Electronic Supplementary Information

Copper-Catalyzed Regioselective 1,2-Thioamidation of Alkenes

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Table of Contents

I. General Information .................................................................................................................. 2
II. Preparation of Starting Materials .............................................................................................. 2
   2.1 Preparation of alkene substrates ....................................................................................... 2
   2.2. Preparation of thiol substrates ....................................................................................... 3
III. Optimization of the Reaction Conditions and the General Procedure .............................. 4
   3.1 Optimization of the reaction conditions ............................................................................ 4
   3.2 General procedure ........................................................................................................... 6
IV X-ray Crystallography of 3j ..................................................................................................... 7
V. Mechanistic Studies .................................................................................................................. 8
VI. Characterization Data ............................................................................................................. 11
VII. Referances ............................................................................................................................. 22
VIII. Copies of ^1H and ^13C NMR Spectra ............................................................................... 23
I. General Information

All the solvents and commercially available reagents were purchased from commercial suppliers. $^1$H NMR, $^{13}$C NMR spectra were recorded on a 400 MHz or/and 500 MHz Bruker FT-NMR spectrometers. All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, $J$, are reported in Hertz (Hz). High Resolution Mass (MS) analysis was obtained using on a LC/MSD TOF spectrometer system with Electrospray Ionization (ESI). Melting points were measured on a Mel-Temp apparatus and are uncorrected. Reactions were monitored by thin-layer chromatography (TLC) carried out on commercial silica gel plates (GF254) under UV light. Flash chromatography was performed on silica gel 60 (200–300 mesh).

II. Preparation of Starting Materials

2.1 Preparation of alkene substrates

Alkenes 1a–1e, and 1m were purchased from commercial sources and used as received, 1f–1l,$^1$ 1n, 1q,$^2$ 1o, 1p and 1r,$^3$ 1s-1t$^4$ were prepared according to literature procedures.
2.2. Preparation of thiol substrates

Thiols 2a–2g and disulfide 2h in the reaction were obtained from commercial sources and used without further purification.
III. Optimization of the Reaction Conditions and the General Procedure

3.1 Optimization of the reaction conditions

In Ar atmosphere, allylbenzene (1a, 1.0 equiv, 0.2 mmol) was added to a solution of 4-methylbenzenethiol (2a, 1.5 equiv, 0.3 mmol), NFSI (1.5 equiv, 0.3 mmol), catalyst (20 mol%) and additive (20 mol%) in CH$_3$CN (1.5 mL) in an oven-dried 10 mL Schlenk tube. The mixture was heated at 45 °C for 12–20 h (monitored by TLC). After the reaction was completed, the resulting solution was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1, Rf = 0.2) to give the desired product N-(3-phenyl-2-(p-tolylthio)propyl)-N-(phenylsulfonyl)benzenesulfonamide (3a) as a colourless oil.

**Table S1. Optimization of the reaction conditions***

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<th>Entry</th>
<th>Catalyst (mol%)</th>
<th>Additive (mol%)</th>
<th>Solvent</th>
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<th>Yield (%)$^b$</th>
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<td>45 / 15</td>
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° Reaction conditions: In Ar atmosphere, 1a (1.0 equiv, 0.2 mmol), 2a (1.5 equiv, 0.3 mmol), NFSI (1.5 equiv, 0.3 mmol), catalyst (0–30 mol%), additive (0–50 mol%) in solvent (1.5 mL). b Isolated yield. c 2a (1.2 equiv, 0.24 mmol) and NFSI (1.2 equiv, 0.24 mmol) were used. d 2a (1.2 equiv, 0.24 mmol) was used. e NFSI (1.2 equiv, 0.24 mmol) was used. f 2a (2.0 equiv, 0.4 mmol) was used. Unless otherwise noted, B₂Pin₂ = Bis(pinacolato)diboron; phen = 1,10-phenanthroline; Bipy = 2,2'-Bipyridine.

3.2 General procedure

In a dry 10 mL Schlenk tube, alkenes 1 (1.0 equiv, 0.2 mmol) and thiols 2 (1.5 equiv, 0.3 mmol), NFSI (1.5 equiv, 0.3 mmol), CuCl (20 mol%), B₂Pin₂ (20 mol%) were mixed in CH₃CN (1.5 mL) in Ar. Then the mixture was heated at 45 °C for 15 h (monitored by TLC). After the reaction was completed, it was cooled to room temperature and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to give the desired products 3 or 4.
IV X-ray Crystallography of 3j

Crystallographic data for compound 3j (CCDC- 1525419) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).

Bond precision: C-C = 0.0039 Å  Wavelength=1.54184

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Correction method= # Reported T Limits: Tmin=0.816 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.000  Theta(max) = 62.380

R(reflections) = 0.0409( 4069)  wR2(reflections) = 0.1087( 4598)

S = 1.038  Npar= 380
V. Mechanistic Studies

5.1 General procedure for the control experiments of 3a

In a dry 10 mL Schlenk tube, allylbenzene (1a, 1.0 equiv, 0.1 mmol) was added to a solution of 4-methylbenzenethiol (2a, 1.5 equiv, 0.15 mmol), NFSI (1.5 equiv, 0.15 mmol), CuCl (20 mol%), B₂Pin₂ (20 mol%) and a radical scavenger, such as, butylated hydroxytoluene (BHT, 1.5 equiv, 0.15 mmol), or 2,2,6,6-tetramethyl-1-piperidinol (TEMPO, 1.5 equiv, 0.15 mmol), or 1,1-diphenylethylene (1.0 equiv, 0.1 mmol) in CH₃CN (1.5 mL) in Ar. Then the mixture was heated at 45 °C for 15 h. After completion of the reaction, it was cooled to room temperature. The residue was detected on High Resolution Mass (MS) analysis using a LC/MSD TOF spectrometer system with Electrospray Ionization (ESI).

