Supporting Information

A General Method for Site-Selective Csp³-S Bond Formation via Cooperative Catalysis

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**Instrumentation and Chemicals**

NMR spectra were recorded on Bruker 400 and 600 M spectrometers, operating at 400 and 600 MHz for $^1$H NMR and 100 and 150 MHz for $^{13}$C NMR spectrophotometer using CDCl$_3$ and TMS as the internal standard. Chemical shift values for $^1$H and $^{13}$C are referenced to residual solvent peaks (CHCl$_3$ in CDCl$_3$: 7.26 ppm for $^1$H, 77.00 ppm for $^{13}$C; Chemical shifts are reported in δ ppm. All coupling constants ($J$ values) were reported in Hertz (Hz). Data for $^1$H NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet), coupling constant (Hz) and integration. Column chromatography was performed on silica gel 200-300 mesh. High-resolution mass spectra (HRMS) were recorded on electron-spray ionization (ESI) technique.

All reactions were carried out under nitrogen atmosphere. Materials were obtained from commercial suppliers or prepared according to standard note procedures unless otherwise noted. Cu(acac)$_2$ was purchased from Shanghai Macklin Bio-Chemical Reagent Co., Ltd., 1,10-phenanthroline was purchased from Alfa Aesar Chemical Co., Ltd., Indium powder was purchased from Meryer Chemical Technology Co., Ltd., Anhydrous DCE was purchased from Energy Chemical Reagent Co., Ltd.

**General Procedure: Preparation of $N$-fluoroamides and disulfides**

**Procedure for $N$-fluoroamides**

\[
\begin{align*}
\text{Tos}^N\text{H} & \quad \text{R}^2 \quad \text{R}^3 \\
1) \text{NaH (2.0 equiv)} & \quad \text{DCM (0.25 M)} & \quad \text{r.t., 30 min} & \quad \begin{array}{c}
\rightarrow \text{F} \\
\text{Tos}^N\text{H} & \quad \text{R}^2 \quad \text{R}^3 
\end{array} \\
2) \text{NFSI (3.0 equiv)} & \quad \text{r.t. 6 h}
\end{align*}
\]

The corresponding N-fluorotosylamides are prepared according to a reported procedure$^1$: To a solution of tosylamine (5 mmol, 1.0 equiv) in dichloromethane (20
mL) was added NaH (0.24 g, 10 mmol, 2.0 equiv) at 0 °C. The mixture was allowed to stir for 30 min at room temperature under nitrogen atmosphere. After that, NFSI (15 mmol, 3.0 equiv) was added portion wise to the resulted mixture. Then the mixture was stirring for another 6 hours and after completion the reaction was quenched by water (20 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (20 mL × 2). The combined organic phase was washed with brine (30 mL), and then dried with anhydrous Na₂SO₄. Evaporation the solvent to give the residue, the residue was washed with DCM and PE (DCM:PE = 1:50) several times. Combining the filtrate and evaporation under reduce pressure to give the crude product. Column chromatography on silica gel (ethyl acetate/PE/DCM = 1:35:0.5 as eluent) afforded corresponding N-fluoroamides as white solid or liquid. N-fluorocarboxyamides 1d and 1e were prepared according to Ref. 2.

The corresponding tosyl amides precursors of 1a, 1b, 1c, 1f, 1g, 1h, 1n, 1o, 1p, 1t, 1u, 1x, 1y, 1z, 1ab, 1ac, 1ad, 1ae, 1af, 1ag, 8a, 8b, 11a were prepared according to Ref. 3.

The corresponding tosyl amides precursors of 1q, 1r, 1v, 1s and 1ai were prepared from the alcohols. A representative example was shown below.

Lithocholic acid (1.0 equiv) was dissolved in THF (0.2 M), LiAlH₄ (2.5 equiv) was added portion wise under 0 °C, then the mixture was refluxing for 12 h. After that, the
reaction was cooled down, the Na$_2$SO$_4$ • 10H$_2$O was added slowly until the mixture was clear to quench the reaction, filtered, solid was washed with Et$_2$O, the combined ether solution was concentrated in vacuo to give the 1.

In an oven dried round bottom flask, PPh$_3$ (1.2 equiv) and TsNHBoc (1.2 equiv) were dissolved in anhydrous THF. Then, a solution of alcohol 1 in THF (1.0 M) was added. The mixture was cooled to 0 ºC and DIAD (1.2 equiv) was slowly added and the reaction was slowly warmed to room temperature and stirred overnight. Upon completion, the reaction was quenched by water (20 mL). The aq. Layer was extracted with EtOAc (25 mL × 3), the combined organic layer dried over Na$_2$SO$_4$. Evaporation and column chromatography on silica gel (EA/PE/DCM = 1:10:0.5 as eluent) afforded 2.

TFA (1.2 equiv) was added to a solution of 2 in DCM (0.5 M), the reaction stirred for 15 min. Then the reaction was quenched by Sat. NaHCO$_3$ solution. The aq. Layer was extracted with DCM (25 mL × 3), the combined organic layer dried over Na$_2$SO$_4$. Evaporation and column chromatography on silica gel (EA/PE/DCM = 1:5:0.5 as eluent) afforded 3

To a solution of 3 (1.0 equiv) in dichloromethane (1.0 M) was added triethylamine (3.0 equiv) at room temperature. Benzoyl chloride (0.95 equiv) was added dropwise under the same temperature. Then the mixture was stirring for 30 min at room temperature (detected by TLC). After that, the mixture was quenched by water (20 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (20 mL × 2). The combined organic phase was washed with brine (30 mL), and then dried over Na$_2$SO$_4$. Evaporation and column chromatography on silica gel (EA/PE/DCM = 1:5:0.5 as eluent) afforded compound 4 as white solid.

The corresponding tosyl amides precursors of 1k, 1l, 1m, 6a, 6c were prepared from the amino alcohols. A representative example was shown below.
In an oven dried round bottom flask was added amino alcohol 5 and dried DCM (0.5 M), the mixture was cooled to 0 °C, Et₃N (3.0 equiv) and TsCl (1.0 equiv) were added slowly, the reaction was warmed to room temperature and stirred overnight. After completion, the solvent was evaporated and the desired residue was dissolved in dried DCM (0.5 M) again, Et₃N (3.0 equiv) and PGCl (1.2 equiv) were added slowly, the reaction was warmed to room temperature and stirred for 8 hours. After that, the mixture was quenched by water (20 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (20 mL × 3). The combined organic phase was washed with brine (30 mL), and then dried over Na₂SO₄. Evaporation and column chromatography on silica gel (EA/PE/DCM = 1:5:0.5 as eluent) afforded compound 6.

Disulfides 2a−2k, 2m−2o are commerical available. 2l was prepared according to Ref. 4. 10a, 10b, 10c were prepared according to Ref. 5.

**List of disulfides:**

![Disulfides](image-url)
List of N-fluoroamides:

1a

1b

1c

1d

1e

1f

1g

1h

1i

1j

1k

1l

1m

1n

1o

1p

1q

1r

1s

1t

1u

1v

1w

1x
Characterization Data for N-fluorotosylamides and disulfides

**N-fluoro-4-methyl-N-octylbenzenesulfonamide (1a)**

![Structure 1a](image)

Yellow solid. mp: 32.3–33.5 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J = 8.2$ Hz, 2H), 7.40 (d, $J = 8.2$ Hz, 2H), 3.20 (dt, $J = 40.8$, 7.0 Hz, 2H), 2.48 (s, 3H), 1.70 (quint, $J = 7.2$ Hz, 2H), 1.35–1.40 (m, 2H), 1.26 (s, 8H), 0.87 (t, $J = 6.8$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 146.12, 129.95, 129.89, 129.04, 53.70 (d, $J = 12.0$ Hz), 31.69, 29.05, 26.57, 26.29, 22.59, 21.75, 14.04.

**N-butyl-N-fluoro-4-methylbenzenesulfonamide (1b)**
Yellow oil. $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J$ = 8.2 Hz, 2H), 7.41 (d, $J$ = 8.2 Hz, 2H), 3.21 (dt, $J$ = 40.8, 7.0 Hz, 2H), 2.48 (s, 3H), 1.69 (quint, $J$ = 7.0 Hz, 2H), 1.38–1.47 (m, 2H), 0.92 (t, $J$ = 7.4 Hz, 3H). $^{13}C$ NMR (100 MHz, CDCl$_3$) $\delta$ 146.14, 129.92, 129.88, 128.96, 53.38 (d, $J$ = 13.0 Hz), 28.25, 21.72, 19.75, 13.52.

$N$-fluoro-$N$-(heptan-4-yl)-4-methylbenzenesulfonamide (1c)

Yellow oil. $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 (d, $J$ = 8.3 Hz, 2H), 7.37 (d, $J$ = 8.2 Hz, 2H), 3.90 (dp, $J$ = 38.8, 6.5 Hz, 1H), 2.46 (s, 3H), 1.51–1.70 (m, 4H), 1.35–1.46 (m, 4H), 0.89 (t, $J$ = 7.3 Hz, 6H). $^{13}C$ NMR (100 MHz, CDCl$_3$) $\delta$ 145.53, 133.12, 129.77, 129.11, 62.95 (d, $J$ = 13.0 Hz), 32.89 (d, $J$ = 6.0 Hz), 21.70, 19.50, 13.81. 

HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{14}$H$_{22}$FNNaO$_2$S, 310.1247; found, 310.1253. 

IR (KBr, cm$^{-1}$): $\nu$ 3517, 3450, 2962, 2873, 1632, 1171.

$N$-(tert-butyl)-$N$-fluoro-2-methylbenzamide (1d)

Yellow oil. $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.28–7.33 (m, 2H), 7.18–7.23 (m, 2H), 2.40 (s, 3H), 1.55 (d, $J$ = 1.9 Hz, 9H). $^{13}C$ NMR (100 MHz, CDCl$_3$) $\delta$ 174.99 (d, $J$ = 10.8 Hz), 135.34 (d, $J$ = 2.4 Hz), 135.08, 130.42, 129.90 (d, $J$ = 1.2 Hz), 127.14 (d, $J$ = 4.4 Hz), 125.31, 64.37 (d, $J$ = 11.0 Hz), 27.18 (d, $J$ = 5.0 Hz), 19.31.

$N$-(tert-butyl)-2-ethyl-$N$-fluorobenzamide (1e)
Yellow oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.35 (t, $J = 7.5$ Hz, 1H), 7.30 (d, $J = 7.5$ Hz, 1H), 7.26 (d, $J = 6.9$ Hz, 1H), 7.21 (t, $J = 7.5$ Hz, 1H), 2.74 (q, $J = 7.5$ Hz, 2H), 1.56 (d, $J = 1.8$ Hz, 9H), 1.24 (t, $J = 7.6$ Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 174.98 (d, $J = 11.0$ Hz), 141.59, 134.65, 129.99, 128.89, 127.10 (d, $J = 4.3$ Hz), 125.33, 64.30 (d, $J = 10.3$ Hz), 27.16 (d, $J = 5.6$ Hz), 26.08, 15.61.

$N$-fluoro-$N$-pentylbenzenesulfonamide (1f)

Yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.73 (d, $J = 8.3$ Hz, 2H), 7.32 (d, $J = 8.1$ Hz, 2H), 3.10 (dt, $J = 40.8$, 7.0 Hz, 2H), 2.39 (s, 3H), 1.62 (quint, $J = 7.1$ Hz, 2H), 1.20–1.30 (m, 4H), 0.80 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 146.14, 129.84, 129.82, 128.76, 53.72 (d, $J = 12.0$ Hz), 28.58, 25.87, 22.06, 21.61, 13.73.

$N$-fluoro-$N$-hexyl-4-methylbenzenesulfonamide (1h)

Yellow oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.82 (d, $J = 8.2$ Hz, 2H), 7.41 (d, $J = 8.2$ Hz, 2H), 3.01 (d, $J = 44.6$ Hz, 2H), 2.48 (s, 3H), 1.24–1.32 (m, 4H), 1.17–1.23 (m, 2H), 0.95 (s, 6H), 0.89 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 146.00, 129.89, 129.79, 129.65, 63.07 (d, $J = 10.5$ Hz), 39.93, 34.25, 25.82, 25.54, 23.37, 21.72, 14.00.

$N$-fluoro-$N$-hexyl-4-methylbenzenesulfonamide (1h)
Yellow solid. mp: 46.3–47.1 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.82 (d, \(J = 8.4\) Hz, 2H), 7.40 (d, \(J = 8.4\) Hz, 2H), 3.20 (dt, \(J = 40.8, 7.0\) Hz, 2H), 2.48 (s, 3H), 1.70 (quint, \(J = 4.8\) Hz, 2H), 1.38 (quint, \(J = 4.8\) Hz, 2H), 1.24–1.31 (m, 16H), 0.88 (t, \(J = 6.9\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 146.12, 129.95, 129.89, 129.06, 53.70 (d, \(J = 12.4\) Hz), 31.89, 29.59, 29.49, 29.40, 29.32, 29.10, 26.58, 26.30, 22.67, 21.75, 14.09.

\(N\)-((1,3-dioxoisindolin-2-yl)pentyl)-\(N\)-fluoro-4-methylbenzenesulfonamide (1i)

Yellow solid. mp: 93.3–94.5 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.84 (dd, \(J = 5.5, 3.0\) Hz, 2H), 7.81 (d, \(J = 8.2\) Hz, 2H), 7.71 (dd, \(J = 5.5, 3.0\) Hz, 2H), 7.40 (d, \(J = 8.2\) Hz, 2H), 3.68 (t, \(J = 7.2\) Hz, 2H), 3.20 (dt, \(J = 40.5, 6.9\) Hz, 2H), 2.48 (s, 3H), 1.68–1.79 (m, 4H), 1.43–1.49 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.38, 146.18, 133.90, 132.09, 129.95, 129.92, 128.89, 123.20, 53.43 (d, \(J = 12.5\) Hz), 37.62, 28.11, 25.90, 23.86, 21.75.

Methyl 6-((\(N\)-fluoro-4-methylphenyl)sulfonamido)hexanoate (1j)

Yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.82 (d, \(J = 8.0\) Hz, 2H), 7.41 (d, \(J = 8.0\) Hz, 2H), 3.66 (s, 3H), 3.21 (dt, \(J = 40.6, 6.9\) Hz, 2H), 2.48 (s, 3H), 2.31 (t, \(J = 7.4\) Hz, 2H), 1.69–1.76 (m, 2H), 1.60–1.67 (m, 2H), 1.40–1.47 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 173.78, 146.20, 129.89 (C×2), 128.82, 53.44 (d, \(J = 12.4\) Hz), 51.44, 33.71, 26.04, 25.96, 24.33, 21.69.

\(N\)-((tert-butyldimethylsilyl)oxy)pentyl)-\(N\)-fluoro-4-methylbenzenesulfonamide(1k)
Yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 3.60 (t, $J = 6.0$ Hz, 2H), 3.21 (dt, $J = 40.7$, 6.9 Hz, 2H), 2.48 (s,3H) 1.73 (quint, $J = 7.2$ Hz, 2H), 1.42–1.54 (m, 4H), 0.88 (s, 9H), 0.03 (s, 3H), 0.03 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 146.14, 129.95, 129.90, 129.03, 62.81, 53.61 (d, $J = 12.4$ Hz), 32.21, 26.11, 25.94, 22.98, 21.75, 18.32, -5.33. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{18}$H$_{32}$FNNaO$_3$Si, 412,1748; found, 412,1750. IR (KBr, cm$^{-1}$): $\nu$ 3573, 3520, 3455, 3391, 2932, 1636.

$N$-(5-((tert-butyldimethylsilyl)oxy)pentyl)-$N$-fluoro-4-methylbenzenesulphonamide (1l)

Yellow oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.81 (d, $J = 8.2$ Hz, 2H), 7.40 (d, $J = 8.2$ Hz, 2H), 3.58 (t, $J = 6.6$ Hz, 2H), 3.20 (dt, $J = 40.8$, 7.0 Hz, 2H), 2.48 (s, 3H), 1.68–1.74 (m, 2H), 1.47–1.53 (m, 2H), 1.38–1.43 (m, 2H), 1.32–1.36 (m, 2H), 0.88 (s, 9H), 0.04 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 146.13, 129.95, 129.90, 129.02, 62.99, 53.64 (d, $J = 12.5$ Hz), 32.59, 26.41, 26.30, 25.95, 25.37, 21.76, 18.34, -5.30. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{19}$H$_{34}$FNNaO$_3$Si, 426.1905; found, 426.1915. IR (KBr, cm$^{-1}$): $\nu$ 3684, 3556, 3474, 3411, 1728.

6-((N-fluoro-4-methylphenyl)sulphonamido)hexyl benzoate (1m)

White solid. mp: 44.6–45.5 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.03 (d, $J = 7.2$ Hz, 2H), 7.82 (d, $J = 8.2$ Hz, 2H), 7.55 (t, $J = 6.8$ Hz, 1H), 7.44 (t, $J = 7.2$ Hz, 2H), 7.40 (d, $J = 8.2$ Hz, 2H), 4.31 (t, $J = 6.6$ Hz, 2H), 3.22 (dt, $J = 40.6$, 6.9 Hz, 2H), 2.48 (s,
3H), 1.63–1.83 (m, 4H), 1.43–1.58 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.62, 146.18, 132.83, 130.40, 129.93, 129.91, 129.52, 128.94, 128.33, 64.76, 53.52 (d, $J$ = 12.5 Hz), 28.53, 26.26, 26.19, 25.61, 21.75. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{20}$H$_{24}$FNNaO$_4$S, 416.1302; found, 416.1299. IR (KBr, cm$^{-1}$): $\nu$ 3714, 3471, 1716, 1280.

N-(2-cyclobutyl-2-methylpropyl)-N-fluoro-4-methylbenzenesulfonamide (1n)

![Structure of 1n]

Yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 (d, $J$ = 8.2 Hz, 2H), 7.40 (d, $J$ = 8.2 Hz, 2H), 2.94 (d, $J$ = 44.8 Hz, 2H), 2.48 (s, 3H), 2.32–2.41 (m, 1H), 1.75–1.81 (m, 5H), 1.61–1.68 (m, 1H), 0.89 (s, 3H), 0.88 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.99, 129.89, 129.78, 129.62, 61.82 (d, $J$ = 10.8 Hz), 43.67, 35.47, 22.83, 22.00, 21.75, 17.12. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{15}$H$_{22}$FNNaO$_2$S, 322.1247; found, 322.1245. IR (KBr, cm$^{-1}$): $\nu$ 3553, 3411, 2967, 1373.

N-(2-cyclopentyl-2-methylpropyl)-4-methylbenzenesulfonamide (1o)

![Structure of 1o]

Yellow solid. mp: 53.3–54.7 °C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J$ = 8.1 Hz, 2H), 7.40 (d, $J$ = 8.1 Hz, 2H), 3.05 (d, $J$ = 44.8 Hz, 2H), 2.48 (s, 3H), 1.84–1.91 (m, 1H), 1.58–1.65 (m, 2H), 1.52–1.58 (m, 2H), 1.45–1.52 (m, 2H), 1.17–1.25 (m, 2H), 0.93 (s, 6H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 145.99, 129.89, 129.78, 129.63, 63.12 (d, $J$ = 10.5 Hz), 47.52, 36.26, 26.73, 25.59, 23.07, 21.75. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{16}$H$_{24}$FNNaO$_2$S, 336.1404; found, 336.1400. IR (KBr, cm$^{-1}$): $\nu$ 3713, 3558, 3474, 3408, 1742.
N-(2-cyclohexyl-2-methylpropyl)-4-methylbenzenesulfonamide (1p)

White solid. mp: 82.1–83.5 ºC; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.82 (d, \(J = 8.2\) Hz, 2H), 7.41 (d, \(J = 8.2\) Hz, 2H), 3.08 (d, \(J = 44.8\) Hz, 2H), 2.49 (s, 3H), 1.26–1.36 (m, 5H), 1.15–1.24 (m, 2H), 1.6–1.15 (m, 2H), 0.87–1.00 (m, 2H), 0.91 (s, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 145.99, 129.91, 129.79, 129.70, 61.80 (d, \(J = 10.5\) Hz), 44.74, 36.66, 27.06, 26.94, 26.58, 23.35, 21.77. HRMS–ESI (m/z): [M+Na]\(^+\) calcd. for C\(_{17}\)H\(_{26}\)FNNaO\(_2\)S, 350.1560; found, 350.1558. IR (KBr, cm\(^{-1}\)): \(\nu\) 3687, 3060, 1727, 1560.

N-(cyclohexylmethyl)-4-methylbenzenesulfonamide (1q)

Yellow solid. mp: 71.5–72.5 ºC; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.82 (d, \(J = 8.0\) Hz, 2H), 7.40 (d, \(J = 8.0\) Hz, 2H), 3.02 (dd, \(J = 42.4, 6.8\) Hz, 2H), 2.48 (s, 3H), 1.79–1.83 (m, 2H), 1.63–1.77 (m, 4H), 1.18–1.31 (m, 3H), 0.92–1.03 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 146.07, 129.89, 129.88, 129.09, 59.54 (d, \(J = 12.0\) Hz), 35.23, 30.80, 26.22, 25.61, 21.73. HRMS–ESI (m/z): [M+Na]\(^+\) calcd. for C\(_{14}\)H\(_{20}\)FNNaO\(_2\)S, 308.1091; found, 308.1087. IR (KBr, cm\(^{-1}\)): \(\nu\) 3711, 3058, 1732, 1371.

