.0\) Hz, 1H), 1.79 (d, \(J = 14.7\) Hz, 1H), 1.65 (s, 3H), 1.64 (d, \(J = 14.7\) Hz, 1H), 1.37 (s, 3H), 1.21 (s, 3H), 1.18-1.11 (m, 1H), 0.93 (s, 9H), 0.65-0.54 (m, 2H), 0.52-0.44 (m, 1H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 144.6, 110.2, 63.4, 53.3, 42.9, 31.9, 31.4, 30.1, 29.2, 27.6, 20.6, 2.7, -0.1.

IR (ATR): \(\tilde{\nu}\) (cm\(^{-1}\)) = 1472, 1368, 1276, 1261, 1139, 1071, 1028, 896, 840, 818, 750.

HRMS (ESI\(^+\)) calcd. for C\(_{15}\)H\(_{30}\)NOS\(^+\) [M+H]\(^+\): 272.2043; found: 272.2043.

(4-Chlorophenyl)(4-(5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)phenyl)((2,4,4-trimethylpentan-2-yl)imino)-\(\lambda^6\)-sulfanone (5o)
Prepared according to **General Procedure D** using sulfilimine 3n (108 mg, 0.189 mmol, 1.0 equiv.), TPAP (3.4 mg, 0.010 mmol, 5.0 mol%), NMO (137 mg, 1.17 mmol, 6.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 10:1) afforded *sulfoximine* 5o as a colourless oil (83 mg, 75%).

**R** 0.5 (petrol/ethyl acetate, 9:1).

**1H NMR** (400 MHz, CDCl₃): δ (ppm) = 7.90 (d, *J* = 8.7 Hz, 2H), 7.84 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 6.1 Hz, 2H), 7.37 (d, *J* = 6.1 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.71 (s, 1H), 2.37 (s, 3H), 1.58 (s, 2H), 1.28 (s, 3H), 1.27 (s, 3H), 1.06 (s, 9H).

**13C NMR** (100 MHz, CDCl₃): δ (ppm) = 145.2, 144.9, 144.0 (q, *2J*CF = 38.3 Hz), 143.8, 141.8, 139.8, 138.4, 129.7, 129.6, 129.2, 129.0, 128.8, 125.9, 125.5, 121.2 (q, *1J*CF = 269.2 Hz), 106.2, 59.3, 58.6, 33.1, 33.0, 32.1, 32.0, 21.5.

**19F NMR** (376 MHz, CDCl₃): δ (ppm) = -62.4

**IR** (ATR): ν (cm⁻¹) = 1472, 1276, 1261, 1235, 1214, 1134, 1088, 975, 909, 750.

**HRMS (ESI⁺)** calcd. for C₃₁H₃₄O₃S₅ClN₃F₃[+M+H]⁺: 588.2058; found: 588.2055.

### 1.2.7 Deprotection of Sulfondiimine

**N-((4-Fluorophenyl)(imino)(methyl)-λ⁵-sulfaneylidene)-4-nitrobenzenesulfonamide (6)**

![Sulfondiimine 4b](image)

Sulfondiimine 4b (1.00 g, 2.14 mmol, 1.0 equiv.) was mixed with TFA (21 mL) and stirred at room temperature for 14 h. The mixture was concentrated *in vacuo* then diluted with CH₂Cl₂ and basified to pH 10-11 using 1 M aq. NaOH solution. The product was extracted with CH₂Cl₂ (3 × 50 mL). The combined extracts were washed with brine, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (petrol/ethyl acetate, 1:1 to 1:3) to afford *sulfondiimine* 6 as a white solid (737 mg, 97%).

**mp** 173-175 °C (CH₂Cl₂)

**R** 0.37 (petrol/ethyl acetate, 1:3).
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 8.29 (d, $J = 8.9$ Hz, 2H), 8.13 (d, $J = 8.9$ Hz, 2H), 8.15-8.08 (m, 2H), 7.29-7.24 (m, 2H), 3.43 (s, 3H), 2.71 (br. s, 1H).

$^{13}$C NMR (100 MHz, (CD$_3$)$_2$CO): $\delta$ (ppm) = 166.7 (d, $^1J_{CF} = 253.7$ Hz), 151.5, 150.5, 138.5 (d, $^4J_{CF} = 3.2$ Hz), 131.6 (d, $^3J_{CF} = 9.6$ Hz), 129.0, 124.8, 117.4 (d, $^2J_{CF} = 23.1$ Hz), 48.5.

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ (ppm) = -102.4 (tt, $J = 8.0, 4.9$ Hz).

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 2978, 1528, 1352, 1296, 1238, 1152, 1086, 1035, 1006, 968.

HRMS (ESI$^+$) calc. for C$_{13}$H$_{13}$FN$_3$O$_4$S$_2$ $[M+H]^+$: 358.0326; found: 358.0323.