![Chemical Reaction Diagram]

(a) Reactants: Ph−C=C−CH₃ (1a), Ph−S−CH₃ (2a), NFSI, CuCl, B₂Pin₂, and a radical scavenger. Products: 3a, N.R. Conditions: CH₃CN, Ar, 45 °C, 15 h, BHT (1.5 eq.).

(b) Reactants: Ph−C=C−CH₃ (1a), Ph−S−CH₃ (2a), NFSI, CuCl, B₂Pin₂, and a radical scavenger. Products: 3a, trace. Conditions: CH₃CN, Ar, 45 °C, 15 h, TEMPO (1.5 eq.).

HRMS detected

Exact Mass: [M+H]+ = 571.2295,
HRMS (ESI) found: 571.2297.
(c) 1a (0.1 mmol) + Ph_2N-SH + SO_3Ph \rightarrow CuCl (20 mol%) BPh_3 (20 mol%) CH_3CN, Ar 45 °C, 15 h \rightarrow 3a, < 5%
HRMS detected
Exact Mass: [M+H]^+ 476.0985, HRMS (ESI) found: 476.0981.

(d) Ph \equiv \rightarrow Ph_2N-SH + SO_3Ph \rightarrow CuCl (20 mol%) BPh_3 (20 mol%) CH_3CN, Ar 45 °C, 15 h \rightarrow PhO_2S \equiv \rightarrow Ph_2N\text{SO}_2Ph
34% yield
and 95% of 2a was recovered
5.2 General procedure for the control experiments of 4a

In a dry 10 mL Schlenk tube, alkene substrate (1n, 1.0 equiv, 0.1 mmol) was added to a solution of 4-methylbenzenethiol (2a, 1.5 equiv, 0.15 mmol), NFSI (1.5 equiv, 0.15 mmol), CuCl (20 mol%), B₂Pin₂ (20 mol%) and a radical scavenger, such as, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 1.5 equiv, 0.15 mmol), or 1,1-diphenylethylene (1.0 equiv, 0.1 mmol) in CH₃CN (1.5 mL) in Ar. Then the mixture was heated at 45 °C for 15 h. After completion of the reaction, it was cooled to room temperature. The residue was detected on High Resolution Mass (MS) analysis using a LC/MSD TOF spectrometer system with Electrospray Ionization (ESI) or monitored by TLC.

(a) \[
\begin{align*}
\text{NH} & \quad \text{SH} \\
\text{Ts} & \quad 1n \\
\text{CuCl} (20 \text{ mol\%}) & \quad \text{NFSI} \\
\text{B₂Pin₂} (20 \text{ mol\%}) & \quad \text{CH₃CN, Ar} \\
45 \degree C, 15 h & \quad \text{TEMPO (1.5 eq.)} \\
\end{align*}
\]

4a, < 5%

(b) \[
\begin{align*}
\text{NH} & \quad \text{SH} \\
\text{Ts} & \quad 1n \\
\text{CuCl} (20 \text{ mol\%}) & \quad \text{B₂Pin₂ (20 mol\%)} \\
\text{CH₃CN, Ar} & \quad 45 \degree C, 15 h \\
\end{align*}
\]

NR

(c) \[
\begin{align*}
\text{NH} & \quad \text{SH} \\
\text{Ts} & \quad 1n (0.1 \text{ mmol}) \\
\text{CuCl} (20 \text{ mol\%}) & \quad \text{B₂Pin₂ (20 mol\%)} \\
\text{CH₃CN, Ar} & \quad 45 \degree C, 15 h \\
\end{align*}
\]

\[
\begin{align*}
2a (0.15 \text{ mmol}) & \quad \text{SO₃Ph} \\
(0.15 \text{ mmol}) & \quad \text{PhO₂S} \\
\text{Ph} & \quad \text{Ph} \\
\text{Ph} & \quad \text{Ph} \\
\end{align*}
\]

4a, trace

21% yield
VI. Characterization Data

\[ \text{N-}(3\text{-phenyl-2-(p-tolylthio)propyl})\text{-N-}(\text{phenylsulfonyl})\text{benzenesulfonamide (3a)} \]

Colourless oil (66.0 mg, 61% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.86-7.84 (m, 4H), 7.63-7.59 (m, 2H), 7.47-7.43 (m, 4H), 7.30-7.23 (m, 5H), 7.11-7.10 (m, 2H), 7.05-7.03 (m, 2H), 3.94-3.89 (m, 1H), 3.86-3.80 (m, 1H), 3.77-3.70 (m, 1H), 3.02 (dd, \( J = 14.0 \text{ Hz}, 5.6 \text{ Hz}, 1H \)), 2.67 (dd, \( J = 15.0 \text{ Hz}, 9.2 \text{ Hz}, 1H \)), 2.34 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 139.06, 138.48, 137.61, 133.87, 132.95, 129.93, 129.76, 129.13, 128.97, 128.57, 128.32, 126.49, 52.13, 49.76, 38.25, 21.09; HRMS (ESI) calcd for C\(_{28}\)H\(_{28}\)NO\(_5\)S\(_3\)^+ [M+H]^+ 538.1175, found 538.1178.

