Supporting Information

Copper-catalyzed 1,3-aminothiocyanation of arylcyclopropanes

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1. General information

All reactions were performed under nitrogen atmosphere unless otherwise stated. Commercially available reagents were used without further purification. Cyclopropane substrates were synthesized according to procedures described in the literature.\(^1\) All reactions were monitored by thin layer chromatography (TLC) using Macherey-Nagel 0.20 mm silica gel 60 plates. \(^1\)H NMR spectra were recorded on 600 MHz spectrometer, \(^13\)C NMR spectra were recorded on a 150 MHz instrument, and \(^19\)F NMR spectra were recorded on a 470, and 565 MHz instrument. \(^1\)H and \(^13\)C NMR spectra are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm for \(^1\)H NMR) and CHCl\(_3\) (77.0 ppm for \(^13\)C NMR), respectively. High-resolution mass spectra (HRMS) were recorded on Bruck microtof or Hybrid Quadrupole-Orbitrap GC-MS/MS system (Q Exactive GC).

2. General procedure for the synthesis of 4a-4ab

\[
\begin{align*}
\text{Cyclicane} + \text{NFSI} + \text{TMSNCS} & \xrightarrow{\text{CuOAc (10 mol%)}} \text{N(SO}_2\text{Ph)}_2 \text{SCN} \\
1a & \quad 2 \quad 3 & \quad \text{DCE, N}_2, 50^\circ\text{C, 15 h} & \quad 4a
\end{align*}
\]

Take 4a as an example: In a nitrogen-filled glove box, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with CuOAc (10 mol%) and L1 (10 mol%). Anhydrous DCE (2.0 mL) was added and the reaction mixture was stirred for 20 min and NFSI (2.0 equiv.) was added. Then cyclopropanes 1a (0.3 mmol), TMSNCS (0.45 mmol, 1.5 equiv) was added at room temperature. The tube was sealed and removed from the glove box. The reaction mixture was stirred at 30 °C. After 15 h the reaction mixture was quenched with water and extracted with CH\(_2\)Cl\(_2\) (3×10 mL) and the combined organic layers were concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (PE/EA, 1:10, PE = petroleum ether, EA = ethyl acetate) to obtain product 4a.
3. Transformation of 4a

In a 25 mL round-bottom flask, 4a (94.4 mg, 0.2 mmol) in CH$_3$CN (3 mL) was added CsCO$_3$ (130.3 mg, 0.4 mmol) and cooled to 0 °C. Then TMSCF$_3$ (56.9 mg, 0.4 mmol) was added at once and the mixture was then stirred at room temperature for 16 h and transformed to 30 °C over 2 h. The resulting mixture was filtered through a short pad of celite and extracted with Et$_2$O. The resulting organic solution was washed with water (10 mL) and brine (10 mL) and dried over MgSO$_4$. After the removal of solvent, the residue was further purified by flash chromatography affording 5a (57.7 mg, 56%).

To a solution of 4a (94.4 mg, 0.2 mmol) in 2 mL of MeCN was added NaBH$_4$ (11.3 mg, 0.3 mmol) at 0 °C. After the mixture had been stirred at 0 °C for 4 h and transferred to room temperature overnight, the reaction was quenched with 20 mL of saturated aqueous NaHCO$_3$. The aqueous layer was extracted with EtOAc, washed with brine, dried over anhydrous Na$_2$SO$_4$, and concentrated. Column chromatography on silica gel (petroleum ether/ EtOAc = 10:1) gave 115.9 mg of 5b (65%).
4. Characterization data of all products

\( \text{N-(3-phenyl-3-thiocyanatopropyl)-N-(phenylsulfonyl)benzenesulfonamide (4a)} \)

Yellow oil (94%, 133.1 mg); \( R_f = 0.5 \) (petroleum ether/ethyl acetate = 10:1, v/v); \( ^1\text{H NMR} \) (600 MHz, CDCl\(_3\)) \( \delta = 7.94 \) (dd, \( J = 7.8 \) Hz, 4H), 7.66 (t, \( J = 7.8 \) Hz, 2H), 7.53 (t, \( J = 8.4 \) Hz, 4H), 7.42-7.36 (m, 3H), 7.32-7.30 (m, 2H), 4.32 (t, \( J = 7.2 \) Hz, 1H), 3.78-3.73 (m, 1H), 3.61-3.55 (m, 1H), 2.66-2.60 (m, 1H), 2.57-2.51 (m, 1H); \( ^{13}\text{C NMR} \) (150 MHz, CDCl\(_3\)) \( \delta = 139.3, 136.9, 134.2, 129.4, 129.3, 129.3, 128.2, 127.6, 110.9, 50.1, 46.4, 35.2; \( \text{HRMS (ESI)} \) calcd for C\(_{22}\)H\(_{20}\)N\(_2\)NaO\(_4\)S\(_3\) ([M + Na]\(^+\)), 495.0477, found 495.0471.

\( \text{N-(phenylsulfonyl)-N-(3-thiocyanato-3-(p-tolyl)propyl)benzenesulfonamide (4b)} \)

White solid (80%, 116.7 mg); \( R_f = 0.5 \) (petroleum ether/ethyl acetate = 10:1, v/v); mp 93-94 °C; \( ^1\text{H NMR} \) (600 MHz, CDCl\(_3\)) \( \delta = 7.95 \) (d, \( J = 7.8 \) Hz, 4H), 7.66 (t, \( J = 7.2 \) Hz, 2H), 7.54 (t, \( J = 7.8 \) Hz, 4H), 7.20 (s, 4H), 4.31 (t, \( J = 7.8 \) Hz, 1H), 3.77-3.72 (m, 1H), 3.61-3.56 (m, 1H), 2.63-2.59 (m, 1H), 2.55-2.52 (m, 1H); \( ^{13}\text{C NMR} \) (150 MHz, CDCl\(_3\)) \( \delta = 139.5, 139.4, 134.3, 133.8, 130.0, 129.4, 128.3, 127.5, 111.1, 50.2, 46.5, 35.3, 21.3; HRMS (ESI) calcd for C\(_{23}\)H\(_{22}\)N\(_2\)NaO\(_4\)S\(_3\) ([M + Na]\(^+\)), 509.0634, found 509.0642.

