Straightforward Access to Thiocyanates via Dealkylative Cyanation of Sulfoxides

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1. General Information

Unless otherwise stated, all glassware was flame-dried before use and all reactions were performed under an atmosphere of argon. All solvents were distilled from appropriate drying agents prior to use. All reagents were used as received from commercial suppliers unless otherwise stated. Trifluoromethanesulfonic anhydride (Tf₂O) was distilled over P₄O₁₀ prior to use and stored under inert atmosphere in the fridge for a maximum of roughly 3 weeks.¹ Reaction progress was monitored by thin layer chromatography (TLC) performed on aluminum plates coated with silica gel F254 with 0.2 mm thickness. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining using potassium permanganate. Flash column chromatography was performed using silica gel 60 (230-400 mesh, Merck and co.). Neat infrared spectra were recorded using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Wavenumbers (νₘₚₓₗ) are reported in cm⁻¹. Mass spectra were obtained using a Bruker maXis UHR-TOF spectrometer with electrospray ionization (ESI) and a Qq-TOF mass analyzer. In several cases, the exact mass was not detected with ESI ionization. These were measured using an Agilent 7200B GC/Q-TOF Spectrometer with electron impact (EI) ionization method and a Q-TOF mass analyzer. The fragmentation pattern for the most significant fragmentations is reported with the relative intensity of the detected mass in percent denoted in parenthesis. Melting points were determined on a capillary apparatus and are uncorrected.

All ¹H NMR and ¹³C NMR spectra were recorded using a Bruker AV-400, AV-500 or AV-600 spectrometer at 300K. Chemical shifts are given in parts per million (ppm, δ), referenced to the solvent peak of CDCl₃, defined at δ = 7.26 ppm (¹H-NMR) and δ = 77.16 (¹³C-NMR). Coupling constants are quoted in Hz (J). ¹H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q) as they appeared in the spectrum. If the appearance of a signal differs from the expected splitting pattern, the observed pattern is designated as apparent (app). Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m) or broad (br).
2. Experimental Procedures

2.1. Synthesis of Starting Materials

Sulfoxide 1n was received from commercial supplier. Sulfoxides 1a, 1a', 1b, 1b', 1c, 1d, 1e, 1f, 1g, 1h, 1i, 1i', 1j, 1m, 1o, 1o', 1o'', 1p are known in the literature and were obtained by oxidation from the corresponding sulfides.

Sulfoxide 1k was obtained from 3-nitroaniline via a two-step literature procedure.\textsuperscript{13}

\textbf{methyl 3-methoxy-4-(methylsulfinyl)-2-naphthoate (1l)}

A solution of sulphenyl chloride (freshly made from dimethyl disulfide and sulfuryl chloride,\textsuperscript{14} 0.5 M in CH\textsubscript{2}Cl\textsubscript{2}, 4.4 mL, 2.2 mmol, 1.1 equiv.) was added to a solution of methyl 3-methoxy-2-naphthoate S1 (432 mg, 2.0 mmol, 1.0 equiv.)\textsuperscript{15} and triethylamine (0.42 mL, 3.0 mmol, 1.5 equiv.) in CH\textsubscript{2}Cl\textsubscript{2} (20 mL, 0.1 M) and the reaction was stirred for 12 h at ambient temperature (23 °C). Water was added (20 mL) and the reaction mixture was extracted with CH\textsubscript{2}Cl\textsubscript{2} (2 × 10 mL). The combined organic phases were dried over anhydrous magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude residue was purified by flash column chromatography (SiO\textsubscript{2}, heptane/ethyl acetate) affording methyl sulfide S2 as a mixture with the starting material in a ratio of 1.15:1 (317.2 mg, 53% purity).