\[ \text{N-}(3\text{-}(4\text{-methoxyphenyl})-2\text{-}(p\text{-tolylthio)propyl})\text{-N-}(\text{phenylsulfonyl})\text{benzenesulfonamide (3b)} \]

Colourless oil (67.0 mg, 59% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.87-7.85 (m, 4H), 7.64-7.60 (m, 2H), 7.48-7.44 (m, 4H), 7.25-7.23 (m, 2H), 7.11-7.09 (m, 2H), 6.97-6.95 (m, 2H), 6.83-6.81 (m, 2H), 3.92-3.86 (m, 1H), 3.85-3.78 (m, 1H), 3.80 (s, 3H), 3.73-3.66 (m, 1H), 2.95 (dd, \( J = 14.4 \text{ Hz}, 5.6 \text{ Hz}, 1H \)), 2.62 (dd, \( J = 14.4 \text{ Hz}, 9.6 \text{ Hz}, 1H \)), 2.34 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 158.29, 139.10, 137.55, 133.87, 132.90, 130.50, 130.11, 130.02, 129.75, 128.97, 128.59, 113.74, 55.24, 52.13, 49.95, 37.38, 21.10; HRMS (ESI) calcd for C\(_{29}\)H\(_{30}\)NO\(_5\)S\(_3\)^+ [M+H]^+ 568.1281, found 568.1290.
**N-(phenylsulfonyl)-N-(2-(p-tolylthio)octyl)benzenesulfonamide (3c)**

Colourless oil (70.0 mg, 66% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.89-7.88 (m, 4H), 7.64-7.62 (m, 2H), 7.51-7.48 (m, 4H), 7.34-7.33 (m, 2H), 7.16-7.14 (m, 2H), 3.87 (dd, $J_1 = 15.0$ Hz, 11.0 Hz, 1H), 3.77 (dd, $J_2 = 15.0$ Hz, 4.5 Hz, 1H), 3.45-3.40 (m, 1H), 2.37 (s, 3H), 1.65-1.63 (m, 2H), 1.29-1.16 (m, 8H), 0.89 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 139.40, 137.42, 133.83, 132.68, 130.06, 129.77, 128.96, 128.37, 53.12, 47.75, 31.65, 30.77, 28.95, 26.90, 22.55, 21.10, 14.04; HRMS (ESI) calcd for C$_{27}$H$_{34}$NO$_4$S$_3$ $^{+}$ [M+H]$^+$ 532.1644, found 532.1648.

**N-(phenylsulfonyl)-N-(2-(p-tolylthio)nonyl)benzenesulfonamide (3d)**

Colourless oil (69.0 mg, 63% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.90-7.88 (m, 4H), 7.64-7.61 (m, 2H), 7.50-7.47 (m, 4H), 7.35-7.33 (m, 2H), 7.16-7.15 (m, 2H), 3.88 (dd, $J_1 = 15.0$ Hz, 10.5 Hz, 1H), 3.78 (dd, $J_2 = 15.0$ Hz, 5.0 Hz, 1H), 3.46-3.39 (m, 1H), 2.37 (s, 3H), 1.68-1.61 (m, 2H), 1.32-1.16 (m, 10H), 0.91 (t, $J = 7.5$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 139.36, 137.42, 133.83, 132.68, 130.06, 129.77, 128.93, 128.33, 53.08, 47.73, 31.73, 30.75, 29.22, 29.10, 26.92, 22.58, 21.07, 14.06; HRMS (ESI) calcd for C$_{28}$H$_{36}$NO$_4$S$_3$ $^{+}$ [M+H]$^+$ 546.1801, found 546.1809.

**Phenylsulfonyl-N-2-(p-tolylthio)cyclohexyl)benzenesulfonamide (3e)**

White solid (25.0 mg, 25% yield) mp 171-173 °C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.30 (br, s, 2H), 7.97 (br, s, 2H), 7.63 (br, s, 2H), 7.52 (br, s, 4H), 7.32-7.30 (m, 2H),
7.11-7.09 (m, 2H), 4.05-4.00 (m, 1H), 3.89-3.84 (m, 1H), 2.32 (s, 3H), 2.30-2.20 (m, 1H), 2.06-2.03 (m, 1H), 1.72-1.71 (m, 2H), 1.60-1.56 (m, 1H), 1.30-1.26 (m, 1H), 1.19-1.15 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): 137.03, 134.08, 133.47, 132.59, 130.65, 129.67, 128.90, 128.52, 67.29, 49.97, 35.84, 32.82, 26.55, 25.53, 21.04; HRMS (ESI) calcd for C$_{25}$H$_{28}$NO$_4$S$_3$ [M+H]$^+$ 502.1175, found 502.1164.

N-((5-phenoxy-2-(p-tolylthio)pentyl)-N-(phenylsulfonyl)benzenesulfonamide (3f)

Colourless oil (61.0 mg, 52% yield). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.90-7.88 (m, 4H), 7.60-7.57 (m, 2H), 7.46-7.43 (m, 4H), 7.38-7.36 (m, 2H), 7.32-7.29 (m, 2H), 7.18-7.16 (m, 2H), 6.98-6.95 (m, 1H), 6.89-6.87 (m, 2H), 3.94-3.89 (m, 1H), 3.88-3.85 (m, 2H), 3.84-3.80 (m, 1H), 3.55-3.49 (m, 1H), 2.38 (s, 3H), 2.21-2.13 (m, 1H), 1.92-1.85 (m, 1H), 1.78-1.70 (m, 1H), 1.50-1.42 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 158.92, 139.18, 137.70, 133.88, 133.03, 129.82 129.53, 129.38, 128.97, 128.36, 120.58, 114.54, 67.37, 52.90, 47.79, 27.58, 26.76, 21.11; HRMS (ESI) calcd for C$_{30}$H$_{32}$NO$_5$S$_3$ [M+H]$^+$ 582.1437, found 582.1404.