1-(4-Fluorophenyl)-1-methyl-N-(2,4,4-trimethylpentan-2-yl)-$\lambda^6$-sulfandiimine (7)

Under an atmosphere of nitrogen, sulfandiimines 4b (1.50 g, 3.20 mmol, 1.0 equiv.) was dissolved in anhydrous MeCN (10 ml). 1-Dodecanethiol (3.80 ml, 15.8 mmol, 5.0 equiv.) was added at room temperature followed by DBU (2.30 mL, 15.4 mmol, 4.75 equiv.). The solution became yellow and was stirred for 20 min under nitrogen until completion of the reaction (TLC). The reaction mixture was then concentrated in vacuo to afford light yellow oil. The crude product was purified by flash column chromatography (petrol/ethyl acetate, 1:1 to 0:1) to afford corresponding sulfandiimine 7 as a colourless oil (806 mg, 89%).

Rf 0.44 (ethyl acetate).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 8.14-8.08 (m, 2H), 7.18-7.08 (m, 2H), 3.05 (s, 3H), 1.97 (br. s, 1H), 1.56 (d, $J = 14.4$ Hz, 1H), 1.52 (d, $J = 14.4$ Hz, 1H), 1.41 (s, 3H), 1.30 (s, 3H), 1.03 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) = 164.6 (d, $^1J_{CF} = 252.7$ Hz), 143.0 (d, $^4J_{CF} = 3.1$ Hz), 129.8 (d, $^3J_{CF} = 9.1$ Hz), 115.7 (d, $^2J_{CF} = 22.4$ Hz), 58.72, 58.70, 51.8, 33.3, 32.3, 32.08, 32.05.

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ (ppm) = -108.7 (tt, $J = 8.3, 5.2$ Hz).

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 2954, 1589, 1488, 1219, 1188, 1152, 1087, 1001, 939.

HRMS (ESI$^+$) calc. for C$_{15}$H$_{26}$FN$_2$S$^+$ $[M+H]^+$: 285.1795; found: 285.1795.
(4-Fluorophenyl)(methyl)-\(\lambda^6\)-sulfanediimine (8)

Under an atmosphere of nitrogen, sulfoniimines 6 (602 mg, 1.69 mmol, 1.0 equiv.) was dissolved in anhydrous MeCN (5.0 ml). 1-Dodecanethiol (2.00 mL, 8.35 mmol, 5.0 equiv.) was added at room temperature followed by DBU (1.20 mL, 8.02 mmol, 4.75 equiv.). The solution became yellow and was stirred for 20 min under nitrogen until completion of the reaction (TLC). The reaction mixture was concentrated in vacuo to afford light yellow oil. The crude product was purified by flash column chromatography (CH\(_2\)Cl\(_2\)/MeOH, 9:1) to afford sulfoniimine 8 as a white solid (285 mg, 98%).

\( mp \) 103-105 °C (CH\(_2\)Cl\(_2\))

Rf 0.48 (CH\(_2\)Cl\(_2\)/MeOH, 9:1).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 8.17-8.08 (m, 2H), 7.18-7.09 (m, 2H), 3.09 (s, 3H), 2.48 (br. s, 2H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 165.2 (d, \(^1\)J\(_{CF}\) = 254.2 Hz), 140.4 (d, \(^4\)J\(_{CF}\) = 3.1 Hz), 129.9 (d, \(^3\)J\(_{CF}\) = 9.3 Hz), 116.1 (d, \(^2\)J\(_{CF}\) = 22.4 Hz), 50.6.

\(^19\)F NMR (376 MHz, CDCl\(_3\)): \( \delta \) (ppm) = -106.7 (tt, \( J = 8.5, 5.1 \) Hz).

IR (ATR): \( \tilde{\nu} \) (cm\(^{-1}\)) = 1589, 1490, 1227, 1057, 933, 839, 661.

HRMS (ESI\(^+\)) calcd. for C\(_7\)H\(_{10}\)FN\(_2\)S\(^+\) [M+H]\(^+\): 173.0543; found: 173.0543.

1.2.8 Deprotection of Sulfilimine

(4-Fluorophenyl)(p-tolyl)-\(\lambda^4\)-sulphaniminium-4-methylbenzenesulfonate (9)

In a 25 mL round bottom flask, sulfilimine 3a (225 mg, 0.652 mmol, 1.0 equiv.) was dissolved in anhydrous CH\(_2\)Cl\(_2\) (6.5 mL). Triflic acid (290 \( \mu \)L, 3.29 mmol, 5.0 equiv.) was added and the
reaction was stirred at room temperature for 1 h. The mixture was diluted with CH$_2$Cl$_2$ and basified to pH 10-11 using 1 M aq. NaOH solution. The separated aqueous phase was extracted with CH$_2$Cl$_2$ (3 × 30 mL). The combined extracts were washed with brine, dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo. Then the crude sulfilimine was dissolved in CH$_2$Cl$_2$ (20 mL), TsOH·H$_2$O (123 mg, 0.715 mmol, 1.1 equiv.) was added and stirred at room temperature for 10 min until a homogeneous solution is formed. The mixture was then concentrated in vacuo and was purified by flash column chromatography (CH$_2$Cl$_2$/MeOH, 20:1 to 5:1) to afford sulfilimium salt 9 as a waxy solid (255 mg, 97%).