N-(cycloheptylmethyl)-4-methylbenzenesulfonamide (1r)

Yellow solid. mp: 57.3–58.3 ºC; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.82 (d, \(J = 8.2\) Hz,
2H), 7.40 (d, J = 8.2 Hz, 2H), 3.01 (dd, J = 41.8, 7.0 Hz, 2H), 2.48 (s, 3H), 1.86–1.94 (m, 1H), 1.78–1.84 (m, 2H), 1.62–1.69 (m, 2H), 1.55–1.61 (m, 2H), 1.36–1.53 (m, 4H), 1.18–1.29 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 146.07, 129.90, 129.88, 129.14, 59.73 (d, J = 12.2 Hz), 36.52, 31.96, 28.28, 26.08, 21.75. HRMS–ESI (m/z): [M+Na]\(^+\) calcd. for C\(_{15}\)H\(_{22}\)FNNaO\(_2\)S, 322.1247; found, 322.1244. IR (KBr, cm\(^{-1}\)): \(\nu\) 3713, 3551, 3479, 3409, 1737, 1170.

\(N\)-(2-((3r,5r,7r)-adamantan-1-yl)ethyl)-4-methylbenzenesulfonamide (1s)

\(1s\)

White solid. mp: 103.3–104.5 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.83 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 3.27 (ddd, J = 40.2, 9.2, 6.4 Hz, 2H), 2.49 (s, 3H), 1.95 (brs, 3H), 1.70 (d, J = 12.0 Hz, 3H), 1.61 (d, J = 12.0 Hz, 3H), 1.54 (m, 1H), 1.52 (t, J = 2.6, 1H), 1.48 (d, J = 2.2 Hz, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 146.12, 129.92, 129.91, 129.26, 48.91 (d, J = 12.7 Hz), 42.24, 39.90, 36.92, 31.74, 28.49, 21.78.

\(N\)-(1-cyclohexyl-3-phenylpropyl)-4-methylbenzenesulfonamide (1t)

\(1t\)

Yellow solid. mp: 83.3–84.3 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.82 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.26 (dd, J = 7.8, 6.8 Hz, 2H), 7.18 (t, J = 6.8 Hz, 1H), 7.08 (d, J = 7.8 Hz, 2H), 3.79 (ddd, J = 39.2, 9.6, 5.1 Hz, 1H), 2.63 (t, J = 8.2 Hz, 2H), 2.46 (s, 3H), 1.82–1.91 (m, 1H), 1.60–1.80 (m, 7H), 1.21–1.30 (m, 2H), 1.05–1.19 (m, 3H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 145.61, 141.33, 132.91, 129.89, 129.17, 128.38, 128.36, 126.03, 67.10 (d, J = 12.0 Hz), 40.12, 33.28, 30.30, 28.68 (d, J = 11.5 Hz), 28.57, 26.35 (d, J = 4.5 Hz), 26.25, 21.71. HRMS–ESI (m/z): [M+Na]\(^+\) calcd. for
C_{22}H_{28}FNNaO_{2}S, 412,1717; found, 412,1716. **IR** (KBr, cm^{-1}): ν 3687, 3472, 3059, 1727, 1560.

**IR** (KBr, cm^{-1}): ν 3687, 3472, 3059, 1727, 1560.

(S)-N-(1-cyclohexylethyl)-N-fluoro-4-methylbenzenesulfonamide (1u)

Yellow solid. mp: 68.1–69.3 °C; **^1H NMR** (400 MHz, CDCl_{3}) δ 7.84 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 3.84 (dp, J = 37.1, 6.7 Hz, 1H), 2.46 (s, 3H), 1.89 (d, J = 12.8 Hz, 1H), 1.71–1.80 (m, 3H), 1.65 (d, J = 10.3 Hz, 1H), 1.51–1.61 (m, 1H), 1.14–1.25 (m, 3H), 1.12 (dd, J = 6.7, 2.3 Hz, 3H), 0.98–1.10 (m, 2H). **^13C NMR** (100 MHz, CDCl_{3}) δ 145.58, 132.77, 129.82, 129.20, 63.03 (d, J = 12.7 Hz), 42.17, 29.45 (d, J = 12.0 Hz), 26.25, 26.06 (d, J = 6.1 Hz), 21.72, 12.18 (d, J = 15.7 Hz). **HRMS–ESI (m/z):** [M+Na]^+ calcd. for C_{15}H_{22}FNNaO_{2}S, 322.1247; found, 322.1246. **IR** (KBr, cm^{-1}): ν 3713, 3556, 3474, 3410, 1740.

N-fluoro-4-methyl-N-((tetrahydrofuran-2-yl)methyl)benzenesulfonamide (1v)

Yellow solid. mp: 83.3–84.3 °C; **^1H NMR** (400 MHz, CDCl_{3}) δ 7.83 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 4.19 (quint, J = 6.4 Hz, 1H), 3.87 (ddd, J = 14.8, 7.8, 7.0 Hz, 1H), 3.77 (ddd, J = 14.8, 7.8, 7.0 Hz, 1H), 3.34 (ddd, J = 21.1, 14.1, 5.6 Hz, 1H), 3.22 (ddd, J = 21.1, 14.1, 5.6 Hz, 1H), 2.48 (s, 3H), 2.05–2.13 (m, 1H), 1.88–1.96 (m, 2H), 1.68–1.77 (m, 1H). **^13C NMR** (100 MHz, CDCl_{3}) δ 146.35, 130.00, 129.96, 128.78, 75.26, 68.38, 57.39 (d, J = 11.1 Hz), 29.76, 25.41, 21.76. **HRMS–ESI (m/z):** [M+Na]^+ calcd. for C_{12}H_{16}FNNaO_{2}S, 296.0727; found, 296.0726. **IR** (KBr, cm^{-1}): ν 3713, 3409, 1732, 1173.
**N-fluoro-4-methyl-N-((tetrahydro-2H-pyran-2-yl)methyl)benzenesulfonamide (1w)**

Yellow solid. mp: 79.9–80.5 °C; **^1H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 3.96–3.99 (m, 1H), 3.63 (dd, $J = 15.6, 10.2, 5.6$ Hz, 1H), 3.43 (ddd, $J = 15.6, 10.2, 5.6$ Hz, 1H), 3.29 (ddd, $J = 21.2, 14.2, 6.2$ Hz, 1H), 3.16 (ddd, $J = 21.2, 14.2, 6.2$ Hz, 1H), 2.47 (s, 3H), 1.85–1.88 (m, 1H), 1.72–1.75 (m, 1H), 1.44–1.62 (m, 3H), 1.24–1.37 (m, 1H). **^13C NMR** (100 MHz, CDCl$_3$) $\delta$ 146.30, 130.00, 129.93, 128.73, 77.32, 68.58, 58.45 (d, $J = 11.6$ Hz), 29.73, 25.67, 22.88, 21.73. **HRMS–ESI** ($m/z$): [M+Na]$^+$ calcd. for C$_{13}$H$_{18}$FNNaO$_3$S, 310.0884; found, 310.0883. **IR** (KBr, cm$^{-1}$): $\nu$ 3711, 3410, 1735, 1172.

**N-fluoro-4-methyl-N-(1-phenylpentyl)benzenesulfonamide (1x)**

Yellow oil. **^1H NMR** (600 MHz, CDCl$_3$) $\delta$ 7.65 (d, $J = 8.1$ Hz, 2H), 7.22–7.26 (m, 5H), 7.21 (d, $J = 8.1$ Hz, 2H), 4.75 (ddd, $J = 37.8, 8.7, 6.3$ Hz, 1H), 2.40 (s, 3H), 2.12–2.18 (m, 1H), 1.92–1.98 (m, 1H), 1.24–1.33 (m, 3H), 1.11–1.19 (m, 1H), 0.84 (t, $J = 7.2$ Hz, 3H). **^13C NMR** (150 MHz, CDCl$_3$) $\delta$ 145.35, 136.64 (d, $J = 3.7$ Hz), 131.86, 129.46, 129.31, 128.66, 128.26, 128.19, 67.76 (d, $J = 12.4$ Hz), 32.65 (d, $J = 4.6$ Hz), 28.11, 22.22, 21.63, 13.80.

**N-fluoro-N-(heptan-2-yl)-4-methylbenzenesulfonamide (1y)**

S16
Yellow oil. ¹H NMR (600 MHz, CDCl₃) δ 7.84 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 4.01 (dtq, J = 37.3, 16.6, 6.6 Hz, 1H), 2.46 (s, 3H), 1.71–1.77 (m, 1H), 1.50–1.56 (m, 1H), 1.36–1.43 (m, 2H), 1.25–1.33 (m, 4H), 1.23 (d, J = 6.5 Hz, 3H), 0.88 (t, J = 6.9 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 145.61, 132.78, 129.78, 129.18, 59.10 (d, J = 13.1 Hz), 34.17 (d, J = 1.9 Hz), 31.39, 25.61, 22.45, 21.67, 15.78 (d, J = 11.3 Hz), 13.95. HRMS–ESI (m/z): [M+Na]⁺ calcd. for C₁₄H₂₂FNNaO₂S, 310.1247; found, 310.1249. IR (KBr, cm⁻¹): ν 3684, 3555, 3412, 1739, 1375, 1176.

N-fluoro-N-(2-isopropylpentyl)-4-methylbenzenesulfonamide (1z)

Yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 3.13 (dddd, J = 42.8, 32.8, 14.2, 6.8 Hz, 2H), 2.49 (s, 3H), 1.85–1.93 (m, 1H), 1.62–1.70 (m, 1H), 1.33–1.41 (m, 1H), 1.22–1.33 (m, 3H), 0.88 (t, J = 6.8 Hz, 3H), 0.86 (d, J = 6.8 Hz, 3H), 0.85 (d, J = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 146.07, 129.89, 129.87, 129.30, 55.09 (d, J = 12.4 Hz), 40.75, 30.92, 28.21, 21.77, 20.48, 19.01, 18.63, 14.26. HRMS–ESI (m/z): [M+Na]⁺ calcd. for C₁₅H₂₄FNNaO₂S, 324.1404; found, 324.1408. IR (KBr, cm⁻¹): ν 3688, 3412, 1739, 1375, 1176.

N-fluoro-4-methyl-N-(5-methylhexyl)benzenesulfonamide (1aa)

Yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 3.20 (dt, J = 40.8, 7.0 Hz, 2H), 2.48 (s, 3H), 1.65–1.72 (m, 2H), 1.47–1.57 (m, 1H), 1.34–1.43 (m, 2H), 1.15–1.20 (m, 2H), 0.87 (s, 3H), 0.85 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 146.14, 129.91, 129.88, 128.95, 53.73 (d, J = 12.4 Hz), 38.36, 27.78, 26.53, 24.36, 22.46, 21.72.

N-fluoro-4-methyl-N-(2,2,4-trimethylpentyl)benzenesulfonamide (1ab)
**N-(3-cyclohexylpropyl)-N-fluoro-4-methylbenzenesulfonamide (1ac)**

White solid. mp: 73.1–74.5 ºC; \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.82 (d, \( J = 8.2 \) Hz, 2H), 7.40 (d, \( J = 8.0 \) Hz, 2H), 3.18 (dt, \( J = 40.7, 7.2 \) Hz, 2H), 2.48 (s, 3H), 1.62–1.76 (m, 7H), 1.20–1.30 (m, 4H), 1.15–1.21 (m, 2H), 0.82–0.90 (m, 2H). \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 146.12, 129.96, 129.89, 129.05, 54.07 (d, \( J = 12.4 \) Hz), 37.25, 34.24, 33.18, 26.57, 26.25, 23.74, 21.76.

**N-(3-cyclohexylpropyl)-N-fluoro-4-methylbenzenesulfonamide (1ac)**

![1ac](image)

**Yellow oil. \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.84 (d, \( J = 8.2 \) Hz, 2H), 7.37 (d, \( J = 8.2 \) Hz, 2H), 4.10–4.31 (m, 3H), 2.47 (s, 3H), 1.69–1.78 (m, 1H), 1.60–1.69 (m, 1H), 1.35–1.43 (m, 2H), 1.25–1.34 (m, 2H), 1.21 (s, 9H), 0.88 (t, \( J = 7.2 \) Hz, 3H). \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 178.13, 145.91, 132.55, 129.86, 129.22, 62.42 (d, \( J = 6.5 \) Hz), 61.77 (d, \( J = 12.2 \) Hz), 38.76, 28.18, 27.70 (d, \( J = 7.0 \) Hz), 27.09, 22.35, 21.72,
13.75. **HRMS–ESI** (m/z): [M+Na]⁺ calcd. for C₁₈H₂₈FNNaO₄S, 396.1615; found, 396.1619. **IR** (KBr, cm⁻¹): ν 3555, 3416, 3235, 1732, 1169.

*(2R,3S)-2-((N-fluoro-4-methylphenyl)sulfonamido)-3-methylpentylbenzoate (1ae)*

![1ae](image)

Yellow oil. **¹H NMR** (400 MHz, CDCl₃) δ 8.06 (d, J = 7.2 Hz, 2H), 7.84 (d, J = 8.2 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.8 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 4.49–4.59 (m, 2H), 4.27 (ddt, J = 36.4, 6.0, 4.0 Hz, 1H), 2.43 (s, 3H), 1.96–2.06 (m, 1H), 1.60–1.68 (m, 1H), 1.29–1.39 (m, 1H), 1.08 (d, J = 6.8 Hz, 3H), 0.95 (t, J = 7.4 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 166.17, 145.84, 133.08, 132.53, 129.85, 129.83, 129.78, 129.22, 128.36, 65.11 (d, J = 10.9 Hz), 60.72 (d, J = 13.4 Hz), 36.06, 25.88, 21.73, 15.85, 11.27. **HRMS–ESI** (m/z): [M+Na]⁺ calcd. for C₂₀H₂₄FNNaO₄S, 416.1302; found, 416.1304. **IR** (KBr, cm⁻¹): ν 3554, 3408, 3235, 1723, 1171.

*(R)-2-((N-fluoro-4-methylphenyl)sulfonamido)-4-methylpentyl benzoate (1af)*

![1af](image)

White solid. mp: 69.3–70.5 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.07 (d, J = 7.2 Hz, 2H), 7.83 (d, J = 8.2 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 4.42–4.59 (m, 3H), 2.45 (s, 3H), 1.74–1.85 (m 2H), 1.52–1.61 (m, 1H), 0.98 (s, 3H), 0.96 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 166.20, 145.86, 133.11, 132.74, 129.85, 129.81, 129.77, 129.21, 128.38, 63.05 (d, J = 7.7 Hz), 59.98 (d, J = 12.3 Hz), 37.07 (d, J = 5.1 Hz), 24.94, 22.34 (d, J = 7.1 Hz), 21.72. **HRMS–ESI** (m/z): [M+Na]⁺ calcd. for C₂₀H₂₄FNNaO₄S, 416.1302; found, 416.1307. **IR** (KBr, cm⁻¹): ν 3711, 3473, 3063, 1719, 1172.
**N-((1S,2S,5R)-2-isopropyl-5-methylcyclohexyl)-4-methylbenzenesulfonamide (1ag)**

White solid. mp: 78.9–79.7 ºC; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.83 (d, $J = 8.1$ Hz, 2H), 7.37 (d, $J = 8.1$ Hz, 2H), 4.43 (d, $J = 50.4$ Hz, 1H), 2.47 (s, 3H), 2.22 (d, $J = 13.8$ Hz, 1H), 1.65–1.82 (m, 4H), 1.25–1.34 (m, 1H), 1.13–1.18 (m, 1H), 1.06–1.12 (m, 1H), 0.97 (d, $J = 6.6$ Hz, 3H), 0.92 (d, $J = 6.6$ Hz, 3H), 0.87 (dd, $J = 21.0$, 8.7 Hz, 1H), 0.79 (d, $J = 6.3$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.48, 133.11, 129.77, 129.13, 58.57 (d, $J = 10.9$ Hz), 48.10, 37.69 (d, $J = 6.9$ Hz), 34.76, 29.18, 28.67 (d, $J = 6.4$ Hz), 25.94 (d, $J = 3.3$ Hz), 22.95, 21.71, 20.97, 20.89. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{17}$H$_{26}$FNNaO$_2$S, 350.1560; found, 350.1556. IR (KBr, cm$^{-1}$): ν 3555, 3468, 3234, 1764, 1616, 1167.

**Methyl(S)-3-((N-fluoro-4-methylphenyl)sulfonamido)methyl)-5-methylhexanoate (1ah)**

Colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.81 (d, $J = 8.1$ Hz, 2H), 7.41 (d, $J = 8.1$ Hz, 2H), 3.64 (s, 3H), 3.28 (ddd, $J = 44.4$, 14.4, 7.5 Hz, 1H), 3.18 (ddd, $J = 44.4$, 14.4, 7.5 Hz, 1H), 2.48 (s, 3H), 2.46–2.50 (m, 1H), 2.30–2.41 (m, 2H), 1.53–1.64 (m, 1H), 1.26–1.32 (m, 1H), 1.20–1.26 (m, 1H), 0.88 (d, $J = 7.8$ Hz, 3H), 0.86 (d, $J = 7.8$ Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 172.63, 146.23, 129.92, 129.84, 129.06, 56.65 (d, $J = 11.7$ Hz), 51.45, 41.25, 36.57, 30.97, 24.99, 22.49, 22.44, 21.71.

White solid. mp: 83.3–84.5 ºC; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.05 (d, $J = 7.2$ Hz, 2H), 7.83 (d, $J = 8.4$ Hz, 2H), 7.54 (t, $J = 7.2$ Hz, 1H), 7.44 (t, $J = 7.8$ Hz, 2H), 7.40 (d, $J = 8.4$ Hz, 2H), 4.95–4.99 (m, 1H), 3.18 (dt, $J = 40.6$, 7.0 Hz, 2H), 2.49 (s, 3H), 1.97 (q, $J = 12.5$ Hz, 2H), 1.84–1.90 (m, 2H), 1.75–1.84 (m, 3H), 1.66–1.68 (m, 1H), 1.56–1.62 (m, 3H), 1.37–1.49 (m, 6H), 1.23–1.30 (m, 3H), 1.15–1.21 (m, 2H), 1.04–1.14 (m, 5H), 0.96 (s, 3H), 0.91 (d, $J = 6.6$ Hz, 3H), 0.82–0.86 (m, 1H), 0.65 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.05, 146.07, 132.59, 130.94, 129.90, 129.85, 129.47, 129.06, 128.18, 74.94, 56.46, 56.04, 54.15 (d, $J = 12.3$ Hz), 42.70, 41.95, 40.48, 40.12, 35.79, 35.34, 35.07, 34.61, 32.76, 32.35, 28.20, 27.03, 26.74, 26.32, 24.13, 23.29, 23.00, 21.70, 20.84, 18.52, 12.00. HRMS–ESI ($m/z$): [M+Na]$^+$ calcd. for C$_{38}$H$_{52}$FNNaO$_4$S, 660.3493; found, 660.3501. IR (KBr, cm$^{-1}$): $\nu$ 3552, 3410, 3234, 1714, 1174.

$N$-fluoro-$N$-(((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahdrophenanthren-1-yl)methyl)-4-methylbenzenesulfonamide (1aj)

White solid. mp: 139.3–140.2 ºC; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 (d, $J = 8.0$ Hz, 2H), 7.39 (d, $J = 8.0$ Hz, 2H), 7.15 (d, $J = 8.2$ Hz, 1H), 6.97 (d, $J = 8.2$ Hz, 1H), 6.86 (s, 1H), 3.13 (ddd, $J = 70.2$, 44.0, 15.6 Hz, 2H), 2.77–2.87 (m, 3H), 2.47 (s, 3H), 2.27 (d, $J = 12.8$ Hz, 1H), 1.63–1.80 (m, 5H), 1.65–1.62 (m, 1H), 1.41–1.45 (m, 2H), 1.21 (s, 3H), 1.20 (d, $J = 6.5$ Hz, 6H), 0.97 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 147.02,
146.03, 145.58, 134.69, 129.93, 129.90, 129.73, 126.81, 124.14, 123.77, 63.17 (d, $J = 9.9$ Hz), 44.62, 38.15, 37.60, 37.52, 36.43, 33.42, 29.94, 25.38, 23.97, 23.94, 21.74, 18.98, 18.92, 18.58.

$N$-(4-((tert-butyldimethylsilyl)oxy)butyl)-$N$-fluoro-4-methylbenzenesulfonamide (6a)

Yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 (d, $J = 8.2$ Hz, 2H), 7.39 (d, $J = 8.2$ Hz, 2H), 3.62 (t, $J = 6.0$ Hz, 2H), 3.24 (dt, $J = 40.8$, 6.8 Hz, 2H), 2.47 (s, 3H), 1.75–1.82 (m, 2H), 1.58–1.65 (m, 2H), 0.87 (s, 9H), 0.02 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 146.13, 129.94, 129.89, 128.96, 62.35, 53.61 (d, $J = 12.4$ Hz), 29.60, 25.89, 23.09, 21.74, 18.25, -5.40. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{17}$H$_{30}$FNNaO$_3$Si, 398.1592; found, 398.1594. IR (KBr, cm$^{-1}$): $\nu$ 3683, 3560, 3473, 3411, 1597, 1177.