N-(phenylsulfonyl)-N-((5-(p-tolyloxy)-2-(p-tolylthio)pentyl)benzenesulfonamide (3g)

Colourless oil (64.0 mg, 54% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.89-7.87 (m, 4H), 7.61-7.57 (m, 2H), 7.47-7.43 (m, 4H), 7.36-7.34 (m, 2H), 7.17-7.15 (m, 2H), 7.10-7.08 (m, 2H), 6.78-6.76 (m, 2H), 3.92-3.86 (m, 1H), 3.84-3.77 (m, 3H), 3.54-3.46 (m, 1H), 2.37 (s, 3H), 2.30 (s, 3H), 2.20-2.09 (m, 1H), 1.90-1.81 (m, 1H), 1.76-1.66 (m, 1H), 1.49-1.39 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 156.84, 139.23, 137.69, 133.89, 133.04, 129.83, 129.77, 129.59, 128.99, 128.40, 114.45, 67.58, 52.92, 47.82, 27.60, 26.82, 21.12, 20.45; HRMS (ESI) calcd for C$_{31}$H$_{34}$NO$_5$S$_3$ [M+H]$^+$
596.1594, found 596.1563.

**N-(5-(4-chlorophenoxy)-2-(p-tolylthio)pentyl)-N-(phenylsulfonyl)benzenesulfonamide (3h)**

Colourless oil (71.0 mg, 58% yield). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.87-7.85 (m, 4H), 7.61-7.58 (m, 2H), 7.46-7.43 (m, 4H), 7.36-7.35 (m, 2H), 7.26-7.23 (m, 2H), 7.17-7.16 (m, 2H), 6.80-6.78 (m, 2H), 3.90 (dd, $J = 15.0$ Hz, 10.5 Hz, 1H), 3.85-3.78 (m, 3H), 3.54-3.48 (m, 1H), 2.38 (s, 3H), 2.19-2.11 (m, 1H), 1.91-1.84 (m, 1H), 1.76-1.68 (m, 1H), 1.49-1.41 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 157.52, 139.15, 137.75, 133.89, 133.00, 129.84, 129.49, 129.23, 128.97, 128.36, 125.42, 115.83, 67.80, 52.87, 47.75, 27.45, 26.61, 21.10; HRMS (ESI) calcd for C$_{30}$H$_{30}$ClN$_6$O$_5$S$_3$ $^{[M+Na]^+}$ 638.0867, found 638.0868.

**N-(5-(4-methoxyphenoxy)-2-(p-tolylthio)pentyl)-N-(phenylsulfonyl)benzenesulfonamide (3i)**

Colourless oil (76.0 mg, 62% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.88-7.86 (m, 4H), 7.61-7.57 (m, 2H), 7.46-7.42 (m, 4H), 7.36-7.34 (m, 2H), 7.17-7.15 (m, 2H), 6.86-6.83 (m, 2H), 6.82-6.79 (m, 2H), 3.89 (dd, $J = 15.0$ Hz, 10.5 Hz, 1H), 3.83-3.76 (m, 3H), 3.78 (s, 3H), 3.55-3.50 (m, 1H), 2.37 (s, 3H), 2.18-2.08 (m, 1H), 1.91-1.82 (m, 1H), 1.75-1.65 (m, 1H), 1.49-1.39 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 153.79, 153.15, 139.22, 137.70, 133.89, 133.03, 129.84, 129.49, 128.99, 128.41, 115.55, 114.64, 68.20, 55.75, 52.91, 47.82, 27.60, 26.86, 21.12; HRMS (ESI) calcd for C$_{31}$H$_{33}$NNaO$_6$S$_3$ $^{[M+Na]^+}$ 634.1362, found 634.1354.
\(N\)-(5-(4-nitrophenoxy)-2-(p-tolylthio)pentyl)-N-(phenylsulfonyl)benzenesulfonamide (3j)

White solid (73.0 mg, 58% yield) mp 119-121 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.21-8.20 (m, 2H), 7.81-7.80 (m, 4H), 7.62-7.59 (m, 2H), 7.46-7.43 (m, 4H), 7.36-7.35 (m, 2H), 7.18-7.16 (m, 2H), 6.92-6.90 (m, 2H), 3.99-3.96 (m, 2H), 3.90 (dd, \(J = 15.0\) Hz, 11.0 Hz, 1H), 3.77 (dd, \(J = 15.0\) Hz, 4.5 Hz, 1H), 3.55-3.49 (m, 1H), 2.38 (s, 3H), 2.23-2.17 (m, 1H), 1.96-1.89 (m, 1H), 1.82-1.73 (m, 1H), 1.52-1.42 (m, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 163.94, 141.38, 138.97, 137.89, 133.95, 132.98, 129.91, 129.33, 128.99, 128.35, 125.88, 114.43, 68.31, 52.77, 47.62, 27.18, 26.37, 21.14; HRMS (ESI) calcd for \(\text{C}_{30}\text{H}_{30}\text{N}_{2}\text{O}_{7}\text{S}_{3}\text{Na}^+\) \([\text{M+Na}]^+\) 649.1107, found 649.1082.