\( \text{N-(3-(3-ethylphenyl)-3-thiocyanatopropyl)-N (phenylsulfonyl)benzenesulfonamide (4c)} \)

Yellow oil (41%, 61.5 mg); \( R_f = 0.5 \) (petroleum ether/ethyl acetate = 10:1, v/v); \( ^1\text{H NMR} \) (600 MHz, CDCl\(_3\)) \( \delta = 7.95 \) (d, \( J = 7.8 \) Hz, 4H), 7.67 (t, \( J = 7.8 \) Hz, 2H), 7.54 (t, \( J = 7.8 \) Hz, 4H), 7.32 (s, 4H), 4.32 (dd, \( J = 7.2, 1.2 \) Hz, 1H), 3.77-3.72 (m, 1H), 3.60-3.55 (m, 1H), 2.87-2.60 (m, 3H), 2.57-2.52 (m, 1H), 1.26 (t, \( J = 7.2 \) Hz, 3H); \( ^{13}\text{C NMR} \) (150 MHz, CDCl\(_3\)) \( \delta = 145.6, 139.2, 139.0, 129.3, 129.3, 128.2, 128.1, 127.6, 111.1, 50.2, 46.5, 35.3, 21.3
134.1, 133.8, 129.2, 128.7, 128.1, 127.4, 110.9, 49.9, 46.3, 35.1, 28.5, 15.3; HRMS (ESI) calcd for C_{24}H_{24}N_{2}NaO_{4}S_{3} ([M + Na]^+), 523.0790, found 523.0788.

![Image of molecule 4c']

**N-(phenylsulfonyl)-N-(3-thiocyanato-3-(4-(1-thiocyanatoethyl)phenyl)propyl)benzenesulfonamide (4c')**

Yellow oil (25%, 41.8 mg); R_{f} = 0.5 (petroleum ether/ethyl acetate = 6:1, v/v); ^1H NMR (600 MHz, CDCl₃) δ = 7.95 (d, J = 7.2 Hz, 4H), 7.67 (t, J = 7.8 Hz, 2H), 7.56 (t, J = 7.8 Hz, 4H), 7.45 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 7.8 Hz, 2H), 4.62 (q, J = 7.2 Hz, 1H), 4.32 (t, J = 7.8 Hz, 1H), 3.80-3.76 (m, 1H), 3.66-3.63 (m, 1H), 2.66-2.62 (m, 1H), 2.56-2.53 (m, 1H), 1.89 (d, J = 6.6 Hz, 3H); ^13C NMR (150 MHz, CDCl₃) δ = 140.5, 139.1, 137.8, 134.2, 129.3, 128.2, 128.1, 127.9, 111.2, 110.5, 49.2, 47.8, 46.2, 34.8, 21.7; HRMS (ESI) calcd for C_{24}H_{24}N_{2}NaO_{4}S_{3} ([M + Na]^+), 580.0464, found 580.0460.

![Image of molecule 4d]

**N-(3-(4-isopropylphenyl)-3-thiocyanatopropyl)-N-(phenylsulfonyl)benzenesulfonamide (4d)**

White solid (75%, 115.6 mg), R_{f} = 0.5 (petroleum ether/ethyl acetate = 10:1, v/v), mp 103-104 °C; ^1H NMR (600 MHz, CDCl₃) 7.95 (d, J = 7.2 Hz, 4H), 7.66 (t, J = 7.8 Hz, 2H), 7.54 (t, J = 7.2 Hz, 4H), 7.27 (q, J = 7.8 Hz, 4H), 4.32-4.30 (t, J = 7.8 Hz, 1H), 3.77-3.72 (m, 1H), 3.59-3.54 (m, 1H), 2.95-2.91 (m, 1H), 2.68-2.61 (m, 1H), 2.57-2.53 (m, 1H), 1.27 (d, J = 6.6 Hz, 6H); ^13C NMR (150 MHz, CDCl₃) δ = 150.2, 139.2, 134.1, 133.9, 129.2, 128.1, 127.5, 127.3, 110.0, 49.9, 46.3, 35.1, 33.8, 23.8; HRMS (ESI) calcd for C_{25}H_{26}N_{2}NaO_{4}S_{3} ([M + Na]^+), 537.0947, found 537.0931.
N-(3-(4-(tert-butyl)phenyl)-3-thiocyanatopropyl)-N-(phenylsulfonyl)benzenesulfonamide (4e)

Light yellow solid (85%, 134.6 mg); Rf = 0.5 (petroleum ether/ethyl acetate = 10:1, v/v); mp 103-104 °C; 1H NMR (600 MHz, CDCl3) δ = 7.95 (d, J = 8.4 Hz, 4H), 7.66 (t, J = 7.2 Hz, 2H), 7.54 (t, J = 8.4 Hz, 4H), 7.42 (d, J = 7.8 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 4.32 (t, J = 7.2 Hz, 1H), 3.77-3.72 (m, 1H), 3.59-3.54 (m, 1H), 2.68-2.63 (m, 1H), 3.59-3.54 (m, 1H), 1.33 (s, 1H); 13C NMR (150 MHz, CDCl3) δ = 152.6, 139.3, 134.2, 133.7, 129.3, 128.2, 127.3, 126.2, 111.1, 49.9, 46.4, 35.2, 34.8, 31.3; HRMS (ESI) calcd for C26H28N2NaO4S3 ([M + Na]+), 551.1103, found 551.1101.