Methyl 3-methoxy-4-(methylthio)-2-naphthoate S2 (53% purity, 247 mg, 0.50 mmol, 1.0 equiv.) was dissolved in methanol (10 mL, 0.05 M). A solution of sodium periodate in water (118.0 mg in 2 mL H\textsubscript{2}O, 0.55 mmol, 1.1 equiv.) was added and the reaction was stirred for 15 h at ambient temperature (23 °C). The precipitate was filtrated and the filtrate was evaporated \textit{in vacuo} to about 20% of its volume. Ethyl acetate (5 mL) and H\textsubscript{2}O (5 mL) were added and the reaction mixture was extracted with ethyl acetate (2 × 5 mL). The combined organic phases were dried
over anhydrous magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude residue was purified by flash column chromatography (SiO₂, heptane/ethyl acetate) affording the title compound (114.5 mg, 26% over 2 steps) as a yellow crystalline solid.

\[ ^1H\text{ NMR (400 MHz, CDCl}_3\text{): } \delta 9.28 (\text{dd, } J = 8.7, 0.8 \text{ Hz, } 1\text{H}), 8.53 (\text{s, } 1\text{H}), 7.97 - 7.88 (\text{m, } 1\text{H}), 7.66 (\text{ddd, } J = 8.6, 6.9, 1.4 \text{ Hz, } 1\text{H}), 7.54 (\text{ddd, } J = 8.1, 6.9, 1.1 \text{ Hz, } 1\text{H}), 4.00 (\text{s, } 3\text{H}), 3.98 (\text{s, } 3\text{H}), 3.11 (\text{s, } 3\text{H}). \]

\[ ^{13}C\text{ NMR (101 MHz, CDCl}_3\text{): } \delta 165.4, 154.8, 137.7, 133.6, 132.0, 130.7, 130.3, 129.8, 126.7, 123.2, 123.1, 64.0, 52.8, 40.7. \]

\[ \text{IR (neat) } \nu_{\text{max}}: 2943, 1721, 1445, 1439, 1209, 1077, 1054, 998, 954, 793, 756 \text{ cm}^{-1}. \]

\[ \text{HRMS (ESI\textsuperscript{+}): exact mass calculated for [M+Na\textsuperscript{+}] (C_{14}H_{14}O_4SNa) m/z 301.0505, found m/z 301.0502.} \]

2.2. Dealkylative cyanation

2.2.1. General Procedure: Dealkylative Cyanation of Sulfoxides

A solution of sulfoxide (1.0 equiv.) in CH₂Cl₂ (0.1 M) was cooled to −78 °C. Trifluoromethanesulfonic anhydride (Tf₂O, 1.0 equiv.) was added and the mixture was stirred for 5 or 15 minutes at this temperature (5 minutes for substrates: 1a-1e, 1h-1j, 1l-1p and 15 minutes for substrates: 1f, 1g, 1k). After this time, trimethylsilyl cyanide (TMSCN, 1.0 equiv.) was added and the resulting mixture was allowed to warm to ambient temperature (23 °C) over the course of 2 h. The reaction was diluted to two times its volume with CH₂Cl₂ and solid sodium bicarbonate (NaHCO₃, 3.0 equiv.) was added. The suspension was stirred for 5 minutes, dried over anhydrous magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude residue was purified by flash column chromatography (SiO₂, heptane/ethyl acetate) affording the products 2.
1-methyl-4-thiocyanatobenzene (2a)

![Chemical structure]

a) Following the general procedure using 1-methyl-4-(methylsulfinyl)benzene 1a (72.0 mg, 0.47 mmol, 1.0 equiv.), trifluoromethanesulfonic anhydride (79 µL, 0.47 mmol, 1.0 equiv.), trimethylsilyl cyanide (58 µL, 0.47 mmol, 1.0 equiv.) and CH$_2$Cl$_2$ (4.7 mL). The title compound was obtained (63.5 mg, 91%) as a colourless liquid.

b) Following the general procedure using 1-(cyclohexylsulfinyl)-4-methylbenzene 1a’ (22.2 mg, 0.10 mmol, 1.0 equiv.), trifluoromethanesulfonic anhydride (17 µL, 0.10 mmol, 1.0 equiv.), trimethylsilyl cyanide (12.5 µL, 0.10 mmol, 1.0 equiv.) and CH$_2$Cl$_2$ (1.0 mL). The title compound was obtained (4.3 mg, 29%) as a colourless liquid.