\(N\)-(phenylsulfonyl)-N-(3-(p-tolylthio)propyl)benzenesulfonamide (3k)

Colourless oil (51.0 mg, 45% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.93-7.91 (m, 4H), 7.62-7.58 (m, 2H), 7.46-7.42 (m, 4H), 7.38-7.36 (m, 2H), 7.17-7.15 (m, 2H), 7.09-7.07 (m, 2H), 6.75-6.73 (m, 2H), 4.26-4.20 (m, 1H), 4.09-4.05 (m, 1H), 4.02-3.92 (m, 2H), 3.89-3.83 (m, 1H), 2.38 (s, 3H), 2.31 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 156.17, 138.90, 137.99, 133.87, 133.32, 130.32, 129.85, 129.81, 129.36, 128.94, 128.50, 114.53, 67.44, 49.32, 47.73, 21.10, 20.45; HRMS (ESI) calcd for \(\text{C}_{29}\text{H}_{29}\text{N}_{2}\text{O}_{7}\text{S}_{3}\text{Na}^+\) \([\text{M+Na}]^+\) 590.1100, found 590.1093.

\(5\)-(N-(phenylsulfonyl)phenylsulfonamido)-4-(p-tolylthio)pentylbenzoate (3l)
Colourless oil (76.0 mg, 62% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.03-8.01 (m, 2H), 7.88-7.86 (m, 4H), 7.60-7.55 (m, 3H), 7.46-7.42 (m, 6H), 7.35-7.33 (m, 2H), 7.15-7.13 (m, 2H), 4.24-4.15 (m, 2H), 3.93-3.80 (m, 2H), 3.49-3.41 (m, 1H), 2.36 (s, 3H), 2.22-2.10 (m, 1H), 1.90-1.82 (m, 1H), 1.70-1.62 (m, 1H), 1.46-1.38 (m, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 166.50, 139.29, 137.82, 133.93, 133.05, 132.84, 130.33, 129.88, 129.63, 129.35, 129.01, 128.35, 128.31, 64.43, 52.97, 47.53, 27.41, 26.27, 21.11; HRMS (ESI) calcd for C\(_{31}\)H\(_{31}\)NNaO\(_2\)S\(_3\)\(\cdot\) [M+Na]\(^+\) 632.1206, found 632.1218.

![Chemical Structure]

\(N\)-(3-phenyl-2-(phenylthio)propyl)-\(N\)-(phenylsulfonyl)benzenesulfonamide (3m)

Colourless oil (64.0 mg, 61% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.91-7.89 (m, 4H), 7.66-7.63 (m, 2H), 7.51-7.47 (m, 4H), 7.39-7.36 (m, 2H), 7.34-7.28 (m, 6H), 7.09-7.07 (m, 2H), 4.00-3.88 (m, 2H), 3.87-3.81 (m, 1H), 3.10-3.05 (m, 1H), 2.76-2.70 (m, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 139.04, 138.35, 133.90, 132.19, 129.12, 129.00, 128.55, 128.35, 127.33, 126.55, 52.13, 49.49, 38.28; HRMS (ESI) calcd for C\(_{27}\)H\(_{25}\)NNaO\(_2\)S\(_3\)\(\cdot\) [M+Na]\(^+\) 546.0838, found 546.0858.

![Chemical Structure]

\(N\)-(3-phenyl-2-(o-tolylthio)propyl)-\(N\)-(phenylsulfonyl)benzenesulfonamide (3n)

Colourless oil (42.0 mg, 39% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.84-7.81 (m, 4H), 7.63-7.59 (m, 2H), 7.47-7.43 (m, 4H), 7.39-7.37 (m, 1H), 7.32-7.21 (m, 3H), 7.19-7.13 (m, 3H), 7.09-7.04 (m, 2H), 3.95-3.82 (m, 2H), 3.80-3.71 (m, 1H), 3.10 (dd, \(J = 14.5\) Hz, 5.0 Hz, 1H), 2.67 (dd, \(J = 14.4\) Hz, 10.0 Hz, 1H), 2.22 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 140.37, 138.96, 138.42, 133.88, 133.14, 132.72, 130.48, 129.15, 128.99, 128.54, 128.28, 127.51, 126.51, 126.45, 52.08, 49.05, 38.29, 20.58; HRMS (ESI) calcd for C\(_{28}\)H\(_{27}\)NNaO\(_2\)S\(_3\)\(\cdot\) [M+Na]\(^+\) 560.0994, found 560.0986.
N-(3-phenyl-2-(m-tolylthio)propyl)-N-(phenylsulfonyl)benzenesulfonamide (3o)

Colourless oil (45.0 mg, 42% yield). \(^1\)H NMR (400 MHz, CDCl₃): \(\delta\) 7.88-7.86 (m, 4H), 7.63-7.60 (m, 2H), 7.48-7.44 (m, 4H), 7.30-7.25 (m, 3H), 7.20-7.14 (m, 3H), 7.07-7.03 (m, 3H), 3.97-3.92 (m, 1H), 3.88-3.78 (m, 2H), 3.04 (dd, \(J = 14.4\) Hz, 5.0 Hz, 1H), 2.68 (dd, \(J = 14.4\) Hz, 9.2 Hz, 1H), 2.31 (s, 3H); \(^1^3\)C NMR (125 MHz, CDCl₃): 139.07, 138.78, 138.39, 133.89, 133.59, 132.51, 129.13, 128.99, 128.94, 128.81, 128.55, 128.32, 128.07, 126.52, 52.23, 49.17, 38.22, 21.24; HRMS (ESI) calcd for C₂₈H₂₇N₂O₄S₃⁺ [M+Na]⁺ 560.0994, found 560.0991.