N-(3-[(1,1'-biphenyl)-4-yl]-3-thiocyanatopropyl)-N-(phenylsulfonyl)benzenesulfonamide (4f)

Light yellow oil (69%, 113.4 mg); Rf = 0.5 (petroleum ether/ethyl acetate = 10:1, v/v); 1H NMR (600 MHz, CDCl3) δ = 7.96 (d, J = 7.8 Hz, 4H), 7.67-7.63 (m, 4H), 7.61 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 8.4 Hz, 4H), 7.48 (t, J = 7.8 Hz, 2H), 7.40-7.38 (m, 3H), 4.38 (t, J = 7.2 Hz, 1H), 3.82-3.77 (m, 1H), 3.65-3.60 (m, 1H), 2.71-2.66 (m, 1H), 2.61-2.56 (m, 1H); 13C NMR (150 MHz, CDCl3) δ = 142.2, 139.9, 139.1, 135.6, 134.1, 129.2, 128.8, 128.1, 127.9, 127.8, 127.7, 127.0, 110.7, 49.8, 46.2, 35.0; HRMS (ESI) calcd for C28H28N2NaO4S3 ([M + Na]+), 571.0790, found 571.0792.

N-(3-(4-fluorophenyl)-3-thiocyanatopropyl)-N-(phenylsulfonyl)benzenesulfonamide (4g)
Pale yellow oil (79%, 116.1 mg); R_f = 0.5 (petroleum ether/ethyl acetate = 10:1, v/v); ^1H NMR (600 MHz, CDCl_3) δ = 7.95 (d, J = 7.2 Hz, 4H), 7.68 (t, J = 7.2 Hz, 2H), 7.56 (t, J = 7.8 Hz, 4H), 7.31-7.30 (m, 2H), 7.11 (t, J = 8.4 Hz, 2H), 4.32(t, J = 7.8 Hz, 1H), 3.79-3.74 (m, 1H), 3.63-3.58 (m, 1H), 2.62-2.52 (m, 2H); ^13C NMR (150 MHz, CDCl_3) δ = 163.8 (d, J = 247.95 Hz), 139.2, 134.2, 132.9 (d, J = 3.3 Hz), 129.4 (d, J = 8.25 Hz), 129.3, 128.1, 116.4 (d, J = 21.75 Hz), 110.6, 49.3, 46.3, 35.1; ^19F NMR (565 MHz, CDCl_3) δ = -111.18 - -111.24 (m, 1F); HRMS (ESI) calcd for C_{22}H_{19}FN_{2}NaO_{2}S_3 ([M + Na]^+), 513.0383, found 513.0379.

![N-(3-(4-chlorophenyl)-3-thiocyanatopropyl)-N-(phenylsulfonfyl)benzenesulfonamide (4h)](image)

N-(3-(4-chlorophenyl)-3-thiocyanatopropyl)-N-(phenylsulfonfyl)benzenesulfonamide (4h)

Light yellow oil (yield 109.3 mg, 72%); R_f = 0.5 (petroleum ether/ethyl acetate = 10:1, v/v); ^1H NMR (600 MHz, CDCl_3) δ = 7.95 (d, J = 7.8 Hz, 4H), 7.68 (t, J = 7.2 Hz, 2H), 7.56 (t, J = 7.8 Hz, 4H), 7.40 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 4.29 (t, J = 7.2 Hz, 1H), 3.79-3.74 (m, 1H), 3.62-3.57 (m, 1H), 2.62-2.56 (m, 1H), 2.54-2.49 (m, 1H); ^13C NMR (150 MHz, CDCl_3) δ = 139.3, 134.2, 133.8, 130.2, 129.3, 128.1, 127.7, 127.7, 110.3, 46.3, 45.4, 34.3; HRMS (ESI) calcd for C_{22}H_{19}ClN_{2}NaO_{2}S_3 ([M + Na]^+), 529.0088, found 529.0078.

![N-(3-(4-bromophenyl)-3-thiocyanatopropyl)-N-(phenylsulfonfyl)benzenesulfonamide (4i)](image)

N-(3-(4-bromophenyl)-3-thiocyanatopropyl)-N-(phenylsulfonfyl)benzenesulfonamide (4i)

Light yellow oil (64%, 105.6 mg); R_f = 0.5 (petroleum ether/ethyl acetate = 10:1, v/v); ^1H NMR (600 MHz, CDCl_3) δ = 7.87 (d, J = 7.8 Hz, 4H), 7.61 (t, J = 7.2 Hz, 2H), 7.49-7.46 (m, 6H), 7.13 (d, J = 8.4 Hz, 2H), 4.21 (t, J = 7.8 Hz, 1H), 3.71-3.67 (m, 1H), 3.54-3.49 (m, 1H), 2.55-2.49 (m, 1H), 2.47-2.41 (m, 1H); ^13C NMR (150 MHz, CDCl_3) δ = 139.1, 136.1, 134.2, 132.5, 129.3, 129.1, 128.1, 123.5, 110.4, 49.2, 46.2, 34.8; HRMS (ESI) calcd for C_{22}H_{18}BrN_{2}NaO_{2}S_3 ([M + Na]^+), 572.9583, found 572.9587.
N-(phenylsulfonyl)-N-(3-thiocyanato-3-(4
(trifluoromethoxy)phenyl)propyl)benzenesulfonamide (4j)