Spectroscopic data was consistent with the literature.$^{16}$

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.43 (d, $J = 8.2$ Hz, 2H), 7.24 (d, $J = 8.0$ Hz, 2H), 2.38 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 140.4, 131.1 (2C), 130.9 (2C), 120.7, 111.2, 21.3.

1-methyl-2-thiocyanatobenzene (2b)

![Chemical structure]

Following the general procedure using 1-methyl-2-(methylsulfinyl)benzene 1b (15.4 mg, 0.10 mmol, 1.0 equiv.), trifluoromethanesulfonic anhydride (17 µL, 0.10 mmol, 1.0 equiv.), trimethylsilyl cyanide (12.5 µL, 0.10 mmol, 1.0 equiv.) and CH$_2$Cl$_2$ (1.0 mL). The title compound was obtained (10.0 mg, 67%) as a yellow oil. Spectroscopic data was consistent with the literature.$^{16}$

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.64 – 7.62 (m, 1H), 7.34 (td, $J = 7.5$, 1.2 Hz, 1H), 7.31 – 7.26 (m, 2H), 2.48 (s, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 139.5, 132.1, 131.6, 130.4, 127.9, 123.8, 110.6, 20.6.
1,3,5-trimethyl-2-thiocyanatobenzene (2c)

Following the general procedure using 1,3,5-trimethyl-2-(methylsulfinyl)benzene 1c (18.2 mg, 0.10 mmol, 1.0 equiv.), trifluoromethanesulfonic anhydride (17 µL, 0.10 mmol, 1.0 equiv.), trimethylsilyl cyanide (12.5 µL, 0.10 mmol, 1.0 equiv.) and CH₂Cl₂ (1.0 mL). The title compound was obtained (17.6 mg, 99%) as a colourless liquid. Spectroscopic data was consistent with the literature.¹⁷

¹H NMR (600 MHz, CDCl₃): δ 7.01 (s, 2H), 2.55 (s, 6H), 2.30 (s, 3H).

¹³C NMR (151 MHz, CDCl₃): δ 142.9 (2C), 141.6, 130.2 (2C), 119.2, 111.0, 22.0 (2C), 21.2.

1-bromo-4-thiocyanatobenzene (2d)

Following the general procedure using 1-bromo-4-(methylsulfinyl)benzene 2c (21.9 mg, 0.10 mmol, 1.0 equiv.), trifluoromethanesulfonic anhydride (17 µL, 0.10 mmol, 1.0 equiv.), trimethylsilyl cyanide (12.5 µL, 0.10 mmol, 1.0 equiv.) and CH₂Cl₂ (1.0 mL). The title compound was obtained (13.8 mg, 65%) as colourless crystals. Spectroscopic data was consistent with the literature.¹⁸

¹H NMR (500 MHz, CDCl₃): δ 7.60 – 7.55 (m, 2H), 7.43 – 7.38 (m, 2H).

¹³C NMR (126 MHz, CDCl₃): δ 133.6 (2C), 131.7 (2C), 124.3, 123.6, 110.0.
1-chloro-2-thiocyanatobenzene (2e)

Following the general procedure using 1-chloro-2-(methylsulfinyl)benzene 1e (17.5 mg, 0.10 mmol, 1.0 equiv.), trifluoromethanesulfonic anhydride (17 µL, 0.10 mmol, 1.0 equiv.), trimethylsilyl cyanide (12.5 µL, 0.10 mmol, 1.0 equiv.) and CH₂Cl₂ (1.0 mL). The title compound was obtained (14.9 mg, 88%) as colourless crystals. Spectroscopic data was consistent with the literature.¹⁹

¹H NMR (600 MHz, CDCl₃): δ 7.71 (dd, J = 7.8, 1.5 Hz, 1H), 7.46 (dd, J = 7.8, 1.3 Hz, 1H), 7.41 – 7.31 (m, 2H).

¹³C NMR (151 MHz, CDCl₃): δ 132.9, 130.5, 130.3, 129.9, 128.6, 125.0, 109.4.