N-(2-((4-methoxyphenyl)thio)-3-phenylpropyl)-N-(phenylsulfonyl)benzenesulfonamide (3p)

Colourless oil (67.0 mg, 60% yield). \(^1\)H NMR (400 MHz, CDCl₃): \(\delta\) 7.86-7.84 (m, 4H), 7.64-7.60 (m, 2H), 7.48-7.44 (m, 4H), 7.31-7.24 (m, 5H), 7.05-7.03 (m, 2H), 6.84-6.82 (m, 2H), 3.90 (dd, \(J = 15.0\) Hz, 6.4 Hz, 1H), 3.86-3.78 (m, 1H), 3.81 (s, 3H), 3.67-3.60 (m, 1H), 2.97 (dd, \(J = 14.4\) Hz, 5.6 Hz, 1H), 2.66 (dd, \(J = 14.4\) Hz, 9.6 Hz, 1H); \(^1^3\)C NMR (125 MHz, CDCl₃): 159.75, 139.07, 138.59, 135.66, 133.87, 129.16, 128.97, 128.60, 128.33, 126.48, 123.73, 114.58, 55.33, 52.11, 50.52, 38.29; HRMS (ESI) calcd for C₂₈H₂₇N₂O₄S₃⁺ [M+Na]⁺ 576.0944, found 576.0931.

N-(phenylsulfonyl)-N-(2-(phenylthio)-5-(p-tolyloxy)pentyl)benzenesulfonamide (3q)
Colourless oil (58.0 mg, 50% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.90-7.89 (m, 4H), 7.61-7.57 (m, 2H), 7.47-7.43 (m, 6H), 7.37-7.29 (m, 3H), 7.11-7.09 (m, 2H), 6.79-6.76 (m, 2H), 3.92 (dd, $J$ = 15.2 Hz, 10.4 Hz, 1H), 3.85-3.77 (m, 3H), 3.63-3.56 (m, 1H), 2.31 (s, 3H), 2.20-2.09 (m, 1H), 1.93-1.85 (m, 1H), 1.77-1.67 (m, 1H), 1.53-1.43 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 156.80, 139.16, 133.91, 133.61, 132.19, 129.82, 129.78, 129.07, 129.00, 128.37, 127.36, 114.42, 67.52, 52.87, 47.47, 27.67, 26.80, 20.44; HRMS (ESI) calcd for C$_{30}$H$_{31}$NaO$_5$S$_3^+$ [M+Na]$^+$ 604.1257, found 604.1261.

**N-(2-((4-methoxyphenylthio)octyl)-N-(phenylsulfonfonyl)benzenesulfonamide (3r)**

Colourless oil (44.0 mg, 40% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.87-7.85 (m, 4H), 7.65-7.61 (m, 2H), 7.51-7.47 (m, 4H), 7.39-7.36 (m, 2H), 6.89-6.87 (m, 2H), 3.88-3.83 (m, 1H), 3.83 (s, 3H), 3.77-3.72 (m, 1H), 3.33-3.27 (m, 1H), 1.62-1.60 (m, 2H), 1.27-1.17 (m, 8H), 0.88 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 159.68, 139.38, 135.50, 133.84, 128.97, 128.39, 123.69, 114.60, 55.36, 53.08, 48.50, 31.67, 30.73, 28.96, 26.88, 22.57, 14.06; HRMS (ESI) calcd for C$_{27}$H$_{33}$NaO$_5$S$_3^+$ [M+Na]$^+$ 570.1413, found 570.1414.

**N-(2-(benzylthio)-3-(4-methoxyphenyl)propyl)-N-(phenylsulfonfonyl)benzenesulfonamide (3t)**

Colourless oil (31.0 mg, 27% yield). Colourless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.91-7.89 (m, 4H), 7.65-7.61 (m, 2H), 7.50-7.46 (m, 4H), 7.27-7.26 (m, 3H), 7.19-7.17 (m, 2H), 6.75-6.73 (m, 2H), 6.68-6.66 (m, 2H), 4.05 (dd, $J$ = 15.2 Hz, 6.0 Hz, 1H), 3.81 (s, 3H), 3.80-3.72 (m, 1H), 3.67-3.64 (m, 1H), 3.50-3.47 (m, 1H), 2.31 (s, 3H), 1.84 (m, 2H), 1.62-1.58 (m, 1H), 0.85 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 159.96, 139.38, 135.50, 133.84, 128.97, 128.39, 123.69, 114.60, 55.36, 53.08, 48.50, 31.67, 30.73, 28.96, 26.88, 22.57, 14.06; HRMS (ESI) calcd for C$_{27}$H$_{33}$NaO$_5$S$_3^+$ [M+Na]$^+$ 570.1413, found 570.1414.
3.06-2.99 (m, 1H), 2.84 (dd, J = 14.4 Hz, 5.2 Hz, 1H), 2.51 (dd, J = 14.4 Hz, 10.0 Hz, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 158.15, 139.61, 137.88, 133.80, 130.58, 130.15, 129.02, 128.45, 128.41, 126.94, 113.50, 55.26, 52.80, 45.24, 37.66, 35.44; HRMS (ESI) calcd for C\(_{20}\)H\(_{29}\)NNaO\(_3\)S\(_2\)\(^+\) [M+Na]\(^+\) 590.1100, found 590.1107.