Yellow oil (yield 135.1 mg, 81%); Rf = 0.5 (petroleum ether/ethyl acetate = 10:1, v/v); 1H NMR (600 MHz, CDCl3) δ = 7.94 (d, J = 8.4 Hz, 4H), 7.67 (t, J = 7.2 Hz, 2H), 7.54 (t, J = 7.8 Hz, 4H), 7.37 (d, J = 8.4 Hz, 1H), 7.27 (d, J = 7.8 Hz, 1H), 4.32 (t, J = 7.8 Hz, 1H), 3.80-3.76 (m, 1H), 3.62-3.57 (m, 1H), 2.63-2.60 (m, 1H), 2.56-2.53 (m, 1H). 13C NMR (150 MHz, CDCl3) δ = 149.7, 139.1, 135.8, 134.3, 129.4, 129.2, 129.0 (q, J = 256.2 Hz), 128.2, 121.6, 110.4, 48.9, 46.1, 34.9; 19F NMR (565 MHz, CDCl3) δ = -57.76 (s, 1CF3O); HRMS (ESI) calcd for C23H19F3N2O3S3 ([M + Na]+), 579.0300, found 579.0300.

N-(phenylsulfonyl)-N-(3-thiocyanato-3-(m-tolyl)propyl)benzenesulfonamide (4k)

White solid (65%, 94.7 mg); Rf = 0.5 (petroleum ether/ethyl acetate = 10:1, v/v); mp 144-145 ºC; 1H NMR (600 MHz, CDCl3) δ = 7.95 (d, J = 7.8 Hz, 4H), 7.67 (t, J = 7.8 Hz, 2H), 7.55 (t, J = 7.8 Hz, 4H), 7.31 (t, J = 7.8 Hz, 1H), 7.20 (d, J = 7.8 Hz, 1H), 7.11 (s, 1H), 4.29 (t, J = 7.8 Hz, 1H), 3.78-3.73 (m, 1H), 3.60-3.55 (m, 1H), 2.65-2.59 (m, 1H), 2.56-2.51 (m, 1H), 2.38 (s, 3H); 13C NMR (150 MHz, CDCl3) δ = 139.3, 139.2, 136.7, 134.2, 130.2, 129.3, 129.2, 128.2, 124.6, 111.0, 50.2, 46.4, 35.3, 21.5; HRMS (ESI) calcd for C22H23N2O4S3 ([M + Na]+), 509.0634, found 509.0630.

N-3-(1,1'-biphenyl)-3-thiocyanatopropyl)-N-(phenylsulfonyl)benzenesulfonamide (4l)
Pale yellow oil (80%, 132.1 mg); R_f = 0.5 (petroleum ether); ¹H NMR (600 MHz, CDCl₃) δ = 7.94 (d, J = 7.2 Hz, 4H), 7.63 (t, J = 7.8 Hz, 5H), 7.52-7.45 (m, 8H), 7.39 (t, J = 7.2 Hz, 1H), 7.29 (d, J = 7.8 Hz, 1H), 4.38 (t, J = 7.2 Hz, 1H), 3.82-3.77 (m, 1H), 3.64-3.59 (m, 1H), 2.71-2.69 (m, 1H), 2.63-2.59 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ = 142.4, 140.2, 139.2, 137.4, 134.2, 129.3, 129.0, 128.2, 127.9, 127.2, 126.4, 126.3, 110.9, 50.0, 46.4, 35.2; HRMS (ESI) calcd for C₂₈H₂₄N₂N₂O₄S₄ ([M + Na]+), 571.0790, found 571.0791.

![Chemical Structure](image)

N-(3-(3-fluorophenyl)-3-thiocyanatopropyl)-N-(phenylsulfonyl)benzenesulfonamide (4m)

Light yellow oil (62%, 91.1 mg); R_f = 0.5 (petroleum ether/ethyl acetate = 10:1, v/v); ¹H NMR (600 MHz, CDCl₃) δ = 7.96 (d, J = 7.8 Hz, 4H), 7.68 (t, J = 7.8 Hz, 2H), 7.56 (t, J = 7.8 Hz, 4H), 7.41-7.37 (m, 1H), 7.12-7.08 (m, 2H), 7.02-7.00 (m, 1H), 4.29 (t, J = 7.8 Hz, 1H), 3.81-3.76 (m, 1H), 3.75-3.71 (m, 1H), 3.65-3.60 (m, 1H), 2.60-2.54 (m, 1H), 2.53-2.49 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ = 163.7 (d, J = 246.9 Hz), 139.6 (d, J = 7.05 Hz), 139.2, 134.2, 131.0 (d, J = 8.25 Hz), 129.3, 128.2, 123.2 (d, J = 3.0 Hz), 116.5 (d, J = 20.85 Hz), 114.6 (d, J = 22.35 Hz), 110.3, 49.2, 46.2, 34.9; ¹⁹F NMR (565 MHz, CDCl₃) δ = -111.75 - -111.80 (m, 1F); HRMS (ESI) calcd for C₂₂H₁₉FN₂NaO₄S₄ ([M + Na]+), 513.0383, found 513.0380.

![Chemical Structure](image)

N-(3-(3-chlorophenyl)-3-thiocyanatopropyl)-N-(phenylsulfonyl)benzenesulfonamide (4n)

White solid (56%, 85.0 mg); R_f = 0.5 (petroleum ether/ethyl acetate = 10:1, v/v); ¹H NMR (600 MHz, CDCl₃) δ = 7.96 (d, J = 7.8 Hz, 4H), 7.69 (t, J = 8.4 Hz, 2H), 7.57 (t, J = 7.8 Hz, 4H), 7.37-7.34 (m, 2H), 7.27 (s, 1H), 7.23 (d, J = 6.6 Hz, 1H), 4.26 (t, J = 7.2 Hz, 1H), 3.78-3.76 (m, 1H), 3.63-3.59 (m, 1H), 2.59-2.50 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ = 139.2, 139.1,
135.1, 134.2, 130.6, 129.6, 129.3, 128.2, 127.7, 125.6, 110.3, 49.1, 46.1, 34.9; HRMS (ESI) calcd for C$_{23}$H$_{10}$F$_3$NaO$_4$S$_3$ ([M + Na]$^+$), 529.0088, found 529.0084.