Rf 0.62 (CH$_2$Cl$_2$/MeOH, 5:1).

$^1$H NMR (400 MHz, CD$_3$OD): $\delta$ (ppm) = 7.87-7.81 (m, 2H), 7.70-7.76 (m, 4H), 7.50 (d, $J = 8.1$ Hz, 2H), 7.45-7.39 (m, 2H), 7.19 (d, $J = 7.8$ Hz, 2H), 2.44 (s, 3H), 2.34 (s, 3H).

$^{13}$C NMR (100 MHz, CD$_3$OD): $\delta$ (ppm) = 166.9 (d, $^1J_{CF} = 255.7$ Hz), 146.7, 143.5, 141.6, 132.4, 132.3 (d, $^3J_{CF} = 9.7$ Hz), 130.5, 130.0 (d, $^4J_{CF} = 3.2$ Hz), 129.8, 129.4, 126.9, 119.0 (d, $^2J_{CF} = 23.3$ Hz), 21.5, 21.3.

$^{19}$F NMR (376 MHz, CD$_3$OD): $\delta$ (ppm) = -105.7 (tt, $J = 8.2$, 4.7 Hz).

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 2981, 2361, 2341, 1589, 1494, 1227, 1177, 1122, 1034, 1011, 814, 683.

HRMS (ESI$^+$) calcd. for C$_{13}$H$_{13}$FNS$^+$ [M+H]$^+$: 234.0747; found: 234.0746.

**1.2.9 Deprotection of Sulfoximine**

(4-Fluorophenyl)(imino)(p-tolyl)-$\lambda^6$-sulfanone (10)

Sulfoximine 5d (69 mg, 0.19 mmol, 1.0 equiv.) was mixed with TFA (1.5 mL) and heated to 60 °C for 18 h. The mixture was concentrated in vacuo then diluted with CH$_2$Cl$_2$ and basified to pH 10-11 using 1 M aq. NaOH solution. The product was extracted with CH$_2$Cl$_2$ (3 × 30 mL). The combined extracts were washed with brine, dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo. The crude product was purified by flash column chromatography (petrol/ethyl acetate, 3:1 to 1:2) to afford sulfoximine 10 as a colourless oil (47 mg, 99%).

Rf 0.41 (petrol/ethyl acetate, 1:1).
1H NMR (400 MHz, CDCl₃): δ (ppm) = 8.05-8.00 (m, 2H), 7.89 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 7.14-7.08 (m, 2H), 2.90 (br. s, 1H), 2.37 (s, 3H).

13C NMR (100 MHz, CDCl₃): δ (ppm) = 165.2 (d, 1JCF = 254.4 Hz), 143.7, 140.5, 139.8 (d, 4JCF = 3.1 Hz), 130.7 (d, 3JCF = 9.5 Hz), 130.0, 128.0, 116.4 (d, 2JCF = 22.7 Hz), 21.6.

19F NMR (376 MHz, CDCl₃): δ (ppm) = -106.2 (tt, J = 8.3, 5.1 Hz).

IR (ATR): v (cm⁻¹) = 2981, 2888, 1588, 1489, 1382, 1229, 1130, 1094, 968, 839.

HRMS (ESI⁺) calcd. for C₁₃H₁₃FNOS [M+H]⁺: 250.0696; found: 250.0695.

1.2.10 N-Functionalization of Sulfoniimine

N-((4-Fluorophenyl)(methyl)(phenylimino)-λ⁶-sulfaneylidene)-4-nitrobenzenesulfonamide (11a)

Sulfoniimine 6 (50 mg, 0.14 mmol, 1.0 equiv.), phenylboronic acid (45 mg, 0.37 mmol, 2.5 equiv.), Cu(MeCN)₄PF₆ (26 mg, 0.070 mmol, 0.5 equiv.), N-methylpiperidine (123 mg, 1.24 mmol, 9.0 equiv.) were added to an oven-dried 10 mL vial and dissolved in MeCN (1.4 mL) under oxygen atmosphere. The reaction was stirred at room temperature for 24 h until completion of the reaction (TLC). The reaction was quenched with water and extracted with ethyl acetate (3 × 20 mL). The combined extracts were washed with brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The crude product was purified by flash column chromatography (petrol/ethyl acetate, 4:1 to 2:1) to afford sulfoniimine 11a as a white solid (51 mg, 84%).

mp 177-179 °C (CH₂Cl₂)

Rf 0.39 (petrol/ethyl acetate, 2:1).