1,3-dichloro-2-thiocyanatobenzene (2f)

Following the general procedure using 1,3-dichloro-2-(methylsulfinyl)benzene 1f (20.9 mg, 0.10 mmol, 1.0 equiv.), trifluoromethanesulfonic anhydride (17 µL, 0.10 mmol, 1.0 equiv.), trimethylsilyl cyanide (12.5 µL, 0.10 mmol, 1.0 equiv.) and CH₂Cl₂ (1.0 mL). The title compound was obtained (19.0 mg, 93%) as colourless crystals.

¹H NMR (600 MHz, CDCl₃): δ 7.50 (d, J = 8.1 Hz, 2H), 7.42 – 7.37 (m, 1H).

¹³C NMR (151 MHz, CDCl₃): δ 140.7 (2C), 132.9, 129.6 (2C), 122.7, 108.3.

IR (neat) νmax: 3070, 2161, 1557, 1422, 1401, 1190, 783, 734 cm⁻¹.

This compound was not detected using ESI ionization. LRMS (EI⁺): mass calculated for [M]⁺ (C₇H₃Cl₂NS) m/z 202.9, found m/z 202.9. Fragmentation pattern: 206.9 (13), 204.9 (68), 202.9 (100), 170.0 (29), 168.0 (77), 142.0 (19), 133.0 (24).

Mₚ: 61–63 °C.
**1,3-difluoro-2-thiocyanatobenzene (2g)**

Following the general procedure using 1,3-difluoro-2-(methylsulfinyl)benzene 1g (17.6 mg, 0.10 mmol, 1.0 equiv.), trifluoromethanesulfonic anhydride (17 µL, 0.10 mmol, 1.0 equiv.), trimethylsilyl cyanide (12.5 µL, 0.10 mmol, 1.0 equiv.) and CH₂Cl₂ (1.0 mL). The title compound was obtained (13.1 mg, 76%) as a colourless crystals.

**¹H NMR (600 MHz, CDCl₃):** δ 7.52 (tt, J = 8.5, 6.3 Hz, 1H), 7.12 – 7.05 (m, 2H).

**¹³C NMR (151 MHz, CDCl₃):** δ 162.3 (C-F, ¹JC-F = 255.1, ³JC-F = 3.0 Hz, 2C), 134.0 (C-F, ³JC-F = 10.1 Hz), 112.8 (C-F, ²JC-F = 21.9, ⁴JC-F = 3.7 Hz, 2C), 108.3, 100.5 (C-F, ²JC-F = 21.6 Hz).

**¹⁹F NMR (565 MHz, CDCl₃):** δ -102.34 (t, J = 6.7 Hz).

**IR (neat) νmax:** 2953, 2349, 2323, 2165, 1606, 1469, 1288, 1241, 999, 787, 712, 671, 664, 606 cm⁻¹.

This compound was not detected using ESI ionization. **LRMS (EI):** mass calculated for [M]⁺ (C₇H₃F₂NS) m/z 171.0, found m/z 171.0. Fragmentation pattern: 173.0 (5), 172.0 (9), 171.0 (100), 151.0 (27), 127.1 (27), 101.1 (25), 63.1 (17).

**Mp:** 41–43 °C.

**2-thiocyanatonaphthalene (2h)**

Following the general procedure using 2-(methylsulfinyl)naphthalene 2h (19.0 mg, 0.10 mmol, 1.0 equiv.), trifluoromethanesulfonic anhydride (17 µL, 0.10 mmol, 1.0 equiv.), trimethylsilyl cyanide (12.5 µL, 0.10 mmol, 1.0 equiv.) and CH₂Cl₂ (1.0 mL). The title compound was obtained (16.4 mg, 89%) as colourless crystals. Spectroscopic data was consistent with the literature.²⁰
$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.03 (d, $J = 1.3$ Hz, 1H), 7.91 (d, $J = 8.7$ Hz, 1H), 7.86 (dt, $J = 6.9$, 3.6 Hz, 1H), 7.85 – 7.81 (m, 1H), 7.59 – 7.54 (m, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 133.8, 133.2, 130.4, 130.0, 128.1, 127.8, 127.8, 127.7, 126.4, 121.5, 110.8.