![Structure of compound 4o]

$N$-(phenylsulfonyl)-$N$-(3-thiocyanato-3-(3-(trifluoromethoxy)phenyl)propyl)benzenesulfonamide (4o)

Light yellow oil (61%, 100 mg); $R_f = 0.5$ (petroleum ether/ethyl acetate = 10:1, v/v); $^1$H NMR (600 MHz, CDCl$_3$) $\delta = 7.96$ (d, $J = 7.8$ Hz, 4H), 7.68 (t, $J = 7.8$ Hz, 2H), 7.56 (t, $J = 7.2$ Hz, 4H), 7.47 (t, $J = 7.2$ Hz, 1H), 7.28 (t, $J = 8.4$ Hz, 2H), 7.15 (s, 1H), 4.30 (t, $J = 7.2$ Hz, 1H), 3.80-3.78 (m, 1H), 3.68-3.63 (m, 1H), 2.61-2.50 (m, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta =$ 149.7, 139.6, 139.2, 134.3, 130.8, 129.5 (q, $J$ =239.3 Hz), 129.3, 128.2, 125.8, 121.7, 120.1, 110.2, 49.1, 46.2, 34.8; $^{19}$F NMR (565 MHz, CDCl$_3$) $\delta =$ -57.83 (s, 1CF$_3$O); HRMS (ESI) calcd for C$_{23}$H$_{10}$F$_3$NaO$_4$S$_3$ ([M + Na]$^+$), 579.0300, found 579.0304.

![Structure of compound 4p]

$N$-(phenylsulfonyl)-$N$-(3-thiocyanato-3-(o-tolyl)propyl)benzenesulfonamide (4p)

White solid (82%, 119.6 mg); $R_f = 0.5$ (petroleum ether/ethyl acetate = 10:1, v/v); mp 111-112 °C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta = 7.96$ (d, $J = 8.4$ Hz, 4H), 7.66 (t, $J = 7.8$ Hz, 2H), 7.54 (t, $J = 7.2$ Hz, 4H), 7.34-7.28 (m, 3H), 7.21 (d, $J = 7.2$ Hz, 1H), 4.54 (dd, $J = 7.2$ Hz, 1H), 3.83-3.79 (m, 1H), 3.69-3.64 (m, 1H), 2.73-2.69 (m, 1H), 3.69-3.64 (m, 1H), 2.30(s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta =$ 139.2, 136.3, 134.6, 134.1, 131.1, 129.3, 129.1, 128.1, 127.0, 126.2, 110.9, 46.3, 45.8, 34.9, 19.2; HRMS (ESI) calcd for C$_{23}$H$_{22}$N$_2$NaO$_4$S$_3$ ([M + Na]$^+$), 509.0634, found 509.0634.
N-(3-(2-ethylphenyl)-3-thiocyanatopropyl)-N-(phenylsulfonyl)benzenesulfonamide (4q)

White solid (75%, 112.5 mg); Rf = 0.5 (petroleum ether/ethyl acetate = 10:1, v/v); mp 110-111 °C; ¹H NMR (600 MHz, CDCl₃) δ = 7.95 (d, J = 7.8 Hz, 4H), 7.66 (t, J = 7.8 Hz, 2H), 7.54 (t, J = 7.8 Hz, 4H), 7.37 (dd, J = 6.0, 1.8 Hz,1H), 7.33-7.30 (m, 2H), 7.24-7.23 (m, 1H), 4.62 (t, J = 7.8 Hz, 1H), 3.83-3.78 (m, 1H), 3.63-3.59 (m, 1H), 2.71-2.66 (m, 1H), 2.65-2.60 (m, 3H), 1.21 (t, J = 7.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ = 142.1, 139.2, 134.1, 133.9, 129.3, 129.2, 128.1, 126.9, 126.3, 111.0, 46.3, 45.2, 35.4, 25.4, 15.1; HRMS (ESI) calcd for C₂₅H₂₄N₂NaO₄S₃ ([M + Na]⁺), 523.0790, found 523.0761.

N-(3-(2-isopropylphenyl)-3-thiocyanatopropyl)-N-(phenylsulfonyl)benzenesulfonamide (4r)

White solid (92%, 141.8 mg); Rf = 0.5 (petroleum ether/ethyl acetate = 10:1, v/v); mp 111-112 °C; ¹H NMR (600 MHz, CDCl₃) δ = 7.96 (dd, J = 7.2, 1.2 Hz, 4H), 7.67 (t, J = 7.8 Hz, 2H), 7.55 (t, J = 7.8 Hz, 4H), 7.36-7.33 (m, 3H), 7.30-7.27 (m, 2H), 7.66 (t, J =7.8 Hz, 1H), 3.82-3.77 (m, 1H), 3.62-3.57 (m, 1H), 3.13-3.09 (m, 1H), 2.72-2.67 (m, 1H), 2.65-2.61 (m, 1H), 1.29 (d, J = 7.2 Hz, 3H), 1.16 (d, J = 6.6 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ = 147.0, 139.3, 134.2, 133.0, 129.5, 129.3, 128.2, 126.7, 126.4, 126.3, 111.0, 46.4, 35.7, 28.6, 24.4, 23.6; HRMS (ESI) calcd for C₂₅H₂₆N₂NaO₄S₃ ([M + Na]⁺), 537.0947, found 537.0948.