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\text{N} \quad \text{Ts} \quad \text{S} \quad \text{p-tolylthio)methyl}
\]

2-((p-tolylthio)methyl)-1-tosylpyrrolidine (4a)

Colourless oil (62.0 mg, 86% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.52 (d, J = 8.0 Hz, 2H), 7.36 (d, \(J = 8.0\) Hz, 2H), 7.22 (d, \(J = 8.0\) Hz, 2H), 7.16 (d, \(J = 8.0\) Hz, 2H), 3.65-3.57 (m, 2H), 3.49-3.45 (m, 1H), 3.11-3.06 (m, 1H), 2.74 (dd, \(J = 13.0\) Hz, 10.5 Hz, 1H), 2.39 (s, 3H), 2.36 (s, 3H), 1.89-1.82 (m, 1H), 1.81-1.74 (m, 1H), 1.65-1.58 (m, 1H), 1.53-1.47 (m, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 143.30, 135.99, 133.75, 131.44, 129.64, 129.60, 129.49, 127.34, 58.89, 49.59, 38.91, 30.10, 23.61, 21.35, 20.88; HRMS (ESI) calcd for C\(_{19}\)H\(_{23}\)NNaO\(_3\)S\(_2\)\(^+\) [M+Na]\(^+\) 384.1062, found 384.1067.

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\text{N} \quad \text{Ts} \quad \text{S} \quad \text{p-tolylthio)methyl}
\]

4-Phenyl-2-((p-tolylthio)methyl)-1-tosylpyrrolidine (4b)

Colourless oil (72.0 mg, 82% yield, \(d.r. = 1.7 : 1\)). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.60-7.58 (m, 1.3H), 7.52-7.50 (m, 2.1H), 7.40-7.38 (m, 2.1H), 7.37-7.35 (m, 1.3H), 7.27-7.19 (m, 9.7H), 7.16-7.14 (m, 2.3H), 7.07-7.05 (m, 1.3H), 7.02-7.01 (m, 2.1H), 3.91-3.87 (m, 1.1H), 3.85-3.80 (m, 1.4H), 3.78-3.67 (m, 2.8H), 3.51-3.44 (m, 1.0H), 3.43-3.37 (m, 0.7H), 2.96-2.88 (m, 2.1H), 2.86-2.82 (m, 0.8H), 2.57-2.44 (m, 1.5H), 2.41 (s, 1.8H), 2.39 (s, 3H), 2.36 (s, 3.2H), 2.35 (s, 1.9H), 1.92-1.83 (m, 0.7H), 1.67-1.60 (m, 1.0H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 143.56, 143.51, 139.14, 136.23, 134.45, 133.19, 131.55, 131.21, 130.01, 129.87, 129.75, 129.72, 129.70, 129.58, 128.52, 127.51, 127.40, 126.97, 126.84, 126.80, 59.83, 58.83, 55.45, 55.37, 42.74,
41.13, 40.16, 39.32, 38.89, 36.00, 21.44, 21.42, 20.94; HRMS (ESI) calcd for C_{25}H_{27}NNaO_{2}S_{2}^{+} [M+Na]^{+} 460.1375, found 460.1378.

3-((p-tolythio)methyl)-2-tosyl-2-azaspiro[4.5]decane (4c)

Colourless oil (80.0 mg, 93% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.51 (d, $J$ = 7.5 Hz, 2H), 7.36 (d, $J$ = 7.5 Hz, 2H), 7.20 (d, $J$ = 7.5 Hz, 2H), 7.16 (d, $J$ = 8.0 Hz, 2H), 3.88 (dd, $J$ = 13.5 Hz, 2.0 Hz, 1H), 3.56-3.52 (m, 1H), 3.19 (s, 2H), 2.83 (dd, $J$ = 12.5 Hz, 11.0 Hz, 1H), 2.39 (s, 3H), 2.36 (s, 3H), 1.92-1.88 (m, 1H), 1.59-1.55 (m, 1H), 1.42-1.32 (m, 4H), 1.25-1.07 (m, 4H), 0.74-0.70 (m, 1 H), 0.56-0.53 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 143.28, 136.21, 134.14, 131.74, 130.14, 129.71, 129.42, 127.47, 59.03, 58.36, 44.17, 41.15, 40.51, 36.24, 34.24, 25.74, 23.53, 22.84, 21.43, 20.97; HRMS (ESI) calcd for C$_{24}$H$_{31}$NNaO$_{2}$S$_{2}^{+}$ [M+Na]^{+} 452.1688, found 452.1698.