1H NMR (400 MHz, CDCl₃): δ (ppm) = 8.08-8.04 (m, 2H), 7.91 (d, J = 8.9 Hz, 2H), 7.81 (d, J = 8.9 Hz, 2H), 7.29-7.23 (m, 2H), 6.79-6.73 (m, 2H), 6.69-6.63 (m, 1H), 6.40-6.35 (m, 2H), 3.76 (s, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) = 166.3 (d, $^1J_{CF} = 258.6$ Hz), 149.4, 147.5, 142.6, 131.9 (d, $^4J_{CF} = 3.2$ Hz), 131.1 (d, $^3J_{CF} = 9.7$ Hz), 128.7, 128.3, 123.5, 122.1, 121.9, 117.9 (d, $^2J_{CF} = 23.0$ Hz), 49.1.

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ (ppm) = -101.9 (tt, $J = 8.0, 4.8$ Hz).

IR (ATR): $\nu$ (cm$^{-1}$) = 1592, 1527, 1487, 1350, 1294, 1260, 1156, 1065, 1002, 797, 737, 691

HRMS (ESI$^+$) calcd. for C$_{19}$H$_{17}$FN$_3$O$_4$S$_2$ $[\text{M+H}]^+$: 434.0639; found: 434.0642.

I-(4-Fluorophenyl)-1-methyl-N-phenyl-\(\lambda^6\)-sulfandiimine (11)

![Chemical structure](image)

Under an atmosphere of nitrogen, sulfandiimines 11a (42 mg, 0.10 mmol, 1.0 equiv.) was dissolved in anhydrous MeCN (1.0 ml). 1-Dodecanethiol (0.12 mL, 0.50 mmol, 5.0 equiv.) was added at room temperature followed by DBU (70 µL, 0.47 mmol, 4.8 equiv.). The solution became yellow and was stirred for 20 min under nitrogen until completion of the reaction (TLC). The reaction mixture was concentrated in vacuo to afford light yellow oil. The crude product was purified by flash column chromatography (petrol/ethyl acetate, 1:1 to 0:1) to afford corresponding sulfandiimine 11 as a white solid (19 mg, 80%).

$mp$ 122-123 °C (CH$_2$Cl$_2$)

R$\ell$ 0.39 (ethyl acetate).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 8.23-8.16 (m, 2H), 7.25-7.14 (m, 4H), 7.10-7.06 (m, 2H), 6.90 (tt, $J = 7.5, 1.2$ Hz, 1H), 3.25 (s, 3H), 2.17 (br. s, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) = 165.5 (d, $^1J_{CF} = 254.8$ Hz), 145.8, 138.0 (d, $^4J_{CF} = 3.1$ Hz), 130.7 (d, $^3J_{CF} = 9.4$ Hz), 129.2, 123.2, 121.3, 116.6 (d, $^2J_{CF} = 22.6$ Hz), 48.6.

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ (ppm) = -106.1 (tt, $J = 8.3, 5.2$ Hz).

IR (ATR): $\nu$ (cm$^{-1}$) = 1590, 1486, 1390, 1254, 1153, 1081, 956, 839, 758.

HRMS (ESI$^+$) calcd. for C$_{13}$H$_{14}$FN$_2$S$^+$ $[\text{M+H}]^+$: 249.0856; found: 249.0855.
In an oven-dried flask, sulfondiimine 6 (64 mg, 0.18 mmol, 1.0 equiv.) was dissolved in anhydrous DMSO (0.40 mL). KOH (21 mg, 0.37 mmol, 2.0 equiv.) was added followed by allyl bromide (35 mg, 0.29 mmol, 1.5 equiv.). The reaction mixture was stirred at room temperature for 12 h until completion of the reaction (TLC). The reaction was quenched with water and extracted with CH₂Cl₂ (3 × 20 mL). The combined extracts were washed with brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The crude product was purified by flash column chromatography (petrol/ethyl acetate, 1:1) to afford sulfondiimine 12a as a light yellow oil (58 mg, 81%).

Rf 0.35 (petrol/ethyl acetate, 1:1).

$^1$H NMR (400 MHz, CDCl₃): δ (ppm) = 8.30 (d, J = 9.0 Hz, 2H), 8.18 (d, J = 9.0 Hz, 2H), 8.04-7.96 (m, 2H), 7.41-6.94 (m, 2H), 5.60 (ddt, J = 17.0, 10.3, 5.2 Hz, 1H), 5.05 (dq, J = 17.0, 1.8 Hz, 1H), 4.97 (dq, J = 10.3, 1.8 Hz, 1H), 3.59 (s, 3H), 3.12 (ddt, J = 15.5, 5.2, 1.7 Hz, 1H), 2.90 (ddt, J = 15.5, 5.2, 1.7 Hz, 1H).

$^{13}$C NMR (100 MHz, CDCl₃): δ (ppm) = 166.2 (d, $^1J_{CF} = 258.0$ Hz), 149.7, 149.6, 135.5, 132.4 (d, $^4J_{CF} = 3.2$ Hz), 131.3 (d, $^3J_{CF} = 9.7$ Hz), 128.3, 124.1, 117.5 (d, $^2J_{CF} = 22.7$ Hz), 115.6, 47.6, 46.4.