$N$-(4-(benzyloxy)butyl)-$N$-fluoro-4-methylbenzenesulfonamide (6b)

Yellow solid. mp: 30.4–31.5 ºC; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 (d, $J = 8.2$ Hz, 2H), 7.38 (d, $J = 8.2$ Hz, 2H), 7.36–7.26 (m, 5H), 4.48 (s, 2H), 3.49 (t, $J = 6.0$ Hz, 2H), 3.24 (dt, $J = 40.8$, 6.8 Hz, 2H), 2.47 (s, 3H), 1.79–1.87 (m, 2H), 1.69–1.76 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 146.15, 138.41, 129.94, 129.89, 128.91, 128.36, 127.58, 127.54, 72.89, 69.48, 53.52 (d, $J = 12.4$ Hz), 26.69, 23.36, 21.75. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{18}$H$_{22}$FNNaO$_3$S, 374.1197; found, 374.1199. IR (KBr, cm$^{-1}$): $\nu$ 3712, 3457, 3474, 3509, 1736, 1171.

(R)-$N$-(3-(2-((tert-butyldimethylsilyl)oxy)ethyl)-5-methylhexyl)-$N$-fluoro-4-methylbenzenesulfonamide (6c)
Yellow oil. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.82 (d, \(J = 8.2\) Hz, 2H), 7.40 (d, \(J = 8.2\) Hz, 2H), 3.60 (t, \(J = 6.6\) Hz, 2H), 3.25 (dt, \(J = 40.4, 6.8\) Hz, 2H), 2.48 (s, 3H), 1.66–1.70 (m, 3H), 1.58–1.65 (m, 1H), 1.46–1.52 (m, 1H), 1.39–1.45 (m, 1H), 1.09–1.13 (m, 1H), 0.99–1.08 (m, 1H), 0.87 (s, 9H), 0.85 (d, \(J = 6.6\)Hz, 6H), 0.02 (s, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 146.11, 129.93, 129.89, 129.15, 60.74, 51.61 (d, \(J = 12.4\) Hz), 43.58, 36.64, 30.45, 29.84, 25.92, 25.20, 22.78, 22.73, 21.76, 18.23, -5.38, -5.39. HRMS–ESI (m/z): [M+Na]~ calcd. for C\(_{22}\)H\(_{40}\)FNNaO\(_3\)Si, 468.2374; found, 468.2370. IR (KBr, cm\(^{-1}\)): \(\nu\) 3683, 3556, 3473, 3411, 1725, 1597, 1176.

\(N\)-fluoro-4-methyl-\(N\)-(octan-4-yl)benzenesulfonamide (8a)

Yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.83 (d, \(J = 8.2\) Hz, 2H), 7.37 (d, \(J = 8.2\) Hz, 2H), 3.87 (dp, \(J = 38.8, 6.4\) Hz, 1H), 2.46 (s, 3H), 1.51–1.70 (m, 4H), 1.24–1.46 (m, 6H), 0.89 (t, \(J = 5.6\) Hz, 3H), 0.87 (t, \(J = 5.2\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 145.54, 133.12, 129.78, 129.12, 63.25 (d, \(J = 12.9\) Hz), 32.94 (d, \(J = 5.8\) Hz), 30.49 (d, \(J = 6.2\) Hz), 28.44, 22.45, 21.70, 19.51, 13.88, 13.82. HRMS–ESI (m/z): [M+Na]~ calcd. for C\(_{15}\)H\(_{24}\)FNNaO\(_2\)S, 324.1404; found, 324.1407. IR (KBr, cm\(^{-1}\)) \(\nu\) 3711, 3554, 3477, 3409, 1730, 1596, 1171.

\(N\)-fluoro-4-methyl-\(N\)-(4-methyl-2-propylpentyl)benzenesulfonamide (8b)
White solid. mp: 45.3–46.3 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.81 (d, \(J = 8.2\) Hz, 2H), 7.40 (d, \(J = 8.2\) Hz, 2H), 3.09 (ddd, \(J = 24.4, 14.2, 6.6\) Hz, 1H), 3.03 (ddd, \(J = 24.4, 14.2, 6.6\) Hz, 1H), 2.48 (s, 3H), 1.78–1.88 (m, 1H), 1.61 (quint, \(J = 6.6\) Hz, 1H), 1.35–1.44 (m, 1H), 1.24–1.34 (m, 3H), 1.14–1.24 (m, 2H), 0.87 (t, \(J = 7.0\) Hz, 3H), 0.86 (d, \(J = 6.6\) Hz, 3H), 0.84 (d, \(J = 6.6\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 146.06, 129.85, 129.78, 129.08, 57.53 (d, \(J = 11.9\) Hz), 41.52, 34.30, 33.07, 25.05, 22.74, 22.54, 21.66, 19.16, 14.21. HRMS–ESI (m/z): [M+Na]\(^+\) calcd. for C\(_{16}\)H\(_{26}\)FNNaO\(_2\)S, 338.1560; found, 338.1567. IR (KBr, cm\(^{-1}\)): v 3750, 3558, 3481, 3408, 3234, 1740, 1616, 1172.

\(N-(7\text{-methyloctan-4-yl})\text{-4-methylbenzenesulfonamide (8c)}\)

![Chemical Structure](image)

Colorless oil. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.83 (d, \(J = 8.1\) Hz, 2H), 7.37 (d, \(J = 8.1\) Hz, 2H), 3.83 (dp, \(J = 38.4, 6.3\) Hz, 1H), 2.46 (s, 3H), 1.61–1.67 (m, 2H), 1.56 (dd, \(J = 14.2, 7.8\) Hz, 2H), 1.45–1.51 (m, 1H), 1.38–1.43 (m, 2H), 1.24 (dt, \(J = 12.0, 5.7\) Hz, 2H), 0.89 (t, \(J = 7.3\) Hz, 3H), 0.86 (d, \(J = 6.6\) Hz, 3H), 0.83 (d, \(J = 6.6\) Hz, 3H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 145.55, 133.12, 129.80, 129.12, 63.58 (d, \(J = 12.8\) Hz), 35.40, 33.00 (d, \(J = 5.5\) Hz), 28.64 (d, \(J = 6.4\) Hz), 27.90, 22.47, 22.38, 21.68, 19.51, 13.81. HRMS–ESI (m/z): [M+Na]\(^+\) calcd. for C\(_{16}\)H\(_{26}\)FNNaO\(_2\)S, 338.1560; found, 338.1567. IR (KBr, cm\(^{-1}\)): v 3540, 3474, 3405, 3235, 1728, 1616, 1171.

4-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)disulfaneyl)butanenitrile (10c)
Yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.31 (dd, $J$ = 8.3, 1.9 Hz, 1H), 7.25 (dd, $J$ = 9.6, 4.6 Hz, 2H), 2.92 (dd, $J$ = 8.6, 4.0 Hz, 2H), 2.82 (t, $J$ = 6.8 Hz, 2H), 2.49–2.57 (m, 1H), 2.46 (t, $J$ = 7.1 Hz, 2H), 2.37–2.45 (m, 1H), 2.29 (td, $J$ = 10.6, 4.3 Hz, 1H), 2.12 (dd, $J$ = 12.8, 5.5 Hz, 1H), 2.04–2.10 (m, 3H), 2.00–2.05 (m, 1H), 1.94–1.99 (m, 1H), 1.58–1.64 (m, 2H), 1.50–1.57 (m, 3H), 1.44–1.49 (m, 1H), 0.91 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 220.54, 139.56, 137.73, 133.52, 129.07, 126.27, 126.10, 118.88, 50.43, 47.88, 44.22, 37.95, 36.53, 35.77, 31.51, 29.28, 26.28, 25.63, 24.21, 21.53, 15.66, 13.79. HRMS–ESI ($m/z$): [M+Na]$^+$ calcd. for C$_{22}$H$_{27}$NNaOS$_2$, 408.1426; found, 408.1434. IR (KBr, cm$^{-1}$): v 3440, 2931, 1648, 1630, 552.

$N$-(2,2-dimethylnon-8-en-1-yl)-$N$-fluoro-4-methylbenzenesulfonamide (14a)

Yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J$ = 8.2 Hz, 2H), 7.40 (d, $J$ = 8.1 Hz, 2H), 5.80 (ddt, $J$ = 16.9, 10.2, 6.7 Hz, 1H), 4.98 (dd, $J$ = 16.9, 1.6 Hz, 1H), 4.93 (dd, $J$ = 10.2, 1.6 Hz, 1H), 3.01 (d, $J$ = 44.6 Hz, 2H), 2.49 (s, 3H), 2.03 (q, $J$ = 7.5 Hz, 2H), 1.34–1.42 (m, 2H), 1.18–1.33 (m, 6H), 0.94 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 146.02, 139.07, 129.90, 129.81, 129.62, 114.20, 63.01 (d, $J$ = 10.5 Hz), 40.13, 34.29, 33.73, 29.80, 28.80, 25.56, 23.45, 21.76. HRMS–ESI ($m/z$): [M+Na]$^+$ calcd. for C$_{18}$H$_{28}$FNNaO$_3$S, 364.1717; found, 364.1723. IR (KBr, cm$^{-1}$): v 3711, 3473, 3407, 1731, 1560, 1175.

$N$-(4-cyclopropylbutyl)-$N$-fluoro-4-methylbenzenesulfonamide (16a)
White solid. mp: 31.3–32.5 ºC; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.75 (d, \(J = 8.1\) Hz, 2H), 7.33 (d, \(J = 8.1\) Hz, 2H), 3.14 (dt, \(J = 40.8, 7.0\) Hz, 2H), 2.41 (s, 3H), 1.64–1.69 (m, 2H), 1.40–1.45 (m, 2H), 1.12–1.15 (m, 2H), 0.53–0.60 (m, 1H), 0.28–0.37 (m, 2H), (-0.09)–(-0.07) (m, 2H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 146.14, 129.94, 129.89, 128.98, 53.74 (d, \(J = 12.4\) Hz), 34.12, 26.64, 26.11, 21.75, 10.60, 4.37, 1.00. HRMS–ESI (m/z): [M+Na]^+ calcd. for C\(_{14}\)H\(_{20}\)FNNaO\(_2\)S, 308.1091; found, 308.1089. IR (KBr, cm\(^{-1}\)): \(\nu\) 3576, 3516, 3352, 1636, 1117, 548.

\(N\)-fluoro-\(N\)-(hex-5-en-1-yl)-4-methylbenzenesulfonamide (18a)

Colorless oil. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.82 (d, \(J = 8.1\) Hz, 2H), 7.41 (d, \(J = 8.1\) Hz, 2H), 5.77 (ddt, \(J = 16.9, 10.2, 6.7\) Hz, 1H), 5.00 (dd, \(J = 16.9, 1.5\) Hz, 1H), 4.95 (d, \(J = 10.2\) Hz, 1H), 3.22 (dt, \(J = 40.6, 6.9\) Hz, 2H), 2.48 (s, 3H), 2.05–2.09 (m, 2H), 1.67–1.76 (m, 2H), 1.45–1.55 (m, 2H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 146.18, 138.01, 129.95, 129.91, 128.96, 115.01, 53.47 (d, \(J = 12.3\) Hz), 33.09, 25.74, 25.68, 21.76. HRMS–ESI (m/z): [M+Na]^+ calcd. for C\(_{13}\)H\(_{18}\)FNNaO\(_2\)S, 294.0934; found, 294.0930. IR (KBr, cm\(^{-1}\)): \(\nu\) 3565, 3419, 3337, 2929, 2361, 1638, 1176.

General Procedures for Site-Selective Csp\(^3\)-S Bond Formation

In an oven-dried 8 mL screwed-capped vial Cu(acac)\(_2\) (2.6 mg, 0.01 mmol, 10 mol%),
1,10-phen (1.8 mg, 0.01 mmol, 10 mol%), Na$_2$HPO$_4$ (19.9 mg, 0.14 mmol, 1.4 equiv), 1a (30.1 mg, 0.1 mmol, 1.0 equiv), 2a (26.2 mg, 0.12 mmol, 1.2 equiv) were weighted. Then the vial was transferred into the glove-box, indium powder (19.6 mg, 0.17 mmol, 1.7 equiv) and anhydrous DCE (0.6 mL) were added to the vial. The vial was sealed and moved outside of the glove-box. The vial was kept in a 40 ℃ water bath and irradiated with two 50 W blue LED lamps which were cooled by a fan (2–3 cm away from the vial). After the reaction completion monitored by TLC ($R_f = 0.4$, PE/EA/DCM = 10:1:0.5, about 9 hours), the reaction was quenched by brine (2 mL), and extracted with EtOAc (5 mL × 2), the organic solvent was filtrated through a pad of short anhrdrous Na$_2$SO$_4$ column. Evaporation and flash Silica gel column purification (EtOAc/petroleum ether/DCM = 1:15:0.5 as eluent) of the crude product provided 3a (29.3 mg) in 75% isolated yield.

Characterization Data for Products

$N$-(4-(phenylthio)octyl)-4-methylbenzenesulfonamide (3a)

![Figure S1. two 50 W LED lamps with a fan](image1)

![Figure S2. Before reaction](image2)

![Figure S3. After reaction](image3)
Colourless oil. **^1H NMR** (600 MHz, CDCl$_3$) δ 7.72 (d, $J = 8.1$ Hz, 2H), 7.33 (d, $J = 7.5$ Hz, 2H), 7.30 (d, $J = 8.1$ Hz, 2H), 7.28 (d, $J = 7.5$ Hz, 2H), 7.22 (t, $J = 7.2$ Hz, 1H), 4.29 (t, $J = 6.0$ Hz, 1H), 2.98 (quint, $J = 6.6$ Hz, 1H), 2.88–2.96 (m, 2H), 2.42 (s, 3H), 1.58–1.68 (m, 2H), 1.47–1.54 (m, 3H), 1.33–1.45 (m, 3H), 1.24–1.30 (m, 2H), 0.87 (t, $J = 7.3$ Hz, 3H). **^13C NMR** (150 MHz, CDCl$_3$) δ 143.38, 137.01, 135.23, 132.01, 129.70, 128.86, 127.10, 126.82, 48.71, 43.10, 34.32, 31.39, 28.94, 26.72, 22.54, 21.49, 13.95. **HRMS–ESI** (m/z): [M+Na]$^+$ calcd. for C$_{21}$H$_{29}$NNaO$_2$S$_2$, 414.1532; found, 414.1530. **IR** (KBr, cm$^{-1}$): ν 3554, 3474, 3414, 2928, 1616, 1159.

**N-(4-(p-tolylthio)octyl)-4-methylbenzenesulfonamide (3b)**

Colourless oil. **^1H NMR** (600 MHz, CDCl$_3$) δ 7.72 (d, $J = 8.1$ Hz, 2H), 7.30 (d, $J = 8.1$ Hz, 2H), 7.24 (d, $J = 8.1$ Hz, 2H), 7.08 (d, $J = 8.1$ Hz, 2H), 4.33 (t, $J = 6.0$ Hz, 1H), 2.86–2.95 (m, 3H), 2.42 (s, 3H), 2.33 (s, 3H), 1.59–1.67 (m, 2H), 1.48–1.55 (m, 1H), 1.41–1.48 (m, 3H), 1.32–1.41 (m, 2H), 1.23–1.30 (m, 2H), 0.87 (t, $J = 7.3$ Hz, 3H). **^13C NMR** (150 MHz, CDCl$_3$) δ 143.37, 137.11, 136.98, 132.84, 131.12, 129.69, 129.63, 127.09, 49.11, 43.09, 34.23, 31.29, 28.94, 22.54, 21.49, 21.06, 13.97. **HRMS–ESI** (m/z): [M+Na]$^+$ calcd. for C$_{22}$H$_{31}$NNaO$_2$S$_2$, 428.1688; found, 428.1685. **IR** (KBr, cm$^{-1}$): ν 3698, 3059, 1729, 1561, 900.

**N-(4-((4-methoxyphenyl)thio)octyl)-4-methylbenzenesulfonamide (3c)**

Colourless oil. **^1H NMR** (600 MHz, CDCl$_3$) δ 7.73 (d, $J = 8.1$ Hz, 2H), 7.31 (d, $J = 8.7$ Hz, 2H), 7.30 (d, $J = 8.1$ Hz, 2H), 6.82 (d, $J = 8.7$ Hz, 2H), 4.45 (t, $J = 6.0$ Hz,
1H, 3.80 (s, 3H), 2.87–2.95 (m, 2H), 2.76 (quint, J = 5.4 Hz, 1H), 2.42 (s, 3H), 1.59–1.68 (m, 2H), 1.47–1.51 (m, 1H), 1.38–1.44 (m, 4H), 1.33–1.38 (m, 1H), 1.22–1.29 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 159.40, 143.35, 136.97, 135.60, 129.68, 127.08, 124.72, 114.41, 55.29, 49.87, 43.08, 34.10, 31.17, 28.92, 26.68, 22.52, 21.48, 13.97. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{22}$H$_{31}$NNaO$_4$S$_2$, 444.1638; found, 444.1635. IR (KBr, cm$^{-1}$): ν 3746, 3423, 2930, 1591, 1493, 1159.

4-((1-((4-methylphenyl)sulfonamido)octan-4-yl)thio)phenyl acetate (3d)

![Chemical Structure 3d]

Colourless oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.73 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.7 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.01 (d, J = 8.7 Hz, 2H), 4.32 (t, J = 6.3 Hz, 1H), 2.96–2.90 (m, 3H), 2.42 (s, 3H), 2.30 (s, 3H), 1.60–1.66 (m, 2H), 1.45–1.51 (m, 3H), 1.33–1.44 (m, 3H), 1.24–1.30 (m, 2H), 0.88 (t, J = 7.3 Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 169.26, 149.81, 143.39, 136.98, 133.52, 132.28, 129.71, 127.10, 122.04, 49.27, 43.08, 34.25, 31.36, 28.91, 26.76, 22.53, 21.50, 21.12, 13.96. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{23}$H$_{31}$NNaO$_4$S$_2$, 472.1587; found, 472.1583. IR (KBr, cm$^{-1}$): ν 3472, 1620, 1400, 1119, 619.

$N$-(4-((4-chlorophenyl)thio)octyl)-4-methylbenzenesulfonamide (3e)

![Chemical Structure 3e]

Colourless oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.73 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.7 Hz, 2H), 7.23 (d, J = 8.7 Hz, 2H), 4.34 (t, J = 6.1 Hz, 1H), 2.89–2.98 (m, 3H), 2.43 (s, 3H), 1.60–1.64 (m, 2H), 1.56–1.59 (m, 1H), 1.45–
1.50 (m, 3H), 1.33–1.41 (m, 2H), 1.23–1.30 (m, 2H), 0.87 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 143.43, 137.02, 133.76, 133.36, 132.97, 129.72, 129.02, 127.10, 49.11, 43.07, 34.25, 31.34, 28.90, 26.78, 22.52, 21.49, 13.93. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{21}$H$_{28}$ClNNaO$_2$S$_2$, 448.1142; found, 448.1139. IR (KBr, cm$^{-1}$): $\nu$ 3557, 3417, 2928, 1615, 1158.

$N$-(4-((3,5-dichlorophenyl)thio)octyl)-4-methylbenzenesulfonamide (3f)

![3f](image)

Colourless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.73 (d, $J = 8.1$ Hz, 2H), 7.31 (d, $J = 8.1$ Hz, 2H), 7.17 (t, $J = 1.8$ Hz, 1H), 7.15 (d, $J = 1.8$ Hz, 2H), 4.41 (t, $J = 6.3$ Hz, 1H), 3.04–3.09 (m, 1H), 2.91–2.97 (m, 2H), 2.42 (s, 3H), 1.59–1.64 (m, 3H), 1.49–1.55 (m, 3H), 1.33–1.41 (m, 2H), 1.25–1.31 (m, 2H), 0.89 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 143.47, 139.70, 136.92, 135.07, 129.73, 128.34, 127.09, 126.44, 48.50, 43.02, 34.15, 31.27, 28.77, 26.73, 22.48, 21.50, 13.90. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{21}$H$_{27}$Cl$_2$NNaO$_2$S$_2$, 482.0752; found, 482.0752. IR (KBr, cm$^{-1}$): $\nu$ 3555, 3416, 2929, 1615, 1159.

$N$-(4-((2,4,5-trichlorophenyl)thio)octyl)-4-methyl benzenesulfonamide (3g)

![3g](image)

Colourless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.73 (d, $J = 8.1$ Hz, 2H), 7.47 (s, 1H), 7.36 (s, 1H), 7.30 (d, $J = 8.1$ Hz, 2H), 4.35 (t, $J = 6.3$ Hz, 1H), 3.13–3.17 (m, 1H), 2.91–2.98 (m, 2H), 2.43 (s, 3H), 1.61–1.65 (m, 3H), 1.53–1.56 (m, 3H), 1.35–1.41 (m, 2H), 1.25–1.32 (m, 2H), 0.89 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$
143.48, 137.00, 135.57, 134.01, 131.90, 131.26, 130.94, 130.74, 129.74, 127.10, 47.90, 43.07, 33.97, 31.01, 28.71, 26.68, 22.53, 21.49, 13.89. HRMS–ESI (m/z): [M+Na]^+ calcd. for C_{21}H_{26}Cl_{3}NaO_{2}S_{2}, 516.0363; found, 516.0353. IR (KBr, cm\(^{-1}\)): \(\nu\) 3715, 3415, 2929, 1740, 1435, 1158.