2-((p-tolythio)methyl)-1-tosylpiperidine (4d)

Colourless oil (24.0 mg, 32% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.62 (d, $J$ = 8.5 Hz, 2H), 7.26-7.23 (m, 4H), 7.11 (d, $J$ = 8.0 Hz, 2H), 4.12-4.10 (m, 1H), 3.79-3.77 (m, 1H), 3.06-2.92 (m, 3H), 2.41 (s, 3H), 2.33 (s, 3H), 1.98-1.97 (m, 1H), 1.54-1.51 (m, 2H), 1.44-1.39 (m, 2H), 1.37-1.27 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 142.94, 138.18, 136.51, 131.43, 130.32, 129.73, 129.56, 126.96, 51.73, 40.92, 33.61, 25.25, 24.55, 21.45, 20.99, 18.05; HRMS (ESI) calcd for C$_{20}$H$_{25}$NNaO$_{2}$S$_{2}^{+}$ [M+Na]^{+} 398.1219, found 398.1232.
2-((p-tolylthio)methyl)-1-tosylimidolinone (4e)

White solid (32.0 mg, 39% yield) mp 113-115 °C. $^1$H NMR (500 MHz, CDCl$_3$): δ 7.65 (d, $J = 8.0$ Hz, 1H), 7.40 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 7.22-7.19 (m, 1H), 7.18-7.17 (m, 2H), 7.09 (d, $J = 8.0$ Hz, 2H), 7.05-7.01 (m, 2H), 4.26-4.20 (m, 1H), 3.66 (dd, $J = 13.6$ Hz, 3.4 Hz, 1H), 2.92-2.80 (m, 3H), 2.37 (s, 3H), 2.32 (s, 3H);
$^{13}$C NMR (125 MHz, CDCl$_3$): 143.90, 141.25, 136.34, 134.63, 131.04, 129.85, 129.69, 129.54, 127.79, 126.98, 125.25, 124.70, 116.99, 60.82, 39.14, 33.23, 21.48, 21.02;
HRMS (ESI) calcd for C$_{23}$H$_{23}$N$_2$O$_2$S$_2$Na$^+$ [M+Na]$^+$ 432.1062, found 432.1069.

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\begin{array}{c}
\text{O} \\
\text{N} \\
\text{S} \\
\text{Ts}
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5-((p-tolylthio)methyl)-1-tosylimidazolidin-2-one (4f)

White solid (43.0 mg, 57% yield) mp 104-105 °C. $^1$H NMR (500 MHz, CDCl$_3$): δ 7.80-7.78 (m, 2H), 7.72 (br, s, 1H), 7.28-7.24 (m, 4H), 7.10-7.09 (m, 2H), 4.76-4.70 (m, 1H), 3.84 (t, $J = 10.0$ Hz, 1H), 3.57 (dd, $J = 10.0$ Hz, 7.0 Hz, 1H), 3.27 (dd, $J = 14.0$ Hz, 4.5 Hz, 1H), 2.95 (dd, $J = 14.0$ Hz, 9.0 Hz, 1H), 2.39 (s, 3H), 2.31 (s, 3H);
$^{13}$C NMR (125 MHz, CDCl$_3$): 161.13, 142.80, 134.29, 137.92, 131.57, 130.10, 129.53, 129.24, 126.34, 46.88, 37.73, 21.43, 20.99; HRMS (ESI) calcd for C$_{18}$H$_{20}$N$_2$O$_3$S$_2$Na$^+$ [M+Na]$^+$ 399.0808, found 399.0821.

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\begin{array}{c}
\text{O} \\
\text{N} \\
\text{S} \\
\text{Ts}
\end{array}
\]

1-Methyl-4-((p-tolylthio)methyl)-3-tosylimidazolidin-2-one (4g)

White solid (31.0 mg, 40% yield) mp 133-134 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.86-7.84 (m, 2H), 7.28-7.22 (m, 4H), 7.14-7.12 (m, 2H), 4.76-4.69 (m, 1H), 3.67 (t, $J = 9.2$ Hz, 1H), 3.39 (dd, $J = 9.6$ Hz, 6.4 Hz, 1H), 3.24 (dd, $J = 14.0$ Hz, 4.4 Hz, 1H), 2.90 (s, 3H), 2.82 (dd, $J = 14.0$ Hz, 9.6 Hz, 1H), 2.39 (s, 3H), 2.33 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 157.57, 142.18, 140.02, 138.04, 131.52, 130.16, 129.37, 128.91,
127.05, 51.67, 37.57, 31.77, 21.43, 21.01; HRMS (ESI) calcd for C_{19}H_{22}N_{2}NaO_{3}S_{2}^{+} [M+Na]^{+} 413.0964, found 413.0974.

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\begin{align*}
\text{PhO}_2\text{S} & \quad \text{Ph} \\
\text{N} & \quad \text{SO}_2\text{Ph} \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]

\text{N-\(\text{(2,2-diphenylvinyl)-N-(phenylsulfonyl)benzenesulfonyl}\text{amidade}\)}^{5}

White solid. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.71-7.68 (m, 4H), 7.57-7.54 (m, 2H), 7.40-7.35 (m, 4H), 7.34-7.31 (m, 3H), 7.29-7.17 (m, 7H), 6.13 (s, 1H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): 152.22, 139.85, 138.80, 136.75, 133.73, 129.86, 129.03, 128.74, 128.63, 128.35, 128.20, 128.08, 116.40.

**VII. References**


VIII. Copies of $^1$H and $^{13}$C NMR Spectra
3d
(500 MHz, CDCl₃)

3d
(125 MHz, CDCl₃)
31
(400 MHz, CDCl₃)

31
(125 MHz, CDCl₃)
S35
$3\rho$

(400 MHz, CDCl$_3$)

$3\rho$

(125 MHz, CDCl$_3$)
**4a**

(500 MHz, CDCl$_3$)

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**4a**

(125 MHz, CDCl$_3$)
4c
(500 MHz, CDCl₃)

4c
(125 MHz, CDCl₃)
4d
(500 MHz, CDCl₃)

4d
(125 MHz, CDCl₃)
4f
(500 MHz, CDCl$_3$)

4f
(125 MHz, CDCl$_3$)