$^{19}$F NMR (376 MHz, CDCl₃): δ (ppm) = -102.7 (tt, J = 8.0, 4.9 Hz).

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1526, 1390, 1153, 1084, 956.

HRMS (ESI⁺) calcd. for C₁₆H₁₇FN₃O₄S₂⁺ [M+H]⁺: 398.0639; found: 398.0644.

$\text{N-}\text{Allyl-1-(4-fluorophenyl)-1-methyl-}\lambda^6\text{-sulfanediimine (12)}$

Under an atmosphere of nitrogen, sulfondiimines 12a (45 mg, 0.11 mmol, 1.0 equiv.) was dissolved in anhydrous MeCN (1.1 ml). 1-Dodecanethiol (0.13 mL, 0.54 mmol, 5.0 equiv.) was added at room temperature followed by DBU (78 µL, 0.52 mmol, 4.75 equiv.). The solution became yellow
and was stirred for 20 mins under nitrogen until completion of the reaction (TLC). The reaction mixture was concentrated in vacuo to afford light yellow oil. The crude product was purified by flash column chromatography (CH$_2$Cl$_2$/MeOH, 15:1 to 9:1) to afford corresponding sulfoniimine 12 as a light yellow oil (22 mg, 94%).

R f 0.43 (CH$_2$Cl$_2$ / MeOH = 9:1).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 8.16-8.01 (m, 2H), 7.23-7.17 (m, 2H), 5.96 (ddt, $J$ = 17.0, 10.1, 5.6 Hz, 1H), 5.25 (dq, $J$ = 17.0, 1.8 Hz, 1H), 5.05 (dq, $J$ = 10.1, 1.8 Hz, 1H), 3.68 (ddt, $J$ = 15.2, 5.6, 1.6 Hz, 1H), 3.53 (ddt, $J$ = 15.2, 5.6, 1.6 Hz, 1H), 3.12 (s, 3H), 2.25 (br. s, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) = 165.3 (d, $^1$J$_{CF}$ = 254.1 Hz), 138.5, 137.6 (d, $^4$J$_{CF}$ = 3.0 Hz), 130.6 (d, $^3$J$_{CF}$ = 9.3 Hz), 116.4 (d, $^2$J$_{CF}$ = 22.5 Hz), 114.8, 48.5, 45.7.

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ (ppm) = -106.7 (tt, $J$ = 8.3, 5.1 Hz).

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 1490, 1389, 1253, 1153, 1076, 956.

HRMS (ESI$^+$) calcd. for C$_{10}$H$_{14}$FN$_2$S$^+$ [M+H]$^+$: 213.0856; found: 213.0860.

N-((4-Fluorophenyl)(methyl)((2,4,4-trimethylpentan-2-yl)imino)-$\lambda^6$-sulfaneylidene)acetamide (13a)

Under an atmosphere of argon, sulfoniimine 7 (40 mg, 0.14 mmol, 1.0 equiv.) was dissolved in anhydrous CH$_2$Cl$_2$ (1.5 mL). Triethylamine (30 $\mu$L, 0.22 mmol, 1.5 equiv.) was added at 0°C followed by acetic anhydride (20 $\mu$L, 0.21 mmol, 1.5 equiv.) and DMAP (4.1 mg, 0.034 mmol, 0.25 equiv.). The reaction mixture was stirred at room temperature for 12 h. Sat. aq. NH$_4$Cl (30 mL) was added and the product was extracted with CH$_2$Cl$_2$ (3 x 10 mL). The combined extracts were washed with brine, dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo. The crude product was purified by flash column chromatography (petrol/ethyl acetate, 1.5:1) to afford sulfoniimine 13a as a white solid (45 mg, 99%).

mp 64-65 °C (CH$_2$Cl$_2$)

R f 0.37 (petrol/ethyl acetate, 1.5:1).
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 8.12-8.02 (m, 2H), 7.23-7.12 (m, 2H), 3.36 (s, 3H), 2.12 (s, 3H), 1.52 (d, $J = 14.4$ Hz, 1H), 1.47 (d, $J = 14.4$ Hz, 1H), 1.32 (s, 3H), 1.13 (s, 3H), 1.02 (s, 9H).

$^{13}$C NMR (100 MHz, (CD$_3$)$_2$CO): $\delta$ (ppm) = 179.6, 166.0 (d, $^1J_{CF} = 251.7$ Hz), 141.5 (d, $^4J_{CF} = 3.2$ Hz), 131.6 (d, $^3J_{CF} = 9.1$ Hz), 117.0 (d, $^2J_{CF} = 23.0$ Hz), 59.6, 59.0, 47.9, 32.7, 32.6, 32.4, 32.2, 27.5.