\(N\)-(4-((4-bromophenyl)thio)octyl)-4-methylbenzenesulfonamide (3h)

\[\text{Colourless oil. } ^1H\text{ NMR (600 MHz, CDCl}_3) \delta 7.72 (d, J = 8.1 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 4.30 (t, J = 6.0 Hz, 1H), 2.94–2.91 (m, 1H), 2.88–2.95 (m, 2H), 2.43 (s, 3H), 1.58–1.65 (m, 2H), 1.45–1.52 (m, 3H), 1.33–1.42 (m, 2H), 1.22–1.31 (m, 3H), 0.88 (t, J = 7.2 Hz, 3H). \]

\(\text{^13C NMR (150 MHz, CDCl}_3) \delta 143.45, 136.94, 134.47, 133.44, 131.94, 129.72, 127.09, 120.84, 48.92, 43.05, 34.22, 31.30, 28.89, 26.75, 22.52, 21.51, 13.95. } \]

HRMS–ESI (m/z): [M+Na]^+ calcd. for C_{21}H_{26}BrNNaO_{2}S_{2}, 492.0637; found, 492.0633. IR (KBr, cm\(^{-1}\)): \(\nu\) 3558, 3417, 3234, 2927, 1615.

\(N\)-(4-((4-fluorophenyl)thio)octyl)-4-methylbenzenesulfonamide (3i)

\[\text{Colourless oil. } ^1H\text{ NMR (400 MHz, CDCl}_3) \delta 7.73 (d, J = 8.1 Hz, 2H), 7.28–7.36(m, 4H), 6.95–6.99(m, 2H), 4.41 (t, J = 6.3 Hz, 1H), 2.92 (q, J = 6.9 Hz, 2H), 2.86 (quint, J = 6.6 Hz, 1H), 2.43 (s, 3H), 1.60–1.67 (m, 2H), 1.49–1.56 (m, 1H), 1.40–1.49 (m, 3H), 1.33–1.41 (m, 1H), 1.21–1.31 (m, 3H), 0.87 (t, J = 7.2 Hz, 3H). \]

\(\text{^13C NMR (150 MHz, CDCl}_3) \delta 162.29 (d, J = 247.5 Hz), 143.42, 136.99, 135.05 (d, J = 8.0 Hz), 129.79 (d, J = 3.2 Hz), 129.70, 127.09, 115.94 (d, J = 21.8 Hz), 49.73, 43.07, 34.16, \)
N-(4-((4-nitrophenyl)thio)octyl)-4-methylbenzenesulfonamide (3j)

Yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.11 (d, $J = 8.8$ Hz, 2H), 7.72 (d, $J = 8.2$ Hz, 2H), 7.33 (d, $J = 8.8$ Hz, 2H), 7.30 (d, $J = 8.2$ Hz, 2H), 4.37 (t, $J = 6.2$ Hz, 1H), 3.25–3.32 (m, 1H), 2.95 (q, $J = 6.2$ Hz, 2H), 2.42 (s, 3H), 1.67–1.74 (m, 1H), 1.59–1.67 (m, 4H), 1.35–1.44 (m, 2H), 1.26–1.34 (m, 3H), 0.89 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 146.99, 145.33, 143.54, 136.87, 129.75, 127.99, 127.06, 123.97, 47.08, 42.94, 34.18, 31.22, 28.87, 26.79, 22.53, 21.50, 13.91. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{21}$H$_{28}$FNNaO$_2$S$_2$, 459.1383; found, 459.1380. IR (KBr, cm$^{-1}$): ν 3717, 3560, 2929, 1742, 1512, 1336.

N-(4-((3-nitrophenyl)thio)octyl)-4-methylbenzenesulfonamide (3k)

Yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.12 (s, 1H), 8.03 (d, $J = 8.2$ Hz, 1H), 7.72 (d, $J = 8.0$ Hz, 2H), 7.62 (d, $J = 7.8$ Hz, 1H), 7.44 (t, $J = 8.0$ Hz, 1H), 7.30 (d, $J = 8.0$ Hz, 2H), 4.41 (t, $J = 6.2$ Hz, 1H), 3.12–3.20 (m, 1H), 2.94 (q, $J = 6.2$ Hz, 2H), 2.42 (s, 3H), 1.60–1.70 (m, 2H), 1.54–1.59 (m, 3H), 1.36–1.44 (m, 2H), 1.23–1.34 (m, 3H), 0.88 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 148.49, 143.50, 138.87, 136.91, 136.32, 129.73, 129.58, 127.06, 124.74, 121.13, 48.51, 43.00, 34.16, 31.27,
28.83, 26.78, 22.50, 21.49, 13.90. **HRMS–ESI** \((m/z)\): [M+Na]\(^+\) calcd. for C\(_{21}\)H\(_{28}\)N\(_2\)NaO\(_4\)S\(_2\), 459.1383; found, 459.1386. **IR** (KBr, cm\(^{-1}\)): \(\nu\) 3715, 2930, 1734, 1527, 1348, 1158.

**N-(4-(naphthalen-2-ylthio)octyl)-4-methylbenzenesulfonamide (3l)**

![3l](image)

Colourless oil. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.79 (brs, 2H), 7.74 (t, \(J = 7.5\) Hz, 2H), 7.70 (d, \(J = 8.1\) Hz, 2H), 7.43–7.50 (m, 2H), 7.40 (d, \(J = 8.4\) Hz, 1H), 7.25 (d, \(J = 6.3\) Hz, 2H), 4.39 (t, \(J = 6.0\) Hz, 1H), 3.12 (quint, \(J = 6.7\) Hz, 1H), 2.69–2.95 (m, 2H), 2.39 (s, 3H), 1.64–1.71 (m, 2H), 1.59–1.64 (m, 1H), 1.51–1.56 (m, 3H), 1.39–1.46 (m, 2H), 1.23–1.31 (m, 2H), 0.88 (t, \(J = 7.2\) Hz, 3H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 143.35, 136.95, 133.67, 132.79, 132.11, 130.22, 129.45, 128.45, 127.35, 127.25, 127.07, 125.96, 48.61, 43.10, 34.31, 31.41, 28.96, 26.74, 22.55, 21.46, 13.96. **HRMS–ESI** \((m/z)\): [M+Na]\(^+\) calcd. for C\(_{25}\)H\(_{31}\)N\(_2\)NaO\(_2\)S\(_2\), 464.1688; found, 464.1687. **IR** (KBr, cm\(^{-1}\)): \(\nu\) 3727, 3557, 3414, 2929, 1742, 1734, 1576.

**N-(4-(thiophen-2-ylthio)octyl)-4-methylbenzenesulfonamide (3m)**

![3m](image)

Colourless oil. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.74 (d, \(J = 8.1\) Hz, 2H), 7.35 (dd, \(J = 5.4, 1.0\) Hz, 1H), 7.31 (d, \(J = 8.1\) Hz, 2H), 7.05 (dd, \(J = 3.6, 1.0\) Hz, 1H), 6.98 (dd, \(J = 5.4, 3.6\) Hz, 1H), 4.36 (t, \(J = 6.0\) Hz, 1H), 2.95 (q, \(J = 6.3\) Hz, 2H), 2.63–2.68 (m, 1H), 2.43 (s, 3H), 1.67–1.75 (m, 1H), 1.61–1.66 (m, 1H), 1.41–1.52 (m, 5H), 1.33–1.40 (m, 1H), 1.24–1.32 (m, 2H), 0.89 (t, \(J = 7.3\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\)

N-(4-(benzylthio)octyl)-4-methylbenzenesulfonamide (3n)

 Colourless oil. **$^1$H NMR** (400 MHz, CDCl$_3$) δ 7.73 (d, $J = 8.2$ Hz, 2H), 7.39 (s, 5H), 7.30 (d, $J = 8.2$ Hz, 2H), 4.65 (t, $J = 6.2$ Hz, 1H), 4.21 (s, 2H), 2.96–2.84 (m, 2H), 2.68–2.74 (m, 1H), 2.42 (s, 3H), 1.91–1.78 (m, 2H), 1.74–1.64 (m, 2H), 1.61–1.50 (m, 2H), 1.43–1.34 (m, 1H), 1.34–1.26 (m, 3H), 0.89 (t, $J = 7.1$ Hz, 3H). **$^{13}$C NMR** (100 MHz, CDCl$_3$) δ 143.33, 138.76, 137.03, 129.67, 128.84, 128.41, 127.08, 126.88, 44.80, 43.07, 35.10, 34.53, 31.38, 28.84, 26.59, 22.55, 21.48, 13.97. **HRMS–ESI** (m/z): [M+Na]$^+$ calcd. for C$_{22}$H$_{31}$NNaO$_2$S$_2$, 428.1688; found, 428.1687. **IR** (KBr, cm$^{-1}$): ν 3700, 3416, 2929, 1738, 1556.

N-(4-(phenylselanyl)octyl)-4-methylbenzenesulfonamide (3o)

 Colourless oil. **$^1$H NMR** (600 MHz, CDCl$_3$) δ 7.72 (d, $J = 8.1$ Hz, 2H), 7.33 (d, $J = 7.5$ Hz, 2H), 7.30 (d, $J = 8.1$ Hz, 2H), 7.28 (d, $J = 7.5$ Hz, 2H), 7.22 (t, $J = 7.2$ Hz, 1H), 4.29 (t, $J = 6.0$ Hz, 1H), 2.98 (quint, $J = 6.6$ Hz, 1H), 2.88–2.96 (m, 2H), 2.42 (s, 3H), 1.57–1.66 (m, 2H), 1.46–1.50 (m, 3H), 1.37–1.42 (m, 3H), 1.24–1.30 (m, 2H), 0.87 (t, $J = 7.2$ Hz, 3H). **$^{13}$C NMR** (150 MHz, CDCl$_3$) δ 143.53, 137.13, 135.04, 129.81, 129.26, 129.07, 127.59, 127.21, 45.98, 42.91, 35.08, 32.23, 30.22, 28.05,
22.86, 21.91, 14.34. **HRMS–ESI (m/z):** [M+Na]⁺ calcd. for C₂₁H₂₉NNaO₂SSe, 462.0976; found, 462.0972. **IR (KBr, cm⁻¹):** ν 3695, 3476, 3419, 2926, 1912, 1158.

**N-(4-(phenylthio)butyl)-4-methylbenzenesulfonamide (4a)**

 Colourless oil. **¹H NMR** (600 MHz, CDCl₃) δ 7.72 (d, J = 8.1 Hz, 2H), 7.27–7.31 (m, 6H), 7.16–7.20 (m, 1H), 4.26 (t, J = 6.0 Hz, 1H), 2.95 (q, J = 6.6 Hz, 2H), 2.86 (t, J = 6.6 Hz, 2H), 2.42 (s, 3H), 1.60–1.63 (m, 4H). **¹³C NMR** (150 MHz, CDCl₃) δ 143.46, 136.94, 136.19, 129.73, 129.31, 128.93, 127.09, 126.07, 42.69, 33.13, 28.59, 26.02, 21.50. **HRMS–ESI (m/z):** [M+Na]⁺ calcd. for C₁₇H₂₁NNaO₂S, 358.0906; found, 358.0912. **IR (KBr, cm⁻¹):** ν 3483, 3387, 3104, 1758, 1614, 1158.

**N-(1-(phenylthio)heptan-4-yl)-4-methylbenzenesulfonamide (4b)**

 White solid. mp: 58.3–59.5 °C. **¹H NMR** (600 MHz, CDCl₃) δ 7.72 (d, J = 8.1 Hz, 2H), 7.26–7.28 (m, 6H), 7.15–7.20 (m, 1H), 4.25 (d, J = 8.4 Hz, 1H), 3.19–3.24 (m, 1H), 2.77 (t, J = 6.9 Hz, 2H), 2.41 (s, 3H), 1.52–1.57 (m, 2H), 1.46–1.51 (m, 1H), 1.39–1.45 (m, 1H), 1.29–1.35 (m, 1H), 1.17–1.28 (m, 2H), 1.10–1.17 (m, 1H), 0.76 (t, J = 7.2 Hz, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 143.23, 138.26, 136.44, 129.59, 129.10, 128.87, 126.99, 125.91, 53.43, 37.34, 33.74, 33.97, 33.35, 24.76, 21.49, 18.43, 13.75. **HRMS–ESI (m/z):** [M+Na]⁺ calcd. for C₂₀H₂₇NNaO₂S₂, 400.1375; found, 400.1373. **IR (KBr, cm⁻¹):** ν 3718, 3555, 3412, 2925, 1745, 1614.

**N-(tert-butyl)-2-((phenylthio)methyl)benzamide (4c)**
White solid. mp: 66.3–67.5 °C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.40–7.44 (m, 1H), 7.30–7.31 (m, 2H), 7.26–7.29 (m, 4H), 7.19–7.22 (m, 2H), 6.06 (s, 1H), 4.30 (s, 2H), 1.43 (s, 9H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 168.79, 137.95, 135.96, 134.24, 130.65, 129.91, 129.60, 128.93, 127.75, 127.53, 126.63, 51.96, 36.71, 28.74. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{18}$H$_{21}$NaOS, 322.1236; found, 322.1238. IR (KBr, cm$^{-1}$): ν 3742, 3553, 3410, 2968, 1746, 1617.

$N$-($\text{tert}$-butyl)-2-(1-(phenylthio)ethyl)benzamide (4d)

White solid. mp: 67.3–68.2 °C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.57 (d, $J = 7.8$ Hz, 1H), 7.37 (t, $J = 7.5$ Hz, 1H), 7.26–7.29 (m, 3H), 7.19–7.24 (m, 4H), 5.64 (brs, 1H), 4.91 (q, $J = 6.9$ Hz, 1H), 1.64 (d, $J = 6.9$ Hz, 3H), 1.40 (s, 9H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 169.19, 140.46, 137.57, 134.99, 132.14, 129.79, 128.75, 127.71, 127.15, 127.00, 126.71, 51.81, 43.43, 28.69, 22.15. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{19}$H$_{23}$NaOS, 336.1393; found, 336.1393. IR (KBr, cm$^{-1}$): ν 3738, 3554, 3412, 2969, 1762, 1614.

$N$-(4-(phenylthio)pentyl)-4-methylbenzenesulfonamide (4e)

Colourless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.73 (d, $J = 8.1$ Hz, 2H), 7.35 (d, $J = 7.2$ Hz, 2H), 7.27–7.31 (m, 3H), 7.26–7.27 (m, 1H), 7.23 (t, $J = 7.2$ Hz, 1H), 4.47 (t, $J$
= 6.0 Hz, 1H), 3.09–3.15 (m, 1H), 2.89–2.97 (m, 2H), 2.42 (s, 3H), 1.60–1.65 (m, 2H),
1.47–1.56 (m, 2H), 1.22 (d, J = 6.6 Hz, 3H). 13C NMR (150 MHz, CDCl3) δ 143.41, 136.93, 134.79, 132.15, 129.70, 128.84, 127.08, 126.93, 42.98, 42.87, 33.39, 26.97, 21.49, 21.17. HRMS–ESI (m/z): [M+Na]+ calcd. for C18H23NNaO2S2, 372.1062; found, 372.1061. IR (KBr, cm⁻¹): ν 3731, 3550, 2925, 1747, 1158, 1092.

**N-(2,2-dimethyl-4-(phenylthio)hexyl)-4-methylbenzenesulfonamide (4f)**

![Structure 4f](image)

Colourless oil. 1H NMR (600 MHz, CDCl3) δ 7.69 (d, J = 8.1 Hz, 2H), 7.25–7.16 (m, 4H), 7.21–7.24 (m, 3H), 5.04 (t, J = 8.1 Hz, 1H), 2.87–2.91 (m, 1H), 2.71–2.78 (m, 2H), 2.39 (s, 3H), 1.57–1.63 (m, 1H), 1.51 (dd, J = 15.9, 7.5 Hz, 2H), 1.42 (dd, J = 15.4, 2.7 Hz, 1H), 0.98 (s, 3H), 0.93 (t, J = 7.2 Hz, 3H), 0.90 (s, 3H). 13C NMR (150 MHz, CDCl3) δ 143.11, 137.13, 135.11, 131.70, 129.63, 128.95, 127.05, 127.01, 52.03, 45.96, 42.95, 34.36, 30.23, 26.81, 25.10, 21.48, 10.71. HRMS–ESI (m/z): [M+Na]+ calcd. for C21H29NNaO2S2, 414.1532; found, 414.1528. IR (KBr, cm⁻¹): ν 3720, 3553, 2967, 1740, 1614, 1560.

**N-(4-(phenylthio)hexyl)-4-methyl benzenesulfonamide (4g)**

![Structure 4g](image)

Colourless oil. 1H NMR (600 MHz, CDCl3) δ 7.72 (d, J = 8.4 Hz, 2H), 7.31–7.34 (m, 2H), 7.28–7.30 (m, 2H), 7.25–7.27 (m, 2H), 7.19–7.24 (m, 1H), 4.32 (t, J = 6.3 Hz, 1H), 2.96–3.01 (m, 1H), 2.89–2.95 (m, 2H), 2.42 (s, 3H), 1.59–1.69 (m, 2H), 1.52–1.56 (m, 1H), 1.44–1.52 (m, 3H), 1.35–1.43 (m, 2H), 1.21–1.31 (m, 10H), 0.88 (t, J = 7.2 Hz, 3H). 13C NMR (150 MHz, CDCl3) δ 143.37, 136.99, 135.23, 132.01, 129.69, 128.84, 127.09, 126.80, 48.75, 43.09, 34.63, 31.84, 31.40, 29.46, 29.44, 29.23, 26.77, 26.71, 22.64, 21.49, 14.08. HRMS–ESI (m/z): [M+Na]+ calcd. for C25H37NNaO2S2, 470.2158; found, 470.2152. IR (KBr, cm⁻¹): ν 3714, 2926, 1735, 1573, 1573, 1159.
\(N-(5-(1,3\text{-dioxoisindolin-2-yl})-4\text{-}(phenylthio)pentyl)-4\text{-}methylbenzenesulfonamide (4h)\)

Colourless oil. \(^1\text{H NMR}\) (600 MHz, CDCl\(_3\)) \(\delta\) 7.91 (d, \(J = 7.5\) Hz, 2H), 7.79 (d, \(J = 3.0\) Hz, 2H), 7.71 (d, \(J = 7.5\) Hz, 4H), 7.54–7.58 (m, 1H), 7.51 (t, \(J = 7.5\) Hz, 2H), 7.29 (d, \(J = 7.8\) Hz, 2H), 4.65 (t, \(J = 6.0\) Hz, 1H), 4.02 (dd, \(J = 14.1, 6.6\) Hz, 1H), 3.74 (dd, \(J = 14.1, 6.6\) Hz, 1H), 3.70 (t, \(J = 6.0\) Hz, 1H), 2.91–3.01 (m, 2H), 2.42 (s, 3H), 1.93–2.00 (m, 1H), 1.78–1.84 (m, 2H), 1.62–1.68 (m, 1H). \(^{13}\text{C NMR}\) (150 MHz, CDCl\(_3\)) \(\delta\) 167.79, 143.44, 137.37, 136.82, 134.26, 133.89, 131.60, 129.73, 129.29, 128.75, 127.06, 123.50, 60.43, 42.50, 36.65, 26.18, 21.48. HRMS–ESI (\(m/z\)) \([M+Na]^+\) calcd. for C\(_{26}\)H\(_{26}\)NNaO\(_2\)S\(_2\), 517.1226; found, 517.1226. IR (KBr, cm\(^{-1}\)): \(\nu\) 3714, 3552, 2928, 1714, 1589, 1402.

\(\text{Methyl-6-}((4\text{-methylphenyl)sulfonamido})\text{-3-(phenylthio)hexanoate (4i)}\)

Colourless oil. \(^1\text{H NMR}\) (600 MHz, CDCl\(_3\)) \(\delta\) 7.87 (d, \(J = 7.8\) Hz, 2H), 7.72 (d, \(J = 7.5\) Hz, 2H), 7.68 (t, \(J = 7.5\) Hz, 1H), 7.59 (t, \(J = 7.5\) Hz, 2H), 7.31 (d, \(J = 7.8\) Hz, 2H), 4.64 (t, \(J = 6.0\) Hz, 1H), 3.63 (s, 3H), 3.51–3.55 (m, 1H), 2.92 (quint, \(J = 4.8\) Hz,2H), 2.84 (dd, \(J = 16.8, 4.8\) Hz, 1H), 2.43 (s, 3H), 2.42 (t, \(J = 12.4\) Hz, 1H), 1.92–1.96 (m, 1H), 1.65–1.68 (m, 1H), 1.59–1.63 (m, 2H). \(^{13}\text{C NMR}\) (150 MHz, CDCl\(_3\)) \(\delta\) 170.65, 143.50, 137.01, 136.89, 134.11, 129.75, 129.37, 128.98, 127.06, 60.01, 52.34, 42.47, 33.45, 26.63, 25.56, 21.50. HRMS–ESI (\(m/z\)) \([M+Na]^+\) calcd. for C\(_{20}\)H\(_{25}\)NNaO\(_4\)S\(_2\), 430.1117; found, 430.1119. IR (KBr, cm\(^{-1}\)): \(\nu\) 3719, 3553, 3063, 1738, 1560, 1154.