N-(3-(2-chlorophenyl)-3-thiocyanatopropyl)-N-(phenylsulfonyl)benzenesulfonamide (4s)

Light yellow oil (67%, 101.9 mg); Rf = 0.5 (petroleum ether/ethyl acetate = 10:1, v/v); ¹H NMR (600 MHz, CDCl₃) δ = 7.99 (d, J = 7.8 Hz, 4H), 7.67 (t, J = 7.2 Hz, 2H), 7.56 (t, J = 7.8 Hz,
4H), 7.41-7.32 (m, 4H), 4.71 (t, J = 7.8 Hz, 1H), 3.91-3.86 (m, 1H), 3.73-3.68 (m, 1H), 2.66-2.56 (m, 2H); 13C NMR (150 MHz, CDCl3) δ = 139.3, 134.6, 134.2, 133.8, 130.3, 130.2, 129.3, 128.1, 127.7, 127.7, 110.3, 46.3, 45.4, 34.3; HRMS (ESI) calcd for C26H19ClN2NaO3S3 ([M + Na]+), 529.0088, found 529.0088.

N-(phenylsulfonyl)-N-(3-thiocyanato-3-(2-(trifluoromethoxy)phenyl)propyl)benzenesulfonamide (4t)

White solid (65%, yield 105.3 mg); Rf = 0.5 (petroleum ether/ethyl acetate = 25:1, v/v); mp 52-53 °C; 1H NMR (600 MHz, CDCl3) δ = 7.98 (dd, J = 7.2, 1.2 Hz, 4H), 7.68 (t, J = 7.8 Hz, 2H), 7.56 (t, J = 7.8 Hz, 4H), 7.50 (dd, J = 6.0, 1.8 Hz, 1H), 7.46-7.43 (m, 1H), 7.32-7.31 (m, 1H), 4.61 (t, J = 7.2 Hz, 1H), 3.86-3.81 (m, 1H), 3.64-3.60 (m, 1H), 2.63-2.56 (m, 2H); 13C NMR (150 MHz, CDCl3) δ = 146.6, 139.3, 134.2, 130.6, 129.4, 129.2 (q, J = 260.9 Hz), 129.3, 129.2, 128.2, 127.4, 120.2, 110.1, 46.2, 42.2, 34.6; 19F NMR (565 MHz, CDCl3) δ = -56.71 (s, 1CF3O); HRMS (ESI) calcd for C26H19F3N2NaO3S3 ([M + Na]+), 579.0300, found 579.0304.

N-(3-(2,5-dimethylphenyl)-3-thiocyanatopropyl)-N-(phenylsulfonyl)benzenesulfonamide (4u)

Yellow oil (yield 93 mg, 62%); Rf = 0.5 (petroleum ether/ethyl acetate = 10:1, v/v); 1H NMR (600 MHz, CDCl3) δ = 7.96 (dd, J = 8.4, 1.8 Hz, 4H), 7.67 (t, J = 7.2 Hz, 2H), 7.55 (t, J = 8.4 Hz, 4H), 7.15 (s, 1H), 7.09 (s, 2H), 4.53 (t, J = 7.2 Hz, 1H), 3.81-3.76 (m, 1H), 3.67-3.62 (m, 1H), 2.72-2.67 (m, 1H), 2.63-2.58 (m, 1H), 2.37 (s, 3H), 2.27 (s, 3H); 13C NMR (150 MHz, CDCl3) δ = 139.3, 136.6, 134.2, 134.1, 133.2, 131.1, 129.9, 129.3, 128.2, 126.9, 111.0, 46.4, 46.0, 35.0, 21.1, 18.8; HRMS (ESI) calcd for C26H29N2NaO3S3 ([M + Na]+), 523.0790, found 523.0786.
N-(3-(2,4-dimethylphenyl)-3-thiocyanatopropyl)-N-(phenylsulfonyl)benzenesulfonamide (4v)

Yellow oil (52%, 78 mg); R_f = 0.5 (petroleum ether/ethyl acetate = 10:1, v/v); ^1H NMR (600 MHz, CDCl_3) \( \delta = 7.93 \) (dd, \( J = 7.2, 1.2 \) Hz, 4H), 7.66 (t, \( J = 7.2 \) Hz, 2H), 7.53 (t, \( J = 7.8 \) Hz, 4H), 7.15 (d, \( J = 7.2 \) Hz, 1H), 7.08 (d, \( J = 7.8 \) Hz, 1H), 7.02 (d, \( J = 7.8 \) Hz, 1H), 5.10 (t, \( J = 7.8 \) Hz, 1H), 3.80-3.75 (m, 1H), 3.53-3.48 (m, 1H), 2.76-2.69 (m, 1H), 2.58-2.53 (m, 1H), 2.47 (s, 3H), 2.33 (s, 3H); ^13C NMR (150 MHz, CDCl_3) \( \delta = 142.1, 139.2, 134.1, 133.9, 129.3, 129.2, 128.2, 126.9, 126.3, 111.0, 46.3, 45.2, 35.4, 25.4, 15.1 \); HRMS (ESI) calcd for C_{24}H_{24}N_{2}O_{4}S_{3} ([M + Na]^+), 523.0790, found 523.0794.