1-methoxy-2-thiocyanatobenzene (2i)

![Structure](image)

a) Following the general procedure using 1-methoxy-2-(methylsulfinyl)benzene 1i (17.0 mg, 0.10 mmol, 1.0 equiv.), trifluoromethanesulfonic anhydride (17 µL, 0.10 mmol, 1.0 equiv.), trimethylsilyl cyanide (12.5 µL, 0.10 mmol, 1.0 equiv.) and CH$_2$Cl$_2$ (1.0 mL). The title compound was obtained (16.5 mg, quantitative) as a yellow oil.

b) Following the general procedure using 1-(cyclohexylsulfinyl)-2-methoxybenzene 1i’ (23.8 mg, 0.10 mmol, 1.0 equiv.), trifluoromethanesulfonic anhydride (17 µL, 0.10 mmol, 1.0 equiv.), trimethylsilyl cyanide (12.5 µL, 0.10 mmol, 1.0 equiv.) and CH$_2$Cl$_2$ (1.0 mL). The title compound was obtained (8.0 mg, 48%) as a yellow oil.

Spectroscopic data was consistent with the literature.$^{16}$

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.57 (dd, $J = 7.8$, 1.4 Hz, 1H), 7.36 (td, $J = 8.3$, 1.5 Hz, 1H), 7.06 – 7.02 (m, 1H), 6.94 (d, $J = 8.2$ Hz, 1H), 3.92 (s, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 156.6, 130.7, 130.1, 122.2, 113.3, 111.6, 110.6, 56.3.

1,3-dimethoxy-2-thiocyanatobenzene (2j)

![Structure](image)
a) Following the general procedure using 1,3-dimethoxy-2-(methylsulfinyl)benzene 1j (100 mg, 0.50 mmol, 1.0 equiv.), trifluoromethanesulfonic anhydride (84 µL, 0.50 mmol, 1.0 equiv.), trimethylsilyl cyanide (63 µL, 0.50 mmol, 1.0 equiv.) and CH₂Cl₂ (5.0 mL). The title compound was obtained (78.3 mg, 80%) as colourless crystals.

b) Scale up experiment: Following the general procedure using 1,3-dimethoxy-2-(methylsulfinyl)benzene 1j (1.202 g, 6.00 mmol, 1.0 equiv.), commercial trifluoromethanesulfonic anhydride (1.0 mL, 6.00 mmol, 1.0 equiv.), trimethylsilyl cyanide (0.75 mL, 6.00 mmol, 1.0 equiv.) and CH₂Cl₂ (60.0 mL). After the solvent was removed under reduced pressure, the remaining solid was titurated with warm methyl tert-butyl ether (4x50 mL) and decanted leaving behind an oily residue. The combined methyl tert-butyl ether phases were concentrated in vacuo to give title compound (1.027 g, 88%) as colourless crystals.

1H NMR (400 MHz, CDCl₃): δ 7.37 (t, J = 8.4 Hz, 1H), 6.60 (d, J = 8.4 Hz, 2H), 3.92 (s, 6H).

13C NMR (101 MHz, CDCl₃): δ 160.1 (2C), 132.8, 111.1, 104.5 (2C), 98.9, 56.5 (2C).

IR (neat) νmax: 2152, 1576, 1474, 1431, 1256, 1100, 1019, 774, 664, 600 cm⁻¹.

HRMS (ESI⁺): exact mass calculated for [M+Na]⁺ (C₉H₉NO₂SNa) m/z 218.0246, found m/z 218.0243.

Mp: 103–105 °C.

1-nitro-3-thiocyanatobenzene (2k)

Following the general procedure using 1-(methylsulfinyl)-3-nitrobenzene 1k (18.5 mg, 0.10 mmol, 1.0 equiv.), trifluoromethanesulfonic anhydride (17 µL, 0.10 mmol, 1.0 equiv.), trimethylsilyl cyanide (12.5 µL, 0.10 mmol, 1.0 equiv.) and CH₂Cl₂ (1.0 mL). The title compound was obtained (10.1 mg, 56%) as colourless crystals. Spectroscopic data was consistent with the literature.²¹
**1H NMR (600 MHz, CDCl₃):** δ 8.39 (t, J = 2.1 Hz, 1H), 8.28 (ddd, J = 8.3, 2.2, 0.9 Hz, 1H), 7.88 (ddd, J = 7.9, 2.0, 1.0 Hz, 1H), 7.68 (t, J = 8.1 Hz, 1H).