\(N\text{-}(5\text{-}((\text{tert-butyl}d\text{imethyl}silyl)oxy)-4\text{-}(\text{phenylthio})pentyl)-4\text{-}methylbenzenesulfonamide (4j)}\)
Colourless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.85 (d, \(J = 8.2\) Hz, 2H), 7.72 (d, \(J = 8.2\) Hz, 2H), 7.64 (t, \(J = 7.4\) Hz, 1H), 7.54 (t, \(J = 7.8\) Hz, 2H), 7.30 (d, \(J = 7.8\) Hz, 2H), 4.51 (t, \(J = 6.3\) Hz, 1H), 3.86 (dd, \(J = 11.0, 6.4\) Hz, 1H), 3.81 (dd, \(J = 11.0, 6.4\) Hz, 1H), 3.02–3.08 (m, 1H), 2.95 (q, \(J = 6.6\) Hz, 2H), 2.43 (s, 3H), 1.90–1.99 (m, 1H), 1.73–1.79 (m, 2H), 1.39–1.52 (m, 1H), 0.76 (s, 9H), -0.06 (s, 3H), -0.08 (s, 3H).

\(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.46, 138.60, 136.88, 133.67, 129.75, 129.08, 128.78, 127.08, 66.07, 60.43, 42.80, 29.68 (grease), 27.03, 25.70, 22.70, 21.50, 18.09, -5.67, -5.71. HRMS–ESI (m/z): [M+Na]\(^+\) calcd. for C\(_{24}\)H\(_{37}\)NNaO\(_3\)S\(_2\)Si, 502.1876; found, 502.1881.

IR (KBr, cm\(^{-1}\)): \(\nu\) 3718, 3554, 3063, 1736, 1560.

\(N\)-(5-((tert-butyldimethylsilyl)oxy)-4-(phenylthio)pentyl)-4-methylbenzenesulfonamide (4k)

Colourless oil. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.72 (d, \(J = 8.1\) Hz, 2H), 7.34 (d, \(J = 7.5\) Hz, 2H), 7.29 (d, \(J = 8.1\) Hz, 2H), 7.26 (t, \(J = 7.5\) Hz, 2H), 7.21 (t, \(J = 7.2\) Hz, 1H), 4.32 (t, \(J = 6.0\) Hz, 1H), 3.75–3.79 (m, 1H), 3.69–3.73 (m, 1H), 3.21 (dt, \(J = 13.6, 6.9\) Hz, 1H), 2.92 (dt, \(J = 9.9, 6.6\) Hz, 2H), 2.42 (s, 3H), 1.71 (dd, \(J = 12.6, 6.3\) Hz, 2H), 1.66 (dd, \(J = 12.6, 6.6\) Hz, 1H), 1.59–1.64 (m, 2H), 1.47–1.53 (m, 1H), 0.87 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H). \(^1^3\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 143.36, 137.00, 135.20, 131.68, 129.69, 128.86, 127.09, 126.72, 60.25, 45.00, 43.06, 37.78, 31.83, 26.81, 25.91, 21.49, 18.23, -5.37. HRMS–ESI (m/z): [M+Na]\(^+\) calcd. for C\(_{25}\)H\(_{39}\)NNaO\(_3\)S\(_2\)Si, 516.2033; found, 516.2026. IR (KBr, cm\(^{-1}\)): \(\nu\) 3725, 3554, 3408, 2933, 1742, 1562.

6-((4-methylphenyl)sulfonamido)-3-(phenylthio)hexyl benzoate (4l)
Colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (d, $J = 10.8$ Hz, 2H), 7.88 (d, $J = 10.8$ Hz, 2H), 7.70 (d, $J = 8.2$ Hz, 2H), 7.66 (t, $J = 7.6$ Hz, 1H), 7.54–7.60 (m, 3H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.29 (d, $J = 8.2$ Hz, 2H), 4.56 (t, $J = 6.2$ Hz, 1H), 4.35 (t, $J = 6.4$ Hz, 2H), 3.15 (quint, $J = 6.2$ Hz, 1H), 2.93 (q, $J = 6.2$ Hz, 2H), 2.42 (s, 3H), 2.24–2.31 (m, 1H), 1.87–1.99 (m, 2H), 1.61–1.80 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.21, 143.51, 137.31, 136.84, 133.97, 133.26, 129.76, 129.66, 129.56, 129.38, 128.82, 128.48, 127.05, 61.67, 60.92, 42.70, 27.84, 26.69, 25.21, 21.49. HRMS–ESI (m/z): [M+Na]$^+$ calcld. for C$_{26}$H$_{29}$NNaO$_4$S$_2$, 506.1430; found, 506.1427. IR (KBr, cm$^{-1}$): v 3713, 3553, 3063, 1719, 1560, 1276.

$N$-(2-methyl-2-2-(phenylthio)cyclobutyl)propyl)-4-methylbenzenesulfonamide (4m)

Colourless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.73 (d, $J = 8.1$ Hz, 2H), 7.29 (d, $J = 8.1$ Hz, 2H), 7.25–7.27 (m, 4H), 7.20–7.24 (m, 1H), 5.14 (t, $J = 7.2$ Hz, 1H), 3.47 (q, $J = 8.7$ Hz, 1H), 2.68 (dd, $J = 7.2$, 3.9 Hz, 2H), 2.42 (s, 3H), 2.23–2.28 (m, 1H), 2.19 (q, $J = 9.3$ Hz, 1H), 1.83–1.90 (m, 1H), 1.76–1.82 (m, 1H), 1.61–1.65 (m, 1H), 0.89 (s, 3H), 0.81 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 143.14, 137.22, 134.98, 131.01, 129.65, 128.94, 127.03, 126.86, 52.49, 50.38, 42.11, 35.29, 28.06, 22.82, 21.49, 21.06, 19.54. HRMS–ESI (m/z): [M+Na]$^+$ calcld. for C$_{21}$H$_{27}$NNaO$_2$S$_2$, 412.1375; found, 412.1374. IR (KBr, cm$^{-1}$): v 3713, 3284, 3062, 2965, 1730, 1577.

$N$-(2-methyl-2-2-(phenylthio)cyclopentylpropyl)-4-methylbenzenesulfonamide (4n)
Colourless oil. \textbf{\textsuperscript{1}H NMR} (600 MHz, CDCl$_3$) $\delta$ 7.71 (d, $J$ = 8.1 Hz, 2H), 7.26–7.28 (m, 2H), 7.24–7.25 (m, 2H), 7.22 (d, $J$ = 7.8 Hz, 3H), 5.15 (dd, $J$ = 5.7, 5.7 Hz, 1H), 3.22–3.25 (m, 1H), 2.80 (dd, $J$ = 12.9, 5.7 Hz, 1H), 2.74 (dd, $J$ = 12.9, 5.7 Hz, 1H), 2.39 (s, 3H), 1.75–1.82 (m, 3H), 1.70–1.74 (m, 1H), 1.65–1.70 (m, 1H), 1.62–1.63 (m, 1H), 1.28–1.35 (m, 1H), 0.94 (s, 3H), 0.84 (s, 3H). \textbf{\textsuperscript{13}C NMR} (150 MHz, CDCl$_3$) $\delta$ 143.09, 137.14, 136.39, 130.51, 129.64, 128.93, 127.01, 126.65, 53.19, 51.85, 47.36, 36.51, 35.96, 28.37, 24.99, 24.18, 21.47, 20.89. \textbf{HRMS–ESI} ($m/z$): [M+Na$^+$] calcd. for C$_{22}$H$_{29}$NNaO$_2$S$_2$, 426.1532; found, 426.1527. \textbf{IR} (KBr, cm$^{-1}$): $\nu$ 3721, 3397, 3066, 1731, 1563, 1160.

\textbf{N-(2-methyl-2--2-(phenylthio)cyclohexylpropyl)-4-methylbenzenesulfonamide (4o)}

White solid. mp: 168.3–169.5 ºC; \textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl$_3$) $\delta$ 7.72 (d, $J$ = 8.2 Hz, 2H), 7.25–7.26 (m, 7H), 4.75 (dd, $J$ = 5.8, 5.8 Hz, 1H), 3.10–3.14 (m, 1H), 2.94 (dd, $J$ = 12.6, 5.6 Hz, 1H), 2.87 (dd, $J$ = 12.6, 5.6 Hz, 1H), 2.40 (s, 3H), 1.63–1.81 (m, 4H), 1.39–1.51 (m, 2H), 1.16–1.33 (m, 3H), 1.00 (s, 3H), 0.91 (s, 3H). \textbf{\textsuperscript{13}CNMR} (100 MHz, CDCl$_3$) $\delta$ 143.17,137.04, 135.36, 131.95, 129.65, 128.94, 127.10, 127.07, 52.82, 47.44, 45.58, 37.64, 29.91, 25.11, 24.11, 23.00, 22.45, 21.49, 21.11. \textbf{HRMS–ESI} ($m/z$): [M+Na$^+$] calcd. for C$_{23}$H$_{31}$NNaO$_2$S$_2$, 440.1668; found, 440.1691. \textbf{IR} (KBr, cm$^{-1}$): $\nu$ 3710, 3062, 1734, 1559, 1159.

\textbf{N-(-3-(phenylthio)cyclohexylmethyl)-4-methyl benzenesulfonamide (4p)}


White solid. mp: 108.0–109.0 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.72 (d, $J = 8.1$ Hz, 2H), 7.35 (d, $J = 7.2$ Hz, 2H), 7.26–7.30 (m, 4H), 7.22 (t, $J = 7.2$ Hz, 1H), 4.29 (t, $J = 6.3$ Hz, 1H), 3.54–3.55 (m, 1H), 2.81 (td, $J = 6.6$, 2.7 Hz, 2H), 2.42 (s, 3H), 1.89–1.96 (m, 1H), 1.71–1.81 (m, 2H), 1.61–1.69 (m, 3H), 1.48–1.54 (m, 1H), 1.41–1.46 (m, 1H), 0.98–1.09 (m, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 143.37, 137.04, 135.51, 131.48, 129.71, 128.93, 127.06, 126.71, 48.30, 44.37, 34.69, 32.71, 30.97, 29.64, 21.50, 20.63. HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{20}$H$_{25}$NaO$_2$S$_2$, 398.1219; found, 398.1219. IR (KBr, cm$^{-1}$): ν 3721, 3554, 2928, 1733, 1572, 1158.

$N$-(-3-(phenylthio)cycloheptylmethyl)-4-methylbenzenesulfonamide (4q)

White solid. mp: 93.1–94.0 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.70 (d, $J = 8.1$ Hz, 2H), 7.66 (d, $J = 8.1$ Hz, 2H), 7.36–7.38 (m, 2H), 7.32–7.34 (m, 2H), 7.27–7.32 (m, 1/2×8H, 1/2×8H), 7.20–7.26 (m, 1/2×2H, 1/2×2H), 4.47 (t, $J = 6.3$ Hz, 1H), 4.27 (t, $J = 6.3$ Hz, 1H), 3.38–3.42 (m, 1H), 3.15–3.20 (m, 1H), 2.74–2.77 (m, 2H), 2.68–2.73 (m, 1H), 2.62–2.67 (m, 1H), 2.42 (s, 1/2×6H, 1/2×6H), 2.01–2.07 (m, 1H), 1.97–1.99 (m, 1H), 1.79–1.84 (m, 1H), 1.70–1.79 (m, 5H), 1.59–1.68 (m, 5H), 1.51–1.57 (m, 1H), 1.43–1.51 (m, 3H), 1.31–1.34 (m, 2H), 1.24–1.27 (m, 1H), 1.14–1.21 (m, 1H), 1.05–1.11 (m, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 143.38, 143.27, 137.10, 137.04, 135.60 (C×2), 131.89, 131.32, 129.70, 129.65, 129.01, 128.91, 127.09, 127.06, 126.91, 126.64, 49.40, 49.18, 46.81, 45.99, 38.69, 38.59, 36.74, 35.17, 34.76, 34.59, 32.22, 31.88, 27.93, 26.73, 25.55, 25.29, 21.49 (C×2). HRMS–ESI (m/z): [M+Na]$^+$ calcd. for C$_{21}$H$_{27}$NaO$_2$S$_2$, 412.1375; found, 412.1375. IR (KBr, cm$^{-1}$): ν 3724, 3553, 2925, 2856, 1734, 1158.
N-(2-((1r,3s,5R,7S)-2-(phenylthio)adamantan-1-yl)ethyl)-4-methylbenzenesulfonamide (4r)

Colorless oil. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.70 (d, \(J = 7.8\) Hz, 2H), 7.31 (d, \(J = 7.8\) Hz, 2H), 7.23–7.27 (m, 4H), 7.23 (t, \(J = 6.9\) Hz, 1H), 4.25 (t, \(J = 5.4\) Hz, 1H), 3.21 (s, 1H), 2.92–3.03 (m, 2H), 2.40 (s, 3H), 2.24 (d, \(J = 12.6\) Hz, 1H), 1.92–1.95 (m, 3H), 1.76–1.83 (m, 2H), 1.65–1.71 (m, 3H), 1.60 (d, \(J = 12.3\) Hz, 2H), 1.46–1.52 (m, 2H), 1.31–1.37 (m, 1H), 1.27 (d, \(J = 12.9\) Hz, 1H). \(^1\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 143.22, 136.93, 136.00, 131.76, 129.63, 128.96, 127.15, 126.74, 59.64, 42.73, 40.55, 38.92, 38.08, 38.04, 37.04, 36.29, 33.21, 31.26, 28.06, 28.00, 21.49. HRMS–ESI (m/z): [M+Na\(^+\)] calcd. for C\(_{25}\)H\(_{31}\)NNaO\(_2\)S\(_2\), 464.1688; found, 464.1682. IR (KBr, cm\(^{-1}\)): \(\nu\) 3715, 3554, 2925, 1738, 1558, 1372.

N-(3-phenyl-1-(-3-(phenylthio)cyclohexylpropyl)-4-methylbenzenesulfonamide (4s)

Colorless oil. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.73 (d, \(J = 8.1\) Hz, 1/3×2H), 7.70 (d, \(J = 8.1\) Hz, 2/3×2H), 7.33–7.35 (m, 1/3×2H,2/3×2H), 7.25–7.30(m, 1/3×4H,2/3×4H), 7.19–7.24 (m, 1/3×3H,2/3×3H), 7.14–7.17 (m, 1/3×1H,2/3×1H), 6.95 (d, \(J = 7.2\) Hz, 1/3×2H), 6.90 (d, \(J = 7.2\) Hz, 2/3×2H), 4.50 (d, \(J = 9.0\) Hz, 1/3×1H), 4.37 (d, \(J = 9.0\) Hz, 2/3×1H), 3.64 (t, \(J = 3.0\) Hz, 2/3×1H), 3.11–3.18 (m, 1/3×1H,2/3×1H), 2.85–2.89 (m, 1/3×1H), 2.31–2.49 (m, 1/3×1H,2/3×1H), 2.41 (s, 1/3×3H,2/3×3H), 2.40 (t, \(J = 7.2\) Hz, 1/3×2H, 2/3×2H), 1.94–2.00 (m, 1/3×1H, 2/3×1H), 1.76–1.84 (m, 1/3×1H,2/3×1H), 1.62–1.71 (m, 1/3×2H, 2/3×2H), 1.50–1.63 (m, 1/3×2H, 2/3×2H),
1.40–1.49 (m, 1/3×1H, 2/3×1H), 1.08–1.22 (m, 1/3×1H, 2/3×1H), 0.98 (quint, J = 12.3 Hz, 1/3×1H, 2/3×1H), 0.82–0.89 (m, 1/3×1H, 2/3×1H). 13C NMR (150 MHz, CDCl3) δ 143.33, 143.17, 141.19 (C×2), 138.44, 138.40, 135.77, 134.64, 132.03, 131.31, 129.63 (C×2), 128.94, 128.81, 128.38, 128.34, 128.25, 128.21, 127.04, 127.02, 126.85, 126.59, 125.97, 125.91, 58.12, 57.69, 46.19, 45.22, 41.72, 35.46, 35.13, 34.13, 33.75, 33.72, 33.26, 31.94, 31.52, 30.60, 27.37, 27.26, 25.92, 21.51, 21.49, 20.90. HRMS–ESI (m/z): [M+Na]+ calcd. for C28H33NNaO2S2, 502.1845; found, 502.1839. IR (KBr, cm⁻¹): ν 3716, 3554, 3061, 1740, 1558, 1371.

N-((1S)-1-(3-(phenylthio)cyclohexyl)ethyl)-4-methylbenzenesulfonamide (4t)

![4t](image)

White solid. mp: 107.0–108.0 °C; 1H NMR (400 MHz, CDCl3) δ 7.74 (d, J = 8.2 Hz, 2H), 7.34–7.38 (m, 2H), 7.26–7.32 (m, 4H), 7.19–7.24 (m, 1H), 4.12 (d, J = 9.2 Hz, 1H), 3.60–3.61 (m, 1H), 3.14–3.21 (m, 1H), 2.42 (s, 3H), 1.75–1.83 (m, 2H), 1.66–1.75 (m, 3H), 1.5–1.66 (m, 2H), 1.51–1.58 (m, 2H), 0.90 (d, J = 6.7 Hz, 3H). 13C NMR (150 MHz, CDCl3) δ 143.20, 138.28, 135.70, 131.56, 129.64, 128.92, 127.04, 126.70, 53.65, 45.18, 38.14, 33.73, 30.68, 27.44, 21.51, 20.80, 19.07. HRMS–ESI (m/z): [M+Na]+ calcd. for C21H27NNaO2S2, 412.1375; found, 412.1372. IR (KBr, cm⁻¹):

1): ν 3736, 3553, 3034, 1738, 1613, 1557.

N-((5-(phenylthio)tetrahydrofuran-2-yl)methyl)-4-methylbenzenesulfonamide (4u)

![4u](image)

Colourless oil. 1H NMR (600 MHz, CDCl3) δ 7.72 (d, J = 8.4 Hz, 2H), 7.42–7.46 (m, 2H), 7.27–7.31 (m, 4H), 7.23–7.26 (m, 1H), 5.59 (dd, J = 7.2, 4.2 Hz, 1H), 4.69 (t, J =
6.3 Hz, 1H), 4.26–4.31 (m, 1H), 3.19 (ddd, $J = 12.9, 6.3, 3.6$ Hz, 1H), 2.99–3.04 (m, 1H), 2.42 (s, 3H), 2.35–2.40 (m, 1H), 1.95–2.07 (m, 2H), 1.68–1.75 (m, 1H). \[^{13}\text{C}\text{NMR}\] (150 MHz, CDCl\(_3\)) δ 143.50, 136.94, 135.01, 131.49, 129.76, 128.89, 127.18, 127.04, 87.63, 76.47, 46.05, 32.72, 27.37, 21.52. \[^{13}\text{C}\text{NMR}\] \((m/z)\): [M+Na]\(^+\) calcd. for C\(_{18}\)H\(_{21}\)NNaO\(_3\)S\(_2\), 386.0855; found, 386.0854. IR (KBr, cm\(^{-1}\)): ν 3719, 3553, 3059, 1740, 1612, 1557.

\(\text{N-((6-(phenylthio)tetrahydro-2H-pyran-2-yl)methyl)-4-methylbenzenesulfonamide (4v)}\)

Colourless oil. \[^1\text{H}\text{NMR}\] (600 MHz, CDCl\(_3\)) δ 7.63 (d, $J = 8.1$ Hz, 2H), 7.45 (d, $J = 7.5$ Hz, 2H), 7.34 (t, $J = 7.5$ Hz, 2H), 7.29 (t, $J = 7.2$ Hz, 1H), 7.25 (d, $J = 7.5$ Hz, 2H), 5.53 (d, $J = 4.5$ Hz, 1H), 4.42 (dd, $J = 7.5, 3.9$ Hz, 1H), 4.25–4.29 (m, 1H), 3.05–3.10 (m, 1H), 2.80–2.85 (m, 1H), 2.41 (s, 3H), 1.90–1.98 (m, 2H), 1.79–1.84 (m, 1H), 1.68–1.73 (m, 1H), 1.30–1.40 (m, 2H). \[^{13}\text{C}\text{NMR}\] (150 MHz, CDCl\(_3\)) δ 143.23, 136.98, 134.62, 131.91, 129.62, 129.08, 127.35, 127.01, 84.86, 67.76, 47.42, 30.28, 28.23, 21.49, 18.82. \[^{13}\text{C}\text{NMR}\] \((m/z)\): [M+Na]\(^+\) calcd. for C\(_{19}\)H\(_{23}\)NNaO\(_3\)S\(_2\), 400.1012; found, 400.1013. IR (KBr, cm\(^{-1}\)): ν 3703, 3063, 1732, 1557, 1368, 918.