N-(3-(3,5-di-tert-butylphenyl)-3-thiocyanatopropyl)-N-(phenylsulfonyl)benzenesulfonamide (4w)

Light yellow solid (50%, 74.7 mg); R_f = 0.5 (petroleum ether/ethyl acetate = 25:1, v/v); mp 108-109 °C; ^1H NMR (600 MHz, CDCl_3) \( \delta = 7.96 \) (d, \( J = 8.4 \) Hz, 4H), 7.65 (t, \( J = 7.8 \) Hz, 2H), 7.53 (t, \( J = 7.8 \) Hz, 4H), 7.44 (s, 1H), 7.14 (s, 1H), 4.34 (t, \( J = 7.8 \) Hz, 1H), 3.77-3.74 (m, 1H), 3.58-3.53 (m, 1H), 2.73-2.68 (m, 1H), 2.60-2.55 (m, 1H), 1.34 (s, 18H); ^13C NMR (150 MHz, CDCl_3) \( \delta = 152.0, 139.4, 135.7, 134.1, 129.3, 128.2, 123.5, 111.2, 51.0, 46.5, 35.4, 35.0, 31.4 \); HRMS (ESI) calcd for C_{30}H_{36}N_{2}O_{4}S_{3} ([M + Na]^+), 607.1729, found 607.1749.

N-(3-(naphthalen-2-yl)-3-thiocyanatopropyl)-N(phenylsulfonyl)benzenesulfonamide (4x)
Light yellow oil (66%, 103.3 mg); R_f = 0.5 (petroleum ether/ethyl acetate = 10:1, v/v); ¹H NMR (600 MHz, CDCl₃) δ = 7.92 (dd, J = 7.8 Hz, 5H), 7.87-7.85 (m, 2H), 7.77 (s, 1H), 7.64 (t, J = 8.4 Hz, 2H), 7.56-7.55 (q, J = 3.6 Hz, 2H), 7.50 (t, J = 7.8 Hz, 4H), 7.44 (dd, J = 6.6, 1.8 Hz, 1H), 4.51 (t, J = 7.2 Hz, 1H), 3.83-3.78 (m, 1H), 3.63-3.58 (m, 1H), 2.78-2.73 (m, 1H), 2.67-2.62 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ = 139.2, 134.1, 134.0, 133.5, 133.0, 129.5, 129.2, 128.20, 128.16, 127.8, 127.11, 127.09, 126.9, 124.5, 110.8, 50.4, 46.3, 35.1; HRMS (ESI) calcd for C₂₆H₂₂N₂NaO₄S₃ ([M + Na]+), 545.0634, found 545.0621.

![SCN N(SO₂Ph₂)](4y)

**N-(phenylsulfonl)-N-(3-thiocyanoato-3-(thiophen-3-yl)propyl)benzenesulfonamide (4y)**

Light yellow oil (49%, 70.2 mg); R_f = 0.5 (petroleum ether/ethyl acetate = 10:1, v/v); ¹H NMR (600 MHz, CDCl₃) δ = 7.98 (dd, J = 7.8, 1.2 Hz, 2H), 7.69 (t, J = 7.8 Hz, 2H), 7.57 (t, J = 7.2 Hz, 4H), 7.41-7.40 (m, 1H), 7.34-7.33 (m, 1H), 7.11 (dd, J = 3.6, 1.2 Hz, 1H), 4.48 (t, J = 7.8 Hz, 1H), 3.81-3.76 (m, 1H), 3.70-3.65 (m, 1H), 2.66-2.61 (m, 1H), 2.56-2.53 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ = 139.2, 137.5, 134.2, 129.3, 128.2, 127.5, 126.1, 124.2, 110.7, 46.3, 45.3, 35.5; HRMS (ESI) calcd for C₂₀H₁₈N₂NaO₄S₃ ([M + Na]+), 501.0042, found 501.0039.

![SCN N(SO₂Ph₂)](4z)

**N-(4-phenyl-4-thiocyanatobutan-2-yl)-N-(phenylsulfonl)benzenesulfonamide (4z)**

A mixture of two diastereoisomers which are inseparable. The ratio of the two diastereoisomers was determined by ¹H NMR spectroscopy (d.r. = 1:2). The mixture was white solid (65%, 94.7 mg); mp 94-95 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 10:1, v/v); ¹H NMR (600 MHz, CDCl₃) δ = 7.91 (d, J = 7.8 Hz, 4.19H), 7.68-7.65 (m, 3.25H), 7.57-7.54 (m, 3.03H), 7.51-7.48 (m, 3.08H), 7.43-7.35 (m, 5.41H), 7.30 (d, J = 6.6 Hz, 1.14H), 7.25-7.23 (m, 2.22H), 4.24-4.17 (m, 2.58H), 4.15-4.11 (m, 0.57H), 3.01-2.96 (m, 1H), 2.82-2.77 (m, 0.57H), 2.74-2.71 (m, 0.55H), 2.68-2.63 (m, 1.01H), 1.32 (d, J = 7.2 Hz, 3.14H), 1.28 (d, J = 6.6 Hz, 1.60H); ¹³C NMR (150 MHz, CDCl₃) δ = 139.2, 137.5, 134.2, 129.3, 128.2, 127.5, 126.1, 124.2, 110.7, 46.3, 45.3, 35.5; HRMS (ESI) calcd for C₂₀H₁₈N₂NaO₄S₃ ([M + Na]+), 501.0042, found 501.0039.
MHz, CDCl$_3$) $\delta = 137.8$, 137.4, 134.1, 129.3, 129.2, 128.3, 127.6, 127.5, 110.8, 57.3, 50.1, 39.7, 19.6; HRMS (ESI) calcd for C$_{23}$H$_{22}$N$_2$NaO$_4$S$_3$ ([M + Na]$^+$), 509.0634, found 509.0643.

**N-(1,3-diphenyl-3-thiocyanatopropyl)-N-(phenylsulfonfonyl)benzenesulfonamide (4aa)**

4aa and 4aa’ are diastereomers and can be separated by column chromatography.