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ (ppm) = -106.8 (tt, $^J = 8.1$, 5.0 Hz).

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 2980, 1623, 1383, 1360, 1262, 1217, 1153, 1079, 1022, 969, 817.

HRMS (ESI$^+$) calcd. for C$_{17}$H$_{28}$FN$_2$OS$^+$ [M+H]$^+$: 327.1901; found: 327.1897.

$N$-((4-Fluorophenyl)(imino)(methyl)-$\lambda^5$-sulfaneylidene)acetamide (13)

![Chemical structure]

Sulfondiimine 13a (91 mg, 0.28 mmol, 1.0 equiv.) was mixed with TFA (2.8 mL) and stirred at room temperature for 14 h. The mixture was concentrated in vacuo then diluted with CH$_2$Cl$_2$ and basified to pH 10-11 using 1 M aq. NaOH solution. The product was extracted with CH$_2$Cl$_2$ (3 × 20 mL). The combined extracts were washed with brine, dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo. The crude product was purified by flash column chromatography (ethyl acetate, then CH$_2$Cl$_2$/MeOH, 5:1) to afford sulfondiimine 13 as a colourless oil (54 mg, 90%).

$R$ 0.28 (ethyl acetate).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 8.01-7.93 (m, 2H), 7.24-7.17 (m, 2H), 3.16 (s, 3H), 3.04 (br. s, 1H), 2.07 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) = 181.8, 165.6 (d, $^1J_{CF} = 255.6$ Hz), 137.6 (d, $^4J_{CF} = 3.1$ Hz), 129.7 (d, $^3J_{CF} = 9.4$ Hz), 117.0 (d, $^2J_{CF} = 22.9$ Hz), 45.1, 26.0.

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ (ppm) = -105.0 (tt, $J = 8.0$, 5.1 Hz).

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 1587, 1490, 1365, 1281, 1233, 1157, 1083, 1047, 944, 818.

HRMS (ESI$^+$) calcd. for C$_9$H$_{12}$FN$_2$OS$^+$ [M+H]$^+$: 215.0649; found: 215.0648.
1-((4-Fluorophenyl)(methyl)((2,4,4-trimethylpentan-2-yl)imino)-λ₆-sulfaneylidene)-3-phenylurea (14a)

To a solution of sulfondiimine 7 (38 mg, 0.13 mmol, 1.0 equiv.) in anhydrous CH₂Cl₂ (1.3 mL), the phenyl isocyanate (26 mg, 0.22 mmol, 1.5 equiv.) was added dropwise at room temperature under argon atmosphere. The reaction was stirred at room temperature for 24 h until completion of the reaction (TLC). The reaction was quenched with water and extracted with CH₂Cl₂ (3 × 20 mL). The combined extracts were washed with brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The crude product was purified by flash column chromatography (petrol/ethyl acetate, 3:1 to 2:1) to afford sulfondiimine 14a as a white solid (53 mg, 98%).

mp 82-84 °C (CH₂Cl₂)

Rᵣ 0.56 (petrol/ethyl acetate, 2:1).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.15-8.08 (m, 2H), 7.48 (dd, J = 8.6, 1.2 Hz, 1H), 7.27 (dd, J = 8.5, 7.3 Hz, 1H), 7.24-7.18 (m, 2H), 6.99 (tt, J = 7.3, 1.2 Hz, 1H), 6.90 (br. s, 1H), 3.43 (s, 3H), 1.56 (d, J = 14.3 Hz, 1H), 1.51 (d, J = 14.3 Hz, 1H), 1.37 (s, 3H), 1.17 (s, 3H), 1.04 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 165.1 (d, JᵥCF = 254.2 Hz), 159.2, 140.1 (d, JᵥCF = 3.1 Hz), 139.9, 130.2 (d, JᵥCF = 9.4 Hz), 129.0, 122.5, 118.7, 116.4 (d, JᵥCF = 22.8 Hz), 59.4, 58.2, 48.8, 32.1, 32.0, 31.92, 31.89.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) = -106.9. (ddd, J = 13.3, 8.5, 5.1 Hz).

IR (ATR): ν (cm⁻¹) = 1650, 1506, 1389, 1217, 1153, 1088, 962, 836.

HRMS (ESI⁺) calcd. for C₂₂H₃₁FN₃OS⁺ [M+H]⁺: 404.2166; found: 404.1273.