\(\text{N-(1-phenyl-4-(phenylthio)pentyl)-4-methylbenzenesulfonamide (4w)}\)

Colourless oil. \[^1\text{H}\text{NMR}\] (600 MHz, CDCl\(_3\)) δ 7.52 (d, $J = 8.1$ Hz, 1/2×4H, 1/2×4H), 7.29 (d, $J = 7.2$ Hz, 1/2×4H, 1/2×4H), 7.20–7.26 (m,1/2×6H, 1/2×6H),7.12–7.18 (m, 1/2×6H, 1/2×6H), 7.10 (d,J = 8.1 Hz, 2H), 7.09 (d,J = 8.1 Hz, 2H), 6.96–6.99 (m, 1/2×4H, 1/2×4H), 4.80 (d, $J = 7.4$ Hz, 1/2×2H, 1/2×2H), 4.24 (q, $J = 7.4$ Hz, 1/2×2H, 1/2×2H), 3.09 (quint, $J = 13.2$, 6.6 Hz, 1/2×2H, 1/2×2H), 2.34 (s, 1/2×6H,
1.18–1.39 (m, 1/2×12H, 1/2×12H), 1.01 (d, J = 6.6 Hz, 3H), 1.00 (d, J = 6.6 Hz, 3H), 0.94 (t, J = 7.2 Hz, 1/2×6H, 1/2×6H). 13C NMR (150 MHz, CDCl3) δ 143.20, 138.20, 138.19, 135.30, 135.28, 132.00, 131.99, 129.62 (C×2), 128.81, 128.80, 127.02 (C×2), 126.74, 126.72, 50.53, 50.32, 50.19, 49.77, 34.46, 34.43, 29.74 (C×2), 27.58, 27.31, 21.89, 21.86, 21.46 (C×2), 11.09, 11.06. HRMS–ESI (m/z): [M+Na]+ calcd. for C20H27NNaO2S2, 400.1375; found, 400.1375. IR (KBr, cm⁻¹): ν 3718, 3278, 2966, 1734, 1576, 1158.

N-(2-isopropyl-4-(phenylthio)pentyl)-4-methylbenzenesulfonamide (4y)

White solid. mp: 100.3–101.5 °C; 1H NMR (600 MHz, CDCl3) δ 7.73 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 7.8 Hz, 1/2×4, 1/2×4H), 7.25–7.30 (m, 1/2×8H, 1/2×8H), 7.21 (t, J = 7.2 Hz, 1/2×2H, 1/2×2H), 4.37 (d, J = 8.1 Hz, 1/2×2, 1/2×2H), 3.24–3.30 (m, 1/2×2H, 1/2×2H), 2.85–2.92 (m, 1/2×2H, 1/2×2H), 2.41 (s, 1/2×6H, 1/2×6H), 1.40–1.59 (m, 1/2×12H, 1/2×12H), 1.01 (d, J = 6.6 Hz, 3H), 1.00 (d, J = 6.6 Hz, 3H), 0.94 (t, J = 7.2 Hz, 1/2×6H, 1/2×6H). 13C NMR (150 MHz, CDCl3) δ 143.17, 138.20, 138.19, 135.30, 135.28, 132.00, 131.99, 129.62 (C×2), 128.81, 128.80, 127.02 (C×2), 126.74, 126.72, 50.53, 50.32, 50.19, 49.77, 34.46, 34.43, 29.74 (C×2), 27.58, 27.31, 21.89, 21.86, 21.46 (C×2), 11.09, 11.06. HRMS–ESI (m/z): [M+Na]+ calcd. for C20H27NNaO2S2, 400.1375; found, 400.1375. IR (KBr, cm⁻¹): ν 3718, 3278, 2966, 1734, 1576, 1158.
2H), 7.72 (d, \( J = 8.4 \) Hz, 2H), 7.34–7.38 (m, 1/2×4H, 1/2×4H), 7.28–7.31 (m, 1/2×8H, 1/2×8H), 7.22–7.25 (m, 1/2×2H, 1/2×2H), 4.42 (t, \( J = 6.3 \) Hz, 1H), 4.37 (t, \( J = 6.3 \) Hz, 1H), 3.15–3.20 (m, 1H), 3.09–3.18 (m, 1H), 2.93–2.97 (m, 1H), 2.85–2.88 (m, 1H), 2.80–2.89 (m, 1/2×2H, 1/2×2H), 2.43 (s, 3H), 2.42 (s, 3H), 1.70–1.75 (m, 1H), 1.65–1.69 (m, 1H), 1.50–1.54 (m, 1/2×2H, 1/2×2H), 1.36–1.46 (m, 1/2×4H, 1/2×4H), 1.22 (d, \( J = 6.6 \) Hz, 3H), 1.21 (d, \( J = 6.6 \) Hz, 3H), 0.79 (t, \( J = 6.9 \) Hz, 6H), 0.78 (t, \( J = 6.9 \) Hz, 6H).

\[ ^{13}C \text{ NMR (150 MHz, CDCl}_3 \] \( \delta \) 143.38 (C×2), 136.91, 136.86, 134.92, 134.72, 132.31, 132.08, 129.70 (C×2), 128.91, 128.86, 127.14 (C×2), 126.98 (C×2), 44.32, 44.16, 41.87, 41.73, 41.70, 41.12, 36.08, 36.04, 29.69, 28.62, 28.43, 22.44, 21.55, 21.50, 19.31, 19.12, 18.87, 18.68. \[ ^{13}C \text{ HRMS–ESI (m/z): [M+Na]}^+ \text{ calcd. for C}_{21}H_{29}NNaO_2S_2, 414.1532; found, 414.1529. \]

\[ ^{13}C \text{ IR (KBr, cm}^{-1}\text{): } \nu 3741, 3551, 2960, 1748, 1159. \]

**Mixture of \( N-(5\text{-methyl-4-(phenylthio)hexyl})-4\text{-methylbenzenesulfonamide(4z)} \) and \( N-(5\text{-methyl-5-(phenylthio)hexyl})-4\text{-methylbenzenesulfonamide (4z')} \)**

\[ \text{4z} \quad \text{Ts}^+ \quad \text{SPh} \]

\[ \text{4z} \quad \text{Ts}^- \quad \text{SPh} \]

Colourless oil. \[ ^{1}H \text{ NMR (600 MHz, CDCl}_3 \] \( \delta \) 7.75 (d, \( J = 8.1 \) Hz, 2/5×2H), 7.72 (d, \( J = 8.1 \) Hz, 3/5×2H), 7.45 (d, \( J = 6.9 \) Hz, 2/5×2H), 7.34 (d, \( J = 7.2 \) Hz, 3/5×2H), 7.28–7.31 (m, 2/5×3H, 3/5×3H), 7.23–7.26 (m, 2/5×1H, 3/5×1H, 2/5×1H), 7.22 (t, \( J = 7.2 \) Hz, 3/5×1H), 4.56 (t, \( J = 6.0 \) Hz, 2/5×1H), 4.51 (t, \( J = 6.0 \) Hz, 3/5×1H), 2.87–2.95 (m, 3/5×1H, 2/5×1H, 3/5×2H), 2.42 (s, 2/5×3H), 2.41 (s, 3/5×3H), 1.84–1.90 (m, 3/5×1H), 1.69–1.76 (m, 2/5×1H), 1.42–1.45 (m, 2/5×4H), 1.54–1.64 (m, 2/5×2H, 3/5×2H), 1.36–1.38 (m, 3/5×2H), 1.17 (s, 2/5×6H), 0.96 (d, \( J = 6.6 \) Hz, 3/5×3H), 0.93 (d, \( J = 6.6 \) Hz, 3/5×3H).

\[ ^{13}C \text{ NMR (150 MHz, CDCl}_3 \] \( \delta \) 143.33 (C×2), 137.40, 137.06, 137.01, 136.73, 132.18, 131.22, 129.69, 129.68, 128.85, 128.66, 128.46, 127.10, 127.09, 126.38, 56.47, 49.07, 43.15, 43.06, 41.75, 31.90, 29.99, 28.80, 28.71, 27.63, 21.84, 21.47, 21.46, 19.22, 19.15. \[ ^{13}C \text{ HRMS–ESI (m/z): [M+Na]}^+ \text{ calcd. for} \]
\[ \text{C}_{20}\text{H}_{27}\text{NNaO}_2\text{S}_2, \text{ 400.1375;  found, 400.1370.} \text{ IR (KBr, cm}^{-1}\text{): } \nu 3722, 3552, 2959, 1326, 1158. \]

**N-(2,2,4-trimethyl-4-(phenylthio)pentyl)-4-methyl benzenesulfonamide (4aa)**

![4aa](image)

Colourless oil. \(^1\text{H NMR}\) (600 MHz, CDCl\(_3\)) \(\delta\) 7.73 (d, \(J = 8.1\) Hz, 2H), 7.47 (d, \(J = 8.1\) Hz, 2H), 7.38 (t, \(J = 7.2\) Hz, 1H), 7.33 (t, \(J = 7.5\) Hz, 2H), 7.29 (d, \(J = 8.1\) Hz, 2H), 4.91 (t, \(J = 7.2\) Hz, 1H), 2.83 (d, \(J = 7.2\) Hz, 2H), 2.41 (s, 3H), 1.63 (s, 2H), 1.26 (s, 6H), 1.03 (s, 6H).\(^{13}\text{C NMR}\) (150 MHz, CDCl\(_3\)) \(\delta\) 143.22, 137.55, 137.19, 131.79, 129.67, 128.95, 128.57, 127.06, 53.94, 51.06, 49.93, 35.97, 31.02, 27.44, 21.49. \text{HRMS–ESI (m/z): [M+Na]}^+ \text{ calcd. for C}_{21}\text{H}_{29}\text{NNaO}_2\text{S}_2, 414.1532; \text{ found, 414.1531.}

\(\text{IR (KBr, cm}^{-1}\text{): } \nu 3451, 1722, 1572, 619.\)

**N-(3-(1-(phenylthio)cyclohexyl)propyl)-4-methyl benzenesulfonamide (4ab)**

![4ab](image)

Colorless oil. \(^1\text{H NMR}\) (600 MHz, CDCl\(_3\)) \(\delta\) 7.73 (d, \(J = 8.1\) Hz, 2H), 7.40 (d, \(J = 7.2\) Hz, 2H), 7.34 (t, \(J = 7.2\) Hz, 1H), 7.27–7.30 (m, 4H), 4.31 (t, \(J = 6.0\) Hz, 1H), 2.92 (q, \(J = 6.6\) Hz, 2H), 2.42 (s, 3H), 1.69–1.78 (m, 4H), 1.53–1.57 (m, 2H), 1.47–1.52 (m, 1H), 1.38–1.42 (m, 2H), 1.29–1.38 (m, 3H), 1.24–1.28 (m, 2H). \(^{13}\text{C NMR}\) (150 MHz, CDCl\(_3\)) \(\delta\) 143.37, 137.27, 137.04, 131.61, 129.68, 128.69, 128.58, 127.13, 53.46, 43.56, 36.23, 25.84, 23.91, 22.10, 21.49. \text{HRMS–ESI (m/z): [M+Na]}^+ \text{ calcd. for C}_{22}\text{H}_{29}\text{NNaO}_2\text{S}_2, 426.1532; \text{ found, 426.1545.} \text{ IR (KBr, cm}^{-1}\text{): } \nu 3690, 3523, 3451, 1722, 1572, 619.

\((2S)-2-((4\text{-methylphenyl)sulfonamido})-5\text{-}(\text{phenylthio})\text{hexyl pivalate (5a)}\)
Colourless oil. \(^1\text{H NMR}\) (600 MHz, CDCl\(_3\)) \(\delta\) 7.73 (d, \(J = 8.4\) Hz, 2H), 7.72 (d, \(J = 8.4\) Hz, 2H), 7.33 (d, \(J = 7.6\) Hz, 1/2×4H, 1/2×4H), 7.27–7.30 (m, 1/2×8H, 1/2×8H), 7.22–7.24 (m, 1/2×2H, 1/2×2H), 4.71 (d, \(J = 8.4\) Hz, 1H), 4.70 (d, \(J = 8.4\) Hz, 1H), 3.98 (dd, \(J = 11.4\), 4.5 Hz, 1H), 3.96 (dd, \(J = 11.4\), 4.5 Hz, 1H), 3.84 (dd, \(J = 11.4\), 4.5 Hz, 1H), 3.81 (dd, \(J = 11.4\), 4.5 Hz, 1H), 3.42–3.48 (m, 1/2×2H, 1/2×2H), 3.00–3.10 (m, 1/2×2H, 1/2×2H), 2.41 (s, 1/2×6H, 1/2×6H), 1.63–1.71 (m, 1/2×2H, 1/2×2H), 1.51–1.59 (m, 1/2×2H, 1/2×2H), 1.43–1.50 (m, 1/2×2H, 1/2×2H), 1.36–1.43 (m, 1/2×2H, 1/2×2H), 1.17 (s, 9H), 1.17 (d, \(J = 7.5\) Hz, 3H), 1.16 (s, 9H), 1.15 (d, \(J = 7.5\) Hz, 3H). \(^{13}\text{C NMR}\) (150 MHz, CDCl\(_3\)) \(\delta\) 178.19 (C×2), 143.58 (C×2), 137.95, 137.91, 134.74, 134.72, 132.19, 132.16, 129.78, 129.77, 128.86 (C×3), 126.98, 126.95 (C×2), 65.59, 65.49, 53.04, 52.63, 43.09, 42.85, 38.85 (C×2), 32.24, 32.14, 29.49 (C×2), 27.13 (C×2), 21.49, 21.42, 21.10 (C×2). \(\text{HRMS–ESI (m/z): } [\text{M+Na}]^+\) calcd. for C\(_{24}\)H\(_{33}\)NNaO\(_4\)S\(_2\), 486.1743; found, 486.1743. \(\text{IR (KBr, cm}^{-1}\): } \nu 3688, 3375, 3319, 1726, 1573, 1160.

(\(2\text{S}\))-5-((4-methoxyphenyl)thio)-2-((4-methylphenyl)sulfonamido)hexyl pivalate (5b)

Colourless oil. \(^1\text{H NMR}\) (600 MHz, CDCl\(_3\)) \(\delta\) 7.74 (d, \(J = 8.1\) Hz, 1/2×4H, 1/2×4H), 7.30 (d, \(J = 8.4\) Hz, 1/2×4H, 1/2×4H), 7.28 (d, \(J = 8.4\) Hz, 1/2×4H, 1/2×4H), 6.84 (d, \(J = 8.4\) Hz, 2H), 6.83 (d, \(J = 8.4\) Hz, 2H), 4.72 (d, \(J = 8.3\) Hz, 1/2×2H, 1/2×2H), 3.96–3.99 (m, 1/2×2H, 1/2×2H), 3.80–3.85 (m, 1/2×2H, 1/2×2H), 3.80 (s,
1/2×6H, 1/2×6H), 3.42–3.48 (m, 1/2×2H, 1/2×2H), 2.85–2.90 (m, 1H), 2.79–2.84 (m, 1H), 2.41 (s, 3H), 2.40 (s, 3H), 1.62–1.70 (m, 1/2×2H, 1/2×2H), 1.50–1.60 (m, 1/2×2H, 1/2×2H), 1.30–1.44 (m, 1/2×4H, 1/2×4H), 1.17 (s, 1/2×18H, 1/2×18H), 1.11 (d, J = 9.3 Hz, 3H), 1.10 (d, J = 9.3 Hz, 3H). 13C NMR (150 MHz, CDCl3) δ 178.18 (C×2), 159.57, 159.56, 143.54, 143.52, 138.04, 137.99, 135.77, 135.72, 129.76, 129.75, 126.96 (C×2), 124.50, 124.41, 114.44 (C×2), 65.60, 65.50, 55.30 (C×2), 53.08, 52.66, 44.26, 44.02, 38.85 (C×2), 32.13, 32.00, 29.54, 29.49, 27.13 (C×2), 21.46, 21.37, 21.04 (C×2).

HRMS–ESI (m/z): [M+Na]+ calcd. for C25H35NNaO5S2, 516.1849; found, 516.1845. IR (KBr, cm⁻¹): ν 3553, 3412, 3235, 1617, 1160, 617.

(2S)-2-((4-methylphenyl)sulfonamido)-5-(naphthalen-2-ylthio)hexyl pivalate (5c)

![Structural diagram of 5c](image)

Colourless oil. 1H NMR (600 MHz, CDCl3) δ 7.80 (d, J = 6.0 Hz, 1/2×4H, 1/2×4H), 7.75 (t, J = 8.1 Hz, 1/2×4H, 1/2×4H), 7.71 (d, J = 8.1 Hz, 2H), 7.44–7.50 (m, 1/2×4H, 1/2×4H), 7.41 (d, J = 8.4 Hz, 1H), 7.40 (d, J = 8.4 Hz, 1H), 7.22 (d, J = 8.1 Hz, 1/2×4H, 1/2×4H), 4.80 (d, J = 8.4 Hz, 1H), 4.79 (d, J = 8.4 Hz, 1H), 4.00 (dd, J = 11.4, 4.5 Hz, 1H), 3.97 (dd, J = 11.4, 4.5 Hz, 1H), 3.84 (dd, J = 11.4, 4.5 Hz, 1H), 3.84 (dd, J = 11.4, 4.5 Hz, 1H), 3.84 (dd, J = 11.4, 4.5 Hz, 1H), 3.44–3.50 (m, 1/2×2H, 1/2×2H), 3.13–3.23 (m, 1/2×2H, 1/2×2H), 2.37 (s, 3H), 2.36 (s, 3H), 1.68–1.73 (m, 1/2×2H, 1/2×2H), 1.58–1.63 (m, 1/2×2H, 1/2×2H), 1.43–1.54 (m, 1/2×4H, 1/2×4H), 1.21 (t, J = 6.5 Hz, 1/2×6H, 1/2×6H), 1.15 (s, 9H), 1.14 (s, 9H). 13C NMR (150 MHz, CDCl3) δ 178.19 (C×2), 143.53, 143.52, 137.92, 137.89, 133.66, 133.66 (C×2), 132.25, 132.18, 130.54, 130.52, 129.74, 129.73, 129.56 (C×2), 128.34 (C×2), 127.66 (C×2), 127.29, 127.28, 126.91 (C×3), 126.53, 126.51, 126.05 (C×2), 65.59, 65.50, 53.03, 52.67, 43.05, 42.85, 38.83 (C×2), 32.29, 32.19, 29.53, 29.51, 27.11 (C×2), S50
21.44, 21.43, 21.14 (C×2). **HRMS–ESI (m/z):** [M+Na]⁺ calcd. for C_{28}H_{35}NNaO_{4}S_{2}, 536.1900; found, 536.1894. **IR** (KBr, cm⁻¹): ν 3449, 3279, 3053, 1729, 1160, 666.

**(2S)-2-((4-methylphenyl)sulfonamido)-5-(thiophen-2-ylthio)hexyl pivalate (5d)**

![Structure of 5d](image)

Colourless oil. **¹H NMR** (600 MHz, CDCl₃) δ 7.73 (d, J = 7.2 Hz, 2H), 7.38 (d, J = 5.4 Hz, 1H), 7.28 (d, J = 7.8 Hz, 2H), 7.06 (d, J = 3.4 Hz, 1H), 6.99–7.02 (m, 1H), 4.57 (d, J = 8.4 Hz, 1H), 4.00 (dd, J = 11.4, 4.2 Hz, 1H), 3.85 (dd, J = 11.4, 4.2 Hz, 1H), 3.45–3.50 (m, 1H), 2.71–2.77 (m, 1H), 2.41 (s, 3H), 1.59–1.67 (m, 2H), 1.37–1.44 (m, 1H), 1.29–1.35 (m, 1H), 1.17 (s, 9H), 1.15 (d, J = 6.9 Hz, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 178.22, 143.60, 137.92, 135.51, 131.63, 130.15, 129.80, 127.61, 126.99, 65.71, 52.66, 45.70, 38.89, 31.66, 29.64, 27.17, 21.50, 21.41. **HRMS–ESI (m/z):** [M+Na]⁺ calcd. for C_{22}H_{31}NNaO_{2}S_{2}, 492.1307; found, 492.1303. **IR** (KBr, cm⁻¹): ν 3458, 2920, 1729, 1637, 1161, 667.

**(2S)-5-(benzylthio)-2-((4-methylphenyl)sulfonamido)hexyl pivalate (5e)**

![Structure of 5e](image)

Colourless oil. **¹H NMR** (600 MHz, CDCl₃) δ 7.74 (d, J = 8.1 Hz, 2H), 7.73 (d, J = 8.1 Hz, 2H), 7.28–7.31 (m, 1/2×12H, 1/2×12H), 7.20–7.25 (m, 1/2×2H, 1/2×2H), 4.62 (d, J = 8.4 Hz, 1H), 4.59 (d, J = 8.4 Hz, 1H), 3.93 (dd, J = 12.0, 4.2 Hz, 1H), 3.92 (dd, J = 12.0, 4.2 Hz, 1H), 3.79 (dd, J = 12.0, 4.2 Hz, 1H), 3.78 (dd, J = 12.0, 4.2 Hz, 1H), 3.66 (s, 1/2×4H, 1/2×4H), 3.40–3.45 (m, 1H), 3.32–3.36 (m, 1H), 2.51–
2.55 (m, 1H), 2.44–2.50 (m, 1H), 2.41 (s, 1/2×6H, 1/2×6H), 1.50–1.60 (m, 1/2×4H, 1/2×4H), 1.34–1.41 (m, 1/2×4H, 1/2×4H), 1.16 (s, 1/2×18H, 1/2×18H), 1.15 (d, J = 7.8 Hz, 3H), 1.14 (d, J = 7.8 Hz, 3H). 13C NMR (150 MHz, CDCl3) δ 178.19 (C×2), 143.55, 143.53, 138.66, 138.58, 138.09, 138.02, 129.76, 129.75, 128.76 (C×2), 128.48, 128.46, 126.94 (C×3), 126.92, 65.71, 65.52, 53.15, 52.61, 39.31, 38.85, 34.93, 34.75, 32.35, 32.06, 29.68 (C×2), 29.36, 29.32, 27.14 (C×2), 21.48, 21.37, 21.15 (C×2). HRMS–ESI (m/z): [M+Na]⁺ calcd. for C25H35NNaO4S2, 500.1900; found, 500.1984. IR (KBr, cm⁻¹): ν 3506, 3446, 3289, 1730, 1161, 667.