White solid (41%, 67.4 mg); mp 146-147 °C; $R_f = 0.5$ (petroleum ether/ethyl acetate = 10:1, v/v); ¹H NMR (600 MHz, CDCl$_3$) $\delta = 7.60$ (s, 2H), 7.46 (d, $J = 7.2$ Hz, 6H), 7.41-7.31 (m, 8H), 7.17-7.16 (m, 2H), 5.86 (dd, $J = 12$, 3.0 Hz, 1H), 4.04 (dd, $J = 10.8$, 1.8 Hz, 1H), 3.70-3.65 (m, 1H), 2.37-2.32 (m, 1H); ¹³C NMR (150 MHz, CDCl$_3$) $\delta = 138.5$, 133.4, 130.0, 129.2, 129.0, 128.8, 128.3, 127.2, 110.3, 62.2, 51.3, 37.7; HRMS (ESI) calcd for C$_{28}$H$_{32}$N$_2$NaO$_4$S$_3$ ([M + Na]$^+$), 571.0790, found 571.0785.

White solid (29%, 44.2 mg); $R_f = 0.5$ (petroleum ether/ethyl acetate = 8:1, v/v); mp 144-145 °C; ¹H NMR (600 MHz, CDCl$_3$) $\delta = 7.57$ (s, 2H), 7.46-7.33 (m, 15H), 6.92 (d, $J = 7.8$ Hz, 2H), 5.08 (dd, $J = 11.4$, 3.6 Hz, 1H), 4.18 (dd, $J = 10.8$, 4.2 Hz, 1H), 3.73-3.69 (m, 1H), 2.45-2.40 (m, 1H); ¹³C NMR (150 MHz, CDCl$_3$) $\delta = 136.4$, 133.7, 133.5, 129.9, 129.43, 129.36, 129.1, 128.9, 128.1, 127.6, 110.9, 61.6, 50.0, 38.8; HRMS (ESI) calcd for C$_{28}$H$_{32}$N$_2$NaO$_4$S$_3$ ([M + Na]$^+$), 571.0790, found 571.0784.

**N-(3-phenyl-3-((trifluoromethyl)thio)propyl)-N-(phenylsulfonfonyl)benzenesulfonamide (5a)**

Light yellow solid (56%, 57.7 mg); $R_f = 0.5$ (petroleum ether/ethyl acetate = 10:1, v/v); mp 76-77 °C; ¹H NMR (600 MHz, CDCl$_3$) $\delta = 7.91$ (d, $J = 8.4$ Hz, 4H), 7.69 (t, $J = 7.8$ Hz, 2H), 7.57 (t, $J = 7.2$ Hz, 4H), 7.41-7.40 (m, 1H), 7.34-7.33 (m, 1H), 7.11 (dd, $J = 3.6$, 1.2 Hz, 1H), 4.48 (t, $J = 7.8$ Hz, 1H), 3.81-3.76 (m, 1H), 3.70-3.65 (m, 1H), 2.66-2.61 (m, 1H), 2.56-2.53 (m, 1H); ¹³C NMR
(150 MHz, CDCl$_3$) $\delta = 139.2, 137.5, 134.2, 129.3, 128.2, 127.5, 126.1, 124.1, 110.7, 46.3, 45.3, 35.5$; $^{19}$F NMR (565 MHz, CDCl$_3$) $\delta = -39.69$ (s, 1SCF$_3$); HRMS (ESI) calcd for C$_{20}$H$_{18}$N$_2$NaO$_4$S$_4$ ([M + Na]$^+$), 501.0042, found 501.0039.

$N,N'$-(disulfanediylbis(3-phenylpropane-3,1-diyl))bis(N-(phenylsulfonyl)benzenesulfonamide) (5b)

Yellow oil (65%, 115.9 mg); $R_f = 0.5$ (petroleum ether/ethyl acetate = 4:1, v/v); $^1$H NMR (600 MHz, CDCl$_3$) $\delta = 7.93$ (t, $J = 7.8$ Hz, 8H), 7.60 (q, $J = 7.2$ Hz, 4H), 7.54-7.48 (m, 8H), 7.36-7.29 (m, 6H), 7.15-7.12 (m, 4H), 3.57-3.52 (m, 2H), 3.39-3.31 (m, 2H), 3.20-3.18 (m, 1H), 3.13-3.10 (m, 1H), 5.69 (dd, $J = 9.6$, 4.8 Hz, 1H), 3.81-3.76 (m, 1H), 3.65-3.60 (m, 1H), 3.07-3.00 (m, 1H), 2.42-2.34 (m, 2H), 2.26-2.21 (m, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta = 139.51$, 139.49, 139.3, 139.2, 133.90, 133.86, 129.11, 129.08, 128.7, 128.6, 128.3, 128.2, 128.1, 128.0, 127.9, 51.5, 51.3, 47.02, 47.01, 34.0, 33.8; HRMS (ESI) calcd for C$_{42}$H$_{38}$N$_2$NaO$_8$S$_8$ ([M + Na]$^+$), 915.1001, found 915.0996.

S16
5. Reference


6. Copies of NMR Spectra

Compound 4a
Compound 4b
Compound 4c
Compound 4c'
Compound 4d
Compound 4e
Compound 4g
Compound 4h
Compound 4i
Compound 4j
Compound 4l
Compound 4m

[Chemical Structure Image]

[Spectroscopic Data]
Compound 4o
Compound 4q
Compound 4r
Compound 4s
Compound 4u
Compound 4v
Compound 4w
Compound 4y
Compound 4z
Compound 4aa
Compound 5a
Compound 5a
Compound 5b