1-((4-Fluorophenyl)(imino)(methyl)-λ₆-sulfaneylidene)-3-phenylurea (14)
Sulfoniimine 14a (50 mg, 0.12 mmol, 1.0 equiv.) was mixed with TFA (1.2 mL) and stirred at room temperature for 3 days. The mixture was concentrated in vacuo then diluted with CH$_2$Cl$_2$ and basified to pH 10-11 using 1 M aq. NaOH solution. The product was extracted with CH$_2$Cl$_2$ (3 x 20 mL). The combined extracts were washed with brine, dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo. The crude product was purified by flash column chromatography (ethyl acetate) to afford sulfoniimine 14 as a light yellow solid (31 mg, 86%).

mp 55-57 °C (CH$_2$Cl$_2$)

R$_f$ 0.41 (ethyl acetate).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 8.07-8.01 (m, 2H), 7.37 (dd, $J$ = 8.6, 1.2 Hz, 2H), 7.26-7.18 (m, 4H), 7.01 (br. s, 1H), 7.00-6.96 (m, 1H), 3.24 (s, 3H), 2.87 (br. s, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) = 165.7 (d, $^1$J$_{CF}$ = 255.5 Hz), 160.3, 139.3, 138.3(d, $^4$J$_{CF}$ = 3.2 Hz), 130.0 (d, $^3$J$_{CF}$ = 9.5 Hz), 129.0, 122.8, 118.8, 117.0 (d, $^2$J$_{CF}$ = 22.7 Hz), 45.7.

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ (ppm) = -105.2 (ddd, $J$ = 13.2, 8.3, 4.9 Hz).

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) =1591, 1535, 1491, 1438, 1389, 1317, 1236, 1154, 1075, 960, 832.

HRMS (ESI$^+$) calcd. for C$_{14}$H$_{15}$FN$_3$OS$^+$ [M+H]$^+$: 292.0914; found: 292.0915.

1-(4-Fluorophenyl)-1-methyl-N-(4-nitrobenzyl)-N-(2,4,4-trimethylpentan-2-yl)-$\lambda^6$-sulfanediimine (15a)

![Structure](image)

Under an atmosphere of argon, sulfoniimine 7 (91 mg, 0.32 mmol, 1.0 equiv.) was dissolved in anhydrous DCE (1.5 mL). 4 Å Molecular sieves (0.1 g) were added followed by 4-nitrobenzaldehyde (71 mg, 0.47 mmol, 1.3 equiv.) and NaBH(OAc)$_3$ (199 mg, 0.940 mmol, 3.0 equiv.). The reaction mixture was stirred at 50 °C for 18 h. 1 M aq. NaOH solution (30 mL) was added, the product was extracted with CH$_2$Cl$_2$ (3 x 30 mL). The combined extracts were washed with brine, dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo. The crude product was
purified by flash column chromatography (petrol/ethyl acetate, 4:1 to 1.5:1) to afford **sulfondiimine 15a** as a colourless oil (109 mg, 81%).

Rf 0.38 (petrol/ethyl acetate, 1.5:1).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 8.15 (d, $J = 8.8$ Hz, 2H), 8.08-8.01 (m, 2H), 7.55 (d, $J = 8.8$ Hz, 2H), 7.19-7.10 (m, 2H), 4.33 (d, $J = 16.2$ Hz, 1H), 4.08 (d, $J = 16.2$ Hz, 1H), 3.15 (s, 3H), 1.57 (s, 2H), 1.46 (s, 3H), 1.36 (s, 3H), 1.05 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) = 165.2 (d, $^1J_{CF} = 254.5$ Hz), 149.1, 146.9, 137.1 (d, $^4J_{CF} = 2.6$ Hz), 131.0 (d, $^3J_{CF} = 9.2$ Hz), 128.3, 123.6, 116.5 (d, $^2J_{CF} = 22.4$ Hz), 58.9, 58.5, 48.2, 46.2, 32.6, 32.3, 32.04, 32.01.

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ (ppm) = -108.2 (ddd, $J = 13.4$, 8.4, 5.1 Hz).

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 1518, 1487, 1343, 1216, 1146, 1106, 839, 738.

HRMS (ESI$^+$) calcd. for C$_{22}$H$_{31}$FN$_3$O$_2$S$^+$ [M+H]$^+$: 420.2116; found: 420.2114.

1-(4-Fluorophenyl)-1-methyl-N-(4-nitrobenzyl)-1,6-sulfanediimine (15)

![Chemical Structure](image)

Sulfondiimine **15a** (45 mg, 0.11 mmol, 1.0 equiv.) was mixed with TFA (1.1 mL) and stir at room temperature for 6 h. The mixture was concentrated *in vacuo* then diluted with ethyl acetate and basified to pH 10-11 using 1 M aq. NaOH solution. The product was extracted with ethyl acetate (3 × 20 mL). The combined extracts were washed with brine, dried over anhydrous Na$_2$SO$_4$, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (CH$_2$Cl$_2$/MeOH, 20:1) to afford **sulfondiimine 15** as a light yellow solid (29 mg, 88%).

**mp** 131-133 °C (CH$_2$Cl$_2$)

Rf 0.36 (CH$_2$Cl$_2$/MeOH, 9:1).
**H NMR** (400 MHz, CDCl₃): $\delta$ (ppm) = 8.15 (d, $J = 8.7$ Hz, 2H), 8.13-8.08 (m, 2H), 7.55 (d, $J = 8.7$ Hz, 2H), 7.25-7.17 (m, 2H), 4.33 (d, $J = 15.7$ Hz, 1H), 4.18 (d, $J = 15.7$ Hz, 1H), 3.15 (s, 3H), 1.87 (br. s, 1H).