(2R,3S)-3-methyl-2-((4-methylphenyl)sulfonamido)-5-(phenylthio)pentylbenzoate (5f)

Colourless oil. 1H NMR (600 MHz, CDCl3) δ 7.86 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.41 (t, J = 7.5 Hz, 2H), 7.27–7.31 (m, 4H), 7.16–7.21 (m, 1H), 7.10 (d, J = 8.1 Hz, 2H), 4.89 (d, J = 8.4 Hz, 1H), 4.27 (dd, J = 11.7, 6.3 Hz, 1H), 4.10 (dd, J = 11.7, 6.3 Hz, 1H), 3.47–3.51 (m, 1H), 3.00 (ddd, J = 12.8, 8.7, 7.2 Hz, 1H), 2.84 (ddd, J = 12.8, 8.7, 7.2 Hz, 1H), 2.29 (s, 3H), 1.99–2.05 (m, 1H), 1.77–1.83 (m, 1H), 1.42–1.49 (m, 1H), 0.96 (d, J = 6.9 Hz, 3H). 13C NMR (150 MHz, CDCl3) δ 166.36, 143.36, 137.62, 136.11, 133.26, 129.77, 129.69, 129.34, 129.32, 128.94, 128.36, 126.88, 126.09, 63.90, 57.16, 34.85, 32.06, 31.46, 21.47, 15.17. HRMS–ESI (m/z): [M+Na]⁺ calcd. for C26H33NNaO4S2, 506.1430; found, 506.1426. IR (KBr, cm⁻¹): ν 3420, 1720, 1617, 1161, 614.

(2R)-4-methyl-2-((4-methylphenyl)sulfonamido)-5-(phenylthio)pentyl benzoate (5g)
Colourless oil. **H NMR** (400 MHz, CDCl$_3$) δ 7.93 (d, $J = 7.2$ Hz, 2H), 7.64 (d, $J = 8.1$ Hz, 2H), 7.58 (t, $J = 7.5$ Hz, 1H), 7.44 (t, $J = 7.8$ Hz, 2H), 7.28–7.32 (m, 4H), 7.17–7.19 (m, 1H), 7.14 (d, $J = 8.1$ Hz, 2H), 4.58 (d, $J = 8.7$ Hz, 1H), 4.23 (dd, $J = 11.4$, 4.5 Hz, 1H), 4.12 (dd, $J = 11.4$, 4.5 Hz, 1H), 3.64–3.70 (m, 1H), 2.83 (dd, $J = 12.9$, 6.1 Hz, 1H), 2.74 (dd, $J = 12.9$, 6.1 Hz, 1H), 2.34 (s, 3H), 1.79–1.88 (m, 1H), 1.68–1.72 (m, 1H), 1.31–1.39 (m, 1H), 0.87 (d, $J = 6.6$ Hz, 3H). **C NMR** (150 MHz, CDCl$_3$) δ 166.22, 143.43, 137.70, 137.46, 136.55, 133.25, 129.66, 129.53, 129.39, 129.02, 128.42, 126.97, 126.17, 66.91, 51.10, 41.37, 38.88, 29.49, 21.48, 19.24. **HRMS–ESI (m/z):** [M+Na]$^+$ calcd. for C$_{26}$H$_{29}$NNaOS$_4$, 506.1430; found, 506.1430. **IR (KBr, cm$^{-1}$):** ν 3685, 3411, 3083, 1721, 1159, 749.

\[N-((1S,2S,5R)-5-methyl-2-((S)-1-(phenylthio)propan-2-yl)cyclohexyl)-4-methyl benzenesulfonamide (5h)](image)

White solid. mp: 123.3–124.5 °C; **H NMR** (600 MHz, CDCl$_3$) δ 7.71 (d, $J = 8.1$ Hz, 2H), 7.31 (d, $J = 7.5$ Hz, 2H), 7.28 (d, $J = 7.5$ Hz, 2H), 7.24 (d, $J = 8.1$ Hz, 2H), 7.16 (t, $J = 7.2$ Hz, 1H), 4.50 (d, $J = 9.3$ Hz, 1H), 3.64 (dd, $J = 9.3$, 2.8 Hz, 1H), 2.92 (d, $J = 5.1$ Hz, 2H), 2.39 (s, 3H), 1.80–1.83 (m, 1H), 1.67–1.73 (m, 2H), 1.33–1.41 (m, 3H), 1.00 (d, $J = 6.6$ Hz, 3H), 0.76–0.91 (m, 3H), 0.69 (d, $J = 6.1$ Hz, 3H). **C NMR** (150 MHz, CDCl$_3$) δ 143.32, 138.47, 137.42, 129.66, 129.03, 128.80, 126.95, 125.59, 51.26, 43.58, 39.28, 38.66, 34.31, 33.54, 26.09, 24.32, 21.90, 21.49, 17.27. **HRMS–ESI (m/z):** [M+Na]$^+$ calcd. for C$_{23}$H$_{31}$NNaO$_2$S$_2$, 400.1688; found, 400.1683. **IR (KBr, cm$^{-1}$):** ν 3506, 3439, 1631, 749.

\[Methyl(R)-5-methyl-3-(((4-methylphenyl)sulfonamido)methyl)-5-(phenylthio)hexanoate (5i)](image)
Colours oil. \textbf{\textsuperscript{1}H NMR} (600 MHz, CDCl\textsubscript{3}) \(\delta\) 7.73 (d, \(J = 7.5\) Hz, 2H), 7.46 (d, \(J = 7.5\) Hz, 2H), 7.36 (t, \(J = 7.2\) Hz, 1H), 7.30 (t, \(J = 8.4\) Hz, 4H), 4.95 (t, \(J = 6.3\) Hz, 1H), 3.64 (s, 3H), 3.01–3.07 (m, 1H), 2.89–2.95 (m, 1H), 2.49 (dd, \(J = 15.9, 4.8\) Hz, 1H), 2.38–2.43 (m, 1H), 2.41 (s, 3H), 2.31–2.36 (m, 1H), 1.54 (dd, \(J = 15.0, 4.8\) Hz, 1H), 1.47 (dd, \(J = 15.0, 4.8\) Hz, 1H), 1.19 (s, 6H). \textbf{\textsuperscript{13}C NMR} (150 MHz, CDCl\textsubscript{3}) \(\delta\) 173.15, 143.34, 137.37, 137.01, 131.65, 129.69, 128.85, 128.56, 127.08, 51.68, 49.06, 47.63, 44.09, 38.20, 32.06, 29.50, 28.96, 21.47. \textbf{HRMS–ESI} (m/z): [M+Na]\(^+\) calcd. for C\textsubscript{22}H\textsubscript{29}NNaO\textsubscript{4}S\textsubscript{2}, 458.1430; found, 451.432.

\textbf{(3R,5R,8R,9S,10S,13S,14S,17S)-10,13-dimethyl-17-(5-((4-methylphenyl)sulfonamido)-2-(phenylthio)pentan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl benzoate (5j)}

Colorless oil. \textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.04 (d, \(J = 8.1\) Hz, 2H), 7.73 (d, \(J = 8.1\) Hz, 2H), 7.55 (t, \(J = 7.5\) Hz, 1H), 7.39–7.46 (m, 4H), 7.27–7.38 (m, 5H), 4.92–5.01 (m, 1H), 4.31 (t, \(J = 6.3\) Hz, 1H), 2.91 (dd, \(J = 13.8, 6.9\) Hz, 2H), 2.42 (s, 3H), 1.80–1.95 (m, 7H), 1.59–1.72 (m, 5H), 1.50–1.55 (m, 2H), 1.38–1.44 (m, 4H), 1.35–1.38 (m, 1H), 1.30–1.33 (m, 1H), 1.21 (s, 3H), 1.15 (d, \(J = 4.9\) Hz, 2H), 1.06–1.12 (m, 3H), 0.95 (s, 3H), 0.88–0.92 (m, 2H), 0.82 (s, 3H). \textbf{\textsuperscript{13}C NMR} (150 MHz, CDCl\textsubscript{3}) \(\delta\) 166.14, 143.35, 137.50, 137.10, 132.68, 130.94, 129.69, 129.52, 128.57, 128.47, 128.25, 127.13, 127.11, 74.92, 57.37, 56.58, 44.32, 43.59, 41.89, 40.78, 40.38, 38.26, 35.35,
35.06, 34.63, 32.37, 27.03, 26.75, 26.14, 25.37, 24.35, 23.93, 23.85, 23.71, 23.32, 21.52, 20.73, 14.90. **HRMS–ESI** (m/z): [M+Na]$^+$ calcd. for $C_{44}H_{67}NNa_{4}S_{2}$, 750.3621; found, 750.3620. **IR** (KBr, cm$^{-1}$): $\nu$ 3692, 3467, 3410, 3064, 1715, 1566, 750.

$N$-$(((1R,4aS,10aR)-7$-$isopropyl$-1,4a$-dimethyl$-10$-(phenylthio$)-1,2,3,4,4a,9,10,10a$-octahydrophenanthren$-1$-yl)methyl$)-4$-methylbenzenesulfonamide (5k)

White solid. mp: 157.3–158.5 ºC; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.62 (d, $J = 8.1$ Hz, 2H), 7.27–7.31 (m, 3H), 7.20–7.23 (m, 2H), 7.14 (d, $J = 8.1$ Hz, 2H), 7.10 (s, 2H), 6.90 (s, 1H), 5.69 (dd, $J = 15.3$, 5.1 Hz, 1H), 3.53 (t, $J = 6.0$ Hz, 1H), 3.34 (dd, $J = 15.6$, 6.0 Hz, 1H), 2.94 (dd, $J = 13.2$, 5.1 Hz, 1H), 2.87 (sept, $J = 6.9$ Hz, 1H), 2.75 (d, $J = 15.3$ Hz, 1H), 2.67 (dd, $J = 13.2$, 10.2 Hz, 1H), 2.35 (s, 3H), 2.12 (d, $J = 12.9$ Hz, 1H), 1.71–1.87 (m, 3H), 1.54–1.63 (m, 1H), 1.29–1.38 (m, 2H), 1.25 (d, $J = 6.9$ Hz, 6H), 1.24 (s, 3H), 1.12 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 146.59, 146.19, 142.84, 137.38, 134.94, 133.90, 131.52, 129.54, 129.16, 127.45, 127.40, 126.86, 124.76, 121.38, 53.88, 50.59, 45.06, 38.74, 38.61, 38.18, 35.93, 35.59, 33.51, 24.06, 23.99, 22.32, 21.43, 20.02, 18.03. **HRMS–ESI** (m/z): [M+Na]$^+$ calcd. for $C_{33}H_{41}NNaO_{2}S_{2}$, 570.2471; found, 570.2470. **IR** (KBr, cm$^{-1}$): $\nu$ 3686, 3409, 1729, 1572, 1161, 617.

**2-(phenylthio)-1-tosylpyrrolidine (7a)**

Colourless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.75 (d, $J = 8.1$ Hz, 2H), 7.47 (dd, $J = 6.3$, 3.0 Hz, 2H), 7.29–7.33 (m, 3H), 7.28 (d, $J = 8.1$ Hz, 2H), 5.38 (d, $J = 6.3$ Hz, 1H), 3.32–3.39 (m, 2H), 2.42 (s, 3H), 1.90–2.00 (m, 3H), 1.75–1.81 (m, 1H). $^{13}$C NMR
(150 MHz, CDCl$_3$) $\delta$ 143.53, 136.14, 134.14, 133.38, 129.58, 128.99, 128.10, 127.60, 68.98, 47.79, 34.12, 23.55, 21.52. **HRMS–ESI (m/z):** [M+Na]$^+$ calcd. for C$_{17}$H$_{19}$NNaO$_2$S$_2$, 356.0749; found, 356.0758. **IR (KBr, cm$^{-1}$):** $\nu$ 3710, 3553, 3475, 3412, 1747, 1616, 663.

**(4S)-4-isobutyl-2-(phenylthio)-1-tosylpiperidine (7b)**

![Image of compound 7b]

Colourless oil. **$^1$H NMR** (600 MHz, CDCl$_3$) $\delta$ 7.53 (d, $J = 8.1$ Hz, 2H), 7.44 (dd, $J = 6.5$, 1.8 Hz, 2H), 7.27–7.31 (m, 3H), 7.18 (d, $J = 8.1$ Hz, 2H), 5.78 (s, 1H), 3.64–3.66 (m, 1H), 3.21–3.30 (m, 1H), 2.39 (s, 3H), 1.93–1.99 (m, 2H), 1.62–1.65 (m, 1H), 1.54–1.61 (m, 1H), 1.45 (td, $J = 12.7$, 4.5 Hz, 1H), 1.05–1.12 (m, 1H), 0.97–1.05 (m, 2H), 0.85 (d, $J = 6.6$ Hz, 6H). **$^{13}$C NMR** (150 MHz, CDCl$_3$) $\delta$ 143.16, 136.99, 133.62, 133.46, 129.40, 129.04, 127.80, 127.58, 65.02, 45.61, 41.32, 38.12, 31.66, 28.09, 24.44, 22.77, 22.55, 21.49. **HRMS–ESI (m/z):** [M+Na]$^+$ calcd. for C$_{22}$H$_{29}$NNaO$_2$S$_2$, 426.1532; found, 426.1530. **IR (KBr, cm$^{-1}$):** $\nu$ 3552, 3480, 3414, 3234, 1617, 1158, 614.

**N-(7-(phenylthio)octan-4-yl)-4-methylbenzenesulfonamide (9a)**

![Image of compound 9a]

Colourless oil. **$^1$H NMR** (600 MHz, CDCl$_3$) $\delta$ 7.73 (d, $J = 8.4$ Hz, 2H), 7.72 (d, $J = 8.4$ Hz, 2H), 7.31–7.35 (m, 1/2×4H, 1/2×4H), 7.25–7.30 (m, 1/2×8H, 1/2×8H), 7.23 (t, $J = 7.2$ Hz, 1/2×2H, 1/2×2H), 4.35 (d, $J = 8.4$ Hz, 1H), 4.34 (d, $J = 8.4$ Hz, 1H), 3.17–3.24 (m, 1/2×2H, 1/2×2H), 2.98–3.10 (m, 1/2×2H, 1/2×2H), 2.40 (s, 1/2×6H, 1/2×6H), 1.56–1.62(m, 1/2×2H, 1/2×2H), 1.35–1.49 (m, 1/2×6H, 1/2×6H), 1.35–1.49 (m, 1/2×6H, 1/2×6H), 1.35–1.49 (m, 1/2×6H, 1/2×6H).
1.29–1.35 (m, 1/2×2H, 1/2×2H), 1.18–1.28 (m, 1/2×2H, 1/2×2H), 1.11–1.18 (m, 1/2×2H, 1/2×2H), 1.15 (d, J = 6.9 Hz, 3H), 1.14 (d, J = 6.9 Hz, 3H), 0.77 (t, J = 7.2 Hz, 3H), 0.75 (t, J = 7.2 Hz, 3H). 13C NMR (150 MHz, CDCl3) δ 143.17 (C×2), 138.35, 138.32, 134.99, 134.98, 132.06, 132.01, 129.57 (C×2), 128.81, 128.80, 127.01 (C×2), 126.82 (C×2), 53.91, 53.55, 43.23, 43.08, 37.32, 37.29, 32.22 (C×2), 32.08, 32.01, 21.46, 21.37, 21.07 (C×2), 18.45, 18.44, 13.75 (C×2). HRMS–ESI (m/z): [M+Na]+ calcd. for C21H29NNaO2S2, 414.1532; found, 414.1522. IR (KBr, cm⁻¹): ν 3682, 3437, 3279, 1719, 1159, 666.

N-(4-methyl-4-(phenylthio)-2-propylpentyl)-4-methylbenzenesulfonamide (9b)

Colourless oil. 1H NMR (600 MHz, CDCl3) δ 7.75 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H), 7.35 (t, J = 7.2 Hz, 1H), 7.28–7.32 (m, 4H), 4.62 (t, J = 6.3 Hz, 1H), 2.96 (dt, J = 12.0, 6.0 Hz, 1H), 2.88 (dt, J = 12.6, 6.3 Hz, 1H), 2.41 (s, 3H), 1.77 (dt, J = 11.1, 5.4 Hz, 1H), 1.49 (dd, J = 14.7, 5.4 Hz, 1H), 1.42 (dd, J = 14.7, 5.4 Hz, 1H), 1.25–1.34 (m, 2H), 1.18–1.25 (m, 2H), 1.16 (s, 6H), 0.85 (t, J = 7.2 Hz, 3H). 13C NMR (150 MHz, CDCl3) δ 143.28, 137.41, 137.06, 131.90, 129.65, 128.75, 128.50, 127.17, 49.41, 47.26, 44.77, 35.98, 34.44, 29.68, 28.90, 21.46, 19.60, 14.21. HRMS–ESI (m/z): [M+Na]+ calcd. for C22H31NNaO2S2, 428.1688; found, 428.1679. IR (KBr, cm⁻¹): ν 3695, 3523, 3438, 3297, 3079, 1717, 1572, 666.

N-(7-methyl-7-(phenylthio)octan-4-yl)-4-methylbenzenesulfonamide (9c)

Colourless oil. 1H NMR (600 MHz, CDCl3) δ 7.71 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 8.1 Hz, 2H), 7.37 (t, J = 7.2 Hz, 1H), 7.32 (t, J = 7.2 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H),
4.30 (d, $J = 8.7$ Hz, 1H), 3.15 (dt, $J = 8.7$, 6.3 Hz, 1H), 2.38 (s, 3H), 1.60–1.64 (m, 1H), 1.44–1.51 (m, 1H), 1.34–1.41 (m, 1H), 1.24–1.32 (m, 3H), 1.13–1.18 (m, 2H), 1.09 (s, 3H), 1.08 (s, 3H), 0.80 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 143.11, 138.39, 137.34, 132.09, 129.53, 128.74, 128.52, 127.04, 54.29, 48.73, 37.69, 37.61, 30.18, 28.85, 28.71, 21.43, 18.53, 13.80. HRMS–ESI ($m/z$): [M+Na]$^+$ calcd. for C$_{22}$H$_{31}$NNaO$_2$S$_2$, 428.1688; found, 428.1702. IR (KBr, cm$^{-1}$): $\nu$ 3697, 3563, 2958, 1734, 1159.

(2S)-5-((((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)thio)-2-((4-methylphenyl)sulfonamido)hexyl pivalate (11a)

White solid. mp: 73.6–74.9 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.73 (d, $J = 8.1$ Hz, 2H), 7.72 (d, $J = 8.1$ Hz, 2H), 7.28 (d, $J = 8.1$ Hz, 1/2×4H, 1/2×4H), 7.21 (d, $J = 8.1$ Hz, 1/2×2H, 1/2×2H), 7.09–7.13 (m, 1/2×4H, 1/2×4H), 4.63 (d, $J = 8.7$ Hz, 1H), 4.60 (d, $J = 8.7$ Hz, 1H), 3.97 (dd, $J = 11.4$, 4.5 Hz, 1H), 3.95 (dd, $J = 11.4$, 4.5 Hz, 1H), 3.83 (dd, $J = 9.3$, 4.5 Hz, 1H), 3.80 (dd, $J = 9.3$, 4.5 Hz, 1H), 3.42–3.50 (m, 1/2×2H, 1/2×2H), 3.00–3.09 (m, 1H), 2.95–3.00 (m, 1H), 2.87–2.91 (m, 1/2×4H, 1/2×4H), 2.38–2.44 (m, 1/2×2H, 1/2×2H), 2.41 (s, 1/2×6H, 1/2×6H), 2.29 (t, $J = 11.1$ Hz, 1H), 2.26 (t, $J = 11.1$ Hz, 1H), 1.95–2.19 (m, 1/2×9H, 1/2×9H), 1.41–1.71 (m, 1/2×21H, 1/2×21H), 1.18 (d, $J = 7.2$ Hz, 3H), 1.17 (s, 9H), 1.16 (s, 9H), 1.15 (d, $J = 7.2$ Hz, 3H), 0.91 (s, 1/2×6H, 1/2×6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 220.71(C×2), 178.19(C×2), 143.58, 143.56, 139.02(C×2), 137.98, 137.96, 137.31, 137.28, 133.02, 132.98, 131.48, 131.43, 129.87, 129.84, 129.78, 129.76, 126.95(C×2), 125.91(C×2), 125.91(C×2), 125.91(C×2), 125.91(C×2).
65.57, 65.50, 53.05, 52.66, 50.51(C×2), 47.95(C×2), 44.28(C×2), 43.16, 42.94, 38.86(C×2), 38.03(C×2), 35.83(C×2), 32.13(C×2), 31.57(C×2), 29.54, 29.37, 29.25, 29.24, 27.15(C×2), 26.38(C×2), 25.64(C×2), 21.57, 21.55(C×2), 21.51, 21.14(C×2), 13.84(C×2). HRMS–ESI (m/z): [M+Na]⁺ calcd. for C₃₆H₄⁹NNaO₅S₂, 662.2944; found, 662.2943. IR (KBr, cm⁻¹): v3693, 2928, 1736, 1555, 1482.

\( N-(((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-10-(((8R,9S,13S,14S)-8,9,13,14-\text{tetramethyl}-17-\text{oxo}-7,8,9,11,12,13,14,15,16,17-decahydro-6H-\text{cyclopenta[a]}\text{phenanthren-3-yl})thio)-1,2,3,4,4a,9,10,10a-\text{octahydrophenanthren-1-yl})methyl)-4-methylbenzenesulfonamide (12a) \)

White solid. mp: 115.3–116.3 ºC; \(^1\)H NMR (400 MHz, CDCl₃)  \( \delta \) 7.68(d,  \( J = 8.2 \) Hz, 1/3×2H), 7.65 (d,  \( J = 8.2 \) Hz, 2/3×2H), 7.29 (d,  \( J = 8.2 \) Hz, 1/3×2H), 7.23 (d,  \( J = 8.2 \) Hz, 2/3×2H), 7.13–7.19 (m, 1/3×3H, 2/3×3H), 7.09 (s, 1/3×2H, 2/3×2H), 7.06 (s, 2/3×1H), 7.03 (s, 1/3×1H), 7.01 (s, 1/3×1H), 7.00 (s, 2/3×1H), 6.91 (s, 2/3×1H), 6.59 (s, 1/3×1H), 5.81 (dd,  \( J = 9.8, 5.2 \) Hz, 2/3×1H), 5.10 (dd,  \( J = 9.8, 5.2 \) Hz, 1/3×1H), 3.49 (t,  \( J = 6.2 \) Hz, 2/3×1H), 3.28–3.34 (m, 1/3×2H, 2/3×2H), 2.98–3.04 (m, 1/3×1H), 2.49–2.97 (m, 1/3×8H, 2/3×8H), 2.26–2.44 (m, 1/3×4H, 2/3×4H), 2.41 (s, 1/3×3H), 2.36 (s, 2/3×3H), 1.99–2.21 (m, 1/3×6H, 2/3×6H), 1.41–1.87 (m, 1/3×6H, 2/3×6H), 1.20–1.37 (m, 1/3×8H, 2/3×8H), 1.12 (s, 2/3×3H), 1.02 (s, 1/3×3H), 0.94 (s, 2/3×3H), 0.93 (s, 1/3×3H). \(^{13}\)C NMR (100 MHz, CDCl₃)  \( \delta \) 220.55, 220.52, 146.61, 146.57, 146.12, 146.08, 143.03, 142.72, 139.66, 139.59, 137.64, 137.61, 137.58, 137.54, 134.04, 134.00, 133.83, 132.48, 131.74, 129.89, 129.68, 129.54, 129.52, 127.47, 127.42, 126.97, 126.92, 126.84, 126.24, 126.18, 124.74, 124.63, 121.39, 121.31, 121.37.
54.02, 53.79, 50.80, 50.74, 50.51, 49.98, 47.93, 47.92, 45.22, 44.35, 44.29, 38.91, 38.73, 38.68, 38.62, 38.07, 37.99, 36.05, 35.82, 35.39, 34.00, 33.56, 33.50, 31.91, 31.58, 31.42, 30.19, 29.64, 29.35, 29.26, 26.39, 26.33, 25.65, 24.25, 24.05, 24.03, 23.82, 22.67, 22.40, 22.35, 21.59, 21.52, 21.49, 19.98, 19.53, 18.05, 17.94, 14.09, 13.85, 13.82. \textbf{HRMS–ESI} (m/z): [M+Na]$^+$ calcd. for C$_{45}$H$_{57}$NNaO$_3$S$_2$, 747.0642; found, 662.2943. \textbf{IR} (KBr, cm$^{-1}$): v 3693, 3411, 3080, 1735, 1552.

Methyl (R)-5-methyl-3-(((4-methylphenyl)sulfonamido)methyl)-5-(phenylsulfonyl)hexanoate (13a)

![Structure of 13a](image)

White solid. mp: 149.3–150.2 °C; \textbf{1H NMR} (600 MHz, CDCl$_3$)$\delta$ 7.84 (d, $J = 7.5$ Hz, 2H), 7.70 (d, $J = 8.1$ Hz, 2H), 7.67 (t, $J = 7.5$ Hz, 2H), 7.56 (t, $J = 7.8$ Hz, 2H), 7.29 (d, $J = 7.8$ Hz, 1H), 5.11 (t, $J = 6.6$ Hz, 1H), 3.62 (s, 3H), 2.94 (ddd, $J = 13.2$, 6.6, 6.3 Hz, 1H), 2.89 (ddd, $J = 13.2$, 6.6, 6.3 Hz, 1H), 2.41 (s, 3H), 2.39–2.45 (m, 2H), 2.22–2.29 (m, 1H), 1.84 (dd, $J = 14.7$, 4.8 Hz, 1H), 1.68 (dd, $J = 14.7$, 4.8 Hz, 1H), 1.27 (s, 3H), 1.25 (s, 3H). \textbf{13C NMR} (150 MHz, CDCl$_3$) $\delta$ 172.72, 143.45, 136.89, 135.16, 133.74, 130.49, 129.74, 128.82, 126.98, 62.95, 51.71, 47.57, 38.19, 36.39, 31.37, 21.81, 21.46, 21.29. \textbf{HRMS–ESI} (m/z): [M+Na]$^+$ calcd. for C$_{22}$H$_{29}$NNaO$_6$S$_2$, 490.1329; found, 490.1326. \textbf{IR} (KBr, cm$^{-1}$): v 3704, 3556, 3411, 3064, 1735, 1616, 1553.

N-(2,2-dimethyl-3-(2-((phenylthio)methyl)cyclopentyl)propyl)-4-methylbenzenesulfonamide (15a)

![Structure of 15a](image)

Colourless oil. \textbf{1H NMR} (400 MHz, CDCl$_3$) $\delta$ 7.96 (d, $J = 8.4$ Hz, 2H), 7.75 (d, $J = 8.4$ Hz, 2H), 7.67 (t, $J = 7.2$ Hz, 1H), 7.58 (t, $J = 7.8$ Hz, 2H), 7.30 (d, $J = 7.8$ Hz, 2H), S60
5.13 (t, \(J = 7.0\) Hz, 1H), 3.16 (dd, \(J = 14.0, 5.4\) Hz, 1H), 2.91 (dd, \(J = 14.0, 7.8\) Hz, 1H), 2.68 (dd, \(J = 12.8, 6.5\) Hz, 1H), 2.62 (dd, \(J = 12.8, 6.5\) Hz, 1H), 2.41 (s, 3H), 2.37–2.44 (m, 1H), 1.92–1.99 (m, 1H), 1.63–1.75 (m, 2H), 1.49–1.64 (m, 2H), 1.24–1.36 (m, 3H), 0.91–0.95 (m, 1H), 0.89 (s, 3H), 0.83 (s, 3H). \(^{13}\text{C NMR}\) (150 MHz, CDCl\(_3\)) \(\delta\) 143.15, 139.88, 137.20, 133.68, 129.65, 129.37, 127.92, 127.02, 56.27, 52.79, 38.33, 37.77, 37.62, 34.38, 31.91, 30.22, 26.36, 25.40, 21.46, 21.41. \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta\) 143.35, 136.99, 136.49, 130.67, 129.67, 129.17, 128.86, 127.09, 125.88, 42.56, 33.54, 32.11, 29.41, 29.06, 21.50. \(^{13}\text{C NMR}\) (150 MHz, CDCl\(_3\)) \(\delta\) 143.39, 137.06, 135.93,

\((E)\) \(N\)-(7-(phenylthio)hept-4-en-1-yl)-4-methylbenzenesulfonamide (17a)

\[
\text{TsHN} - \text{SPh}
\]

Colorless oil. \(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 7.73 (d, \(J = 8.2\) Hz, 2H), 7.26–7.32 (m, 6H), 7.15–7.19 (m, 1H), 5.32–5.44 (m, 2H), 4.38 (t, \(J = 6.0\) Hz, 1H), 2.93 (dt, \(J = 6.0, 13.4\) Hz, 2H), 2.89 (t, \(J = 7.3\) Hz, 2H), 2.41 (s, 3H), 2.26–2.32 (m, 2H), 1.97–2.02 (m, 2H), 1.49–1.56 (m, 2H). \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta\) 143.35, 136.99, 136.49, 130.67, 129.67, 129.17, 128.86, 127.09, 125.88, 42.56, 33.54, 32.11, 29.41, 29.06, 21.50. \(^{13}\text{C NMR}\) (150 MHz, CDCl\(_3\)) \(\delta\) 143.39, 137.06, 135.93,

\((E)\) \(-N-(6-(phenylthio)hex-4-en-1-yl)-4-methylbenzenesulfonamide (19a)

\[
\text{TsHN} - \text{SPh}
\]

Colorless oil. \(^1\text{H NMR}\) (600 MHz, CDCl\(_3\)) \(\delta\) 7.72 (d, \(J = 8.1\) Hz, 2H), 7.29–7.35 (m, 4H), 7.23–7.25 (m, 2H), 7.15–7.17 (m, 1H), 5.37–5.58 (m, 2H), 4.24 (t, \(J = 5.7\) Hz, 1H), 3.46 (d, \(J = 6.3\) Hz, 2H), 2.83 (dt, \(J = 13.4, 6.6\) Hz, 2H), 2.42 (s, 3H), 1.94–1.98 (m, 2H), 1.42–1.47 (m, 2H). \(^{13}\text{C NMR}\) (150 MHz, CDCl\(_3\)) \(\delta\) 143.39, 137.06, 135.93,
132.39, 130.06, 129.70, 128.74, 126.36, 126.22, 42.42, 36.34, 29.08, 29.04, 21.51. **HRMS–ESI** \((m/z)\): [M+Na]\(^+\) calcd. for \(C_{19}H_{23}NNaO_{2}S_{2}\), 384.1062; found, 384.1062. **IR** (KBr, \(cm^{-1}\)): \(\nu\) 3831, 3509, 2426, 2338, 1636.

1-tosyl-2-vinylpyrrolidine (20a)

Colorless oil. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.72 (d, \(J = 8.1\) Hz, 2H), 7.31 (d, \(J = 8.1\) Hz, 2H), 5.81 (ddd, \(J = 16.9, 10.2, 6.0\) Hz, 1H), 5.27 (d, \(J = 16.9\) Hz, 1H), 5.12 (d, \(J = 10.2\) Hz, 1H), 4.12–4.15 (m, 1H), 3.45 (ddd, \(J = 9.9, 7.5, 4.5\) Hz, 1H), 3.24 (dt, \(J = 9.9, 7.5\) Hz, 1H), 2.43 (s, 3H), 1.86–1.76 (m, 1H), 1.74–1.65 (m, 2H), 1.65–1.59 (m, 1H).

\(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 143.21, 138.68, 135.21, 129.55, 127.53, 115.28, 61.89, 32.28, 23.72, 21.49. **IR** (KBr, \(cm^{-1}\)): \(\nu\) 3704, 3556, 3411, 3064, 1735, 1616, 1553.

**Mechanism Studies:**

1. **Radical Capture Experiments**

   \[ \text{Cu(acac)}_2 \text{(10 mol\%)} \quad 1,10\text{-phen \text{(L1) (10 mol\%)} } \quad \text{In (1.7 equiv)} \quad \text{Na}_2\text{HPO}_4 \text{(1.4 equiv)} \quad \text{DCE (0.17 M), 40 °C, 50 W blue LED, 9 h, BHT (2.0 equiv)} \]

   \[ \begin{align*}
   &\text{1a} + \text{PhSSPh} \rightarrow \text{2a} \\
   \rightarrow &\text{Cu(acac)}_2 \text{(10 mol\%)} \\
   \rightarrow &\text{1,10-phen \text{(L1) (10 mol\%)} } \quad \text{In (1.7 equiv)} \\
   \rightarrow &\text{Na}_2\text{HPO}_4 \text{(1.4 equiv)} \\
   \rightarrow &\text{DCE (0.17 M), 40 °C, 50 W blue LED, 9 h, BHT (2.0 equiv)} \\
   \rightarrow &\text{not observed} \\
   \rightarrow &91\% \text{ }^1\text{H NMR yield} \\
   \end{align*} \]

   \[ \begin{align*}
   &\text{1a} + \text{PhSSPh} \rightarrow \text{2a} \\
   \rightarrow &\text{Cu(acac)}_2 \text{(10 mol\%)} \\
   \rightarrow &\text{1,10-phen \text{(L1) (10 mol\%)} } \quad \text{In (1.7 equiv)} \\
   \rightarrow &\text{Na}_2\text{HPO}_4 \text{(1.4 equiv)} \\
   \rightarrow &\text{DCE (0.17 M), 40 °C, 50 W blue LED, 9 h, BHT (2.0 equiv)} \\
   \rightarrow &\text{not observed} \\
   \rightarrow &91\% \text{ }^1\text{H NMR yield} \\
   \end{align*} \]

   \[ \begin{align*}
   &\text{1a} + \text{PhSSPh} \rightarrow \text{2a} \\
   \rightarrow &\text{Cu(acac)}_2 \text{(10 mol\%)} \\
   \rightarrow &\text{1,10-phen \text{(L1) (10 mol\%)} } \quad \text{In (1.7 equiv)} \\
   \rightarrow &\text{Na}_2\text{HPO}_4 \text{(1.4 equiv)} \\
   \rightarrow &\text{DCE (0.17 M), 40 °C, 50 W blue LED, 9 h, BHT (2.0 equiv)} \\
   \rightarrow &\text{not observed} \\
   \rightarrow &91\% \text{ }^1\text{H NMR yield} \\
   \end{align*} \]

   \[ \begin{align*}
   &\text{1a} + \text{PhSSPh} \rightarrow \text{2a} \\
   \rightarrow &\text{Cu(acac)}_2 \text{(10 mol\%)} \\
   \rightarrow &\text{1,10-phen \text{(L1) (10 mol\%)} } \quad \text{In (1.7 equiv)} \\
   \rightarrow &\text{Na}_2\text{HPO}_4 \text{(1.4 equiv)} \\
   \rightarrow &\text{DCE (0.17 M), 40 °C, 50 W blue LED, 9 h, BHT (2.0 equiv)} \\
   \rightarrow &\text{not observed} \\
   \rightarrow &91\% \text{ }^1\text{H NMR yield} \\
   \end{align*} \]

   \[ \begin{align*}
   &\text{1a} + \text{PhSSPh} \rightarrow \text{2a} \\
   \rightarrow &\text{Cu(acac)}_2 \text{(10 mol\%)} \\
   \rightarrow &\text{1,10-phen \text{(L1) (10 mol\%)} } \quad \text{In (1.7 equiv)} \\
   \rightarrow &\text{Na}_2\text{HPO}_4 \text{(1.4 equiv)} \\
   \rightarrow &\text{DCE (0.17 M), 40 °C, 50 W blue LED, 9 h, BHT (2.0 equiv)} \\
   \rightarrow &\text{not observed} \\
   \rightarrow &91\% \text{ }^1\text{H NMR yield} \\
   \end{align*} \]
2. Control Experiments

\[
\begin{align*}
&\text{F} & \text{N} & \text{H} & \text{tBu} \\
&\text{1a} & 1.0 \text{ eq.} & \text{PhSH} & \text{PhSH} & \text{SPh} & \text{SPh} & \text{N} & \text{Bu} & \text{1a} \\
&\text{2a} & 1.2 \text{ eq.} & \text{Cu(acac)}_2 (10 \text{ mol\%}) & \text{1,10-phen} (L_1) (10 \text{ mol\%}) & \text{In} (1.7 \text{ equiv}) & \text{Na}_2\text{HPO}_4 (1.4 \text{ equiv}) & \text{DCE} (0.17 \text{ M}) & 50 ^\circ \text{C} & 9 \text{h} & \text{blue LED} & \text{3a, 7\%} & \text{4-amide, 90\%} \\
\end{align*}
\]

3. Homolytic cleavage of S-S bond under visible light

\[
\begin{align*}
&\text{S-S} + \text{OEt} & \text{OEt} \\
&\text{2a} & \text{standard conditions} & \text{6} & \text{11\%} \\
\end{align*}
\]

4. Competition experiment

\[
\begin{align*}
&\text{F} & \text{N} & \text{H} & \text{tBu} \\
&\text{1f} & 1.0 \text{ eq.} & \text{PhSSPh} & \text{PhSSPh} & \text{PhSSPh} & \text{COOEt} & \text{COOEt} & \text{COOEt} \\
&\text{2a} & 1.2 \text{ eq.} & \text{Cu(acac)}_2 (10 \text{ mol\%}) & \text{1,10-phen} (L_1) (10 \text{ mol\%}) & \text{In} (1.7 \text{ equiv}) & \text{Na}_2\text{HPO}_4 (1.4 \text{ equiv}) & \text{DCE} (0.17 \text{ M}) & 50 ^\circ \text{C} & 9 \text{h} & \text{blue LED} & \text{4e, 41\%} \\
\end{align*}
\]

Results:

1. By adding TEMPO and 2,6-di-tert-butylphenol to the reaction mixture independently, the desired product 3a can not be observed.

2. The control experiments showed that both of benzenethiol and sodium benzenethiolate could afford thiolation product 3a, but with low efficiency. The defluoro tosylamide is the major product. Thus, the thiol is a possible intermediate in this reaction.

3. The disulfide 2a can be trapped by a Michael acceptor, giving the Michael addition product 6 under the standard condition, or even only under the
irradiation of the 50 W blue LED ($\lambda = 450$ nm). This result indicated that the visible light can promote the homolytic cleavage of S-S bond.

4. The competition experiment between disulfide and ethyl acrylate was carried out. With the addition of 4.0 equiv of ethyl acrylate under the standard condition 41% of the thiolated product 4e was observed indicated the rate of thiolation is very fast. The copper catalyst maybe locate on the carbon center to promote the C-S bond formation.

Direct use of thiophenol can make the reaction system overall redox neutral. Based on this suggestion, we tested thiophenol as the thiolation reagent in the absence of light and In powder, the results were shown in (Eq.1). Different amounts of thiophenol (0.6-2.0 equiv.) were tested. No any desired product was detected. The disulfide can be obtained under this condition. And also, SM 1a can be recovered.

We also test different amounts of thiophenol (0.6-2.0 equiv.) under the standard condition. By using 1.0 equiv. or 0.6 equiv. of thiophenol, 20% or 25% of thiolation product can be obtained (Eq. 2). However, we did not get any disulfide product by using different amounts of thiophenol. Decreasing the amount of thiophenol can increase the product yield, indicated that remained N-F amide may be consumed by the disulfide which generated in situ.

Both of the above results indicated that the disulfide may be the real thiolation reagent.
Furthermore, the thiophenol was subject to the “standard condition” in the absence of N-F amide, to confirm whether corresponding disulfide can be generated under this condition. The blank experiment indicated that this hypothesis was possible (Eq. 3).

Next, according to the referee’s suggestion, the compound In(SPh)₃ was prepared and subjected to the reaction system, however there was no any thiolation product could be detected (Eq. 4-5).

Above experiments indicated that both of PhSH and In(SPh)₃ were not the active thiolation species under this reaction system. Furthermore, we will continue to
explore redox neutral reaction system by using thiophenol based on the referee’s construction and insightful suggestion (future plan).

We state that the visible light promotes the homolysis of the S-S bond of sulfide (Eq. 6-7). However, only a small amount of Michael addition product was obtained. This result indicated that may be PhS \cdot radical was not the major active species in this thiolation reaction.

![Chemical reaction diagram](image)

We also tested whether In powder could reduce the disulfide to generate PhS \cdot radical (Eq. 8). The blank experiment shown that In powder may not reduce the disulfide.

![Chemical reaction diagram](image)

The blank experiments were carried out to confirm the role of each additives in this reaction condition (Eq. 9). The results indicated that each addition cannot induce this reaction independently.
Finally, the real radical clock was carried out. We prepared the N-fluoro-tosylamide precursors with a cyclopropyl group (16a) and a double bond (18a) next to the delta-position, and subjected these two substrates to the reaction system. For the cyclopropane 16a, the ring-opened product was obtained, indicating an intramolecular 1,5-HAT process might be involved (Eq. 10). For 18a, 66% of the linear thiolation was obtained (Eq. 11). Based on this result, we considered that the allylic radical (η₁ or η₃), facilitated by the intramolecular 1,5-HAT process, was intercepted by copper catalyst, due to the steric effect, the linear selectivity is major.

Base on the above all experiments, we proposed the possible mechanism. Ligand exchange between an in situ generated Cu(I) catalyst and disulfide was occurred to generate Cu(I)-I species, which may reduce the N–F amide A to afford the N-centered radical B and Cu(II)-II intermediate. The Cu(II)-II release one molecular of PhSF through the metathesis process to afford the Cu(II)-III. Translocation of N-centered radical B to C-centered radical C via 1,5-HAT occurred, and then the δ C-radical was intercepted by the Cu(II)-III to form the Cu(III)-IV intermediate. Finally, the reductive elimination of Cu(III)-IV to give the desired product D and regenerated active Cu(I) catalyst.
References
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