**C NMR** (100 MHz, CDCl₃): $\delta$ (ppm) = 165.4 (d, $J_{CF} = 254.8$ Hz), 150.0, 146.8, 137.2 (d, $J_{CF} = 3.0$ Hz), 130.6 (d, $J_{CF} = 9.4$ Hz), 128.3, 123.7, 116.6 (d, $J_{CF} = 22.4$ Hz), 48.6, 46.3.

**F NMR** (376 MHz, CDCl₃): $\delta$ (ppm) = -106.0 (ddd, $J = 13.3, 8.2, 5.1$ Hz).

**IR** (ATR): $\tilde{\nu}$ (cm⁻¹) = 1516, 1344, 1153, 839.

**HRMS** (ESI⁺) calcd. for $\text{C}_{14}\text{H}_{15}\text{FN}_{3}\text{O}_{2}\text{S}$ [M+H]⁺: 308.0864; found: 308.0858.
2. NMR Spectra
(3g, 100 MHz, (CD$_3$)$_2$CO)

(3g, 376 MHz, CDCl$_3$)
(3j, 400 MHz, CDCl₃)

(3j, 100 MHz, CDCl₃)
(3k, 400 MHz, CDCl₃)

(3k, 100 MHz, CDCl₃)
(31, 400 MHz, CDCl₃)

(31, 100 MHz, CDCl₃)
(3m, 400 MHz, CDCl₃)

(3m, 100 MHz, CDCl₃)
(3n, 400 MHz, CDCl₃)

(3n, 100 MHz, CDCl₃)
(3n, 376 MHz, CDCl₃)

(3r, 400 MHz, CDCl₃)
(3s, 100 MHz, CDCl₃)

(3t, 400 MHz, CDCl₃)
(3t, 100 MHz, CDCl₃)

(3u, 400 MHz, CDCl₃)
(3u, 100 MHz, CDCl₃)

(4a, 400 MHz, CDCl₃)
(4a, 100 MHz, (CD$_3$)$_2$CO)

(4a, 376 MHz, CDCl$_3$)
(4b, 400 MHz, CDCl₃)

(4b, 100 MHz, (CD₃)₂CO)
(4b, 376 MHz, CDCl₃)

(4c, 400 MHz, CDCl₃)
(4g, 100 MHz, (CD$_3$)$_2$CO)

(4g, 376 MHz, CDCl$_3$)
(4j, 100 MHz, CDCl$_3$)

(4k, 400 MHz, CDCl$_3$)
(4I, 100 MHz, (CD$_3$)$_2$CO)

(4m, 400 MHz, CDCl$_3$)
(4p, 400 MHz, CDCl₃)

(4p, 100 MHz, CDCl₃)
(5a, 400 MHz, CDCl₃)

(5a, 100 MHz, CDCl₃)
(5a, 376 MHz, CDCl₃)

(5b, 400 MHz, CDCl₃)
\[ \text{S90} \]
(5d, 376 MHz, CDCl₃)

(5e, 400 MHz, CDCl₃)
(5h, 400 MHz, CDCl₃)

(5h, 100 MHz, (CD₃)₂CO)
(5j, 400 MHz, CDCl₃)

(5j, 100 MHz, CDCl₃)
(5k, 400 MHz, CDCl₃)

(5k, 100 MHz, CDCl₃)
(5I, 400 MHz, CDCl$_3$)

(5I, 100 MHz, CDCl$_3$)
(5m, 400 MHz, CDCl₃)

(5m, 100 MHz, CDCl₃)
(6, 100 MHz, (CD$_3$)$_2$CO)

(6, 376 MHz, CDCl$_3$)
(7, 376 MHz, CDCl$_3$)

(8, 400 MHz, CDCl$_3$)
(8, 100 MHz, CDCl₃)

(8, 376 MHz, CDCl₃)
(9, 376 MHz, CD$_2$OD)

(10, 400 MHz, CDCl$_3$)
(10, 100 MHz, CDCl₃)

(10, 376 MHz, CDCl₃)
(11a, 376 MHz, CDCl₃)

(11, 400 MHz, CDCl₃)
(11, 100 MHz, CDCl₃)

(11, 376 MHz, CDCl₃)
(12a, 400 MHz, CDCl₃)

(12a, 100 MHz, CDCl₃)
(12, 100 MHz, CDCl₃)

(12, 376 MHz, CDCl₃)
(13, 100 MHz, CDCl₃)

(13, 376 MHz, CDCl₃)
(14a, 376 MHz, CDCl₃)

(14, 400 MHz, CDCl₃)
(14, 100 MHz, CDCl$_3$)

(14, 376 MHz, CDCl$_3$)
3. References

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