**13C NMR (151 MHz, CDCl₃):** δ 149.1, 135.0, 131.4, 127.5, 124.5 (2C), 108.7.

**Methyl 3-methoxy-4-thiocyanato-2-naphthoate (2l)**

Following the general procedure using methyl 3-methoxy-4-(methylsulfinyl)-2-naphthoate **1l** (55.7 mg, 0.20 mmol, 1.0 equiv.), trifluoromethanesulfonic anhydride (34 µL, 0.20 mmol, 1.0 equiv.), trimethylsilyl cyanide (25 µL, 0.20 mmol, 1.0 equiv.) and CH₂Cl₂ (2.0 mL). The title compound was obtained (28.4 mg, 52%) as colourless crystals.

**1H NMR (400 MHz, CDCl₃):** δ 8.58 (s, 1H), 8.38 (d, J = 8.7 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 7.83 – 7.77 (m, 1H), 7.64 – 7.57 (m, 1H), 4.11 (s, 3H), 4.01 (s, 3H).

**13C NMR (101 MHz, CDCl₃):** δ 165.5, 158.9, 137.6, 135.7, 130.9, 130.3, 130.1, 127.0, 125.0, 124.8, 114.4, 110.7, 63.5, 52.9.

**IR (neat) νmax:** 2947, 2158, 1728, 1448, 1336, 1275, 1236, 1149, 1078, 1002, 756 cm⁻¹.

**HRMS (ESI⁺):** exact mass calculated for [M+Na]⁺ (C₁₄H₁₁NO₃SNa) m/z 296.0352, found m/z 296.0354.

**Mp:** 96–98 °C.

**1-thiocyanatoctane (2m)**

Following the general procedure using 1-(methylsulfinyl)octane **1m** (17.6 mg, 0.10 mmol, 1.0 equiv.), trifluoromethanesulfonic anhydride (17 µL, 0.10 mmol, 1.0 equiv.), trimethylsilyl cyanide
(12.5 µL, 0.10 mmol, 1.0 equiv.) and CH₂Cl₂ (1.0 mL). The title compound was obtained (9.7 mg, 57%) as a colourless liquid. Spectroscopic data was consistent with the literature.²¹

**¹H NMR (600 MHz, CDCl₃):** δ 2.95 (t, J = 7.3 Hz, 2H), 1.86 – 1.78 (m, 2H), 1.47 – 1.39 (m, 2H), 1.36 – 1.22 (m, 8H), 0.92 – 0.81 (m, 3H).

**¹³C NMR (151 MHz, CDCl₃):** δ 112.6, 34.2, 31.8, 30.0, 29.2, 29.0, 28.1, 22.7, 14.2.

3,5-dimethyl-4-thiocyanatophenyl methylcarbamate (2n)

Following the general procedure using 3,5-dimethyl-4-(methylsulfinyl)phenyl methylcarbamate 1n (Methiocarb sulfoxide, 33.8 mg, 0.14 mmol, 1.0 equiv.), trifluoromethanesulfonic anhydride (24 µL, 0.14 mmol, 1.0 equiv.), trimethylsilyl cyanide (17.5 µL, 0.14 mmol, 1.0 equiv.) and CH₂Cl₂ (1.5 mL). The title compound was obtained (24.0 mg, 73%) as beige crystals along with the deprotected 3,5-dimethyl-4-thiocyanatophenol (8.4 mg, 25%) as colourless crystals. The title compound appears in ¹H-NMR as a mixture of rotamers denoted as R1 (major) and R2 (minor) in a ratio of 7.6:1.

**¹H NMR (600 MHz, CDCl₃):** δ 7.02 (s, 2H, C₅H₄–H₉₂), 6.99 (s, 2H, C₅H₄–H₉₁), 5.04 (s, 1H, NH₉₁), 4.77 (s, 1H, NH₉₂), 2.95 (d, J = 4.7 Hz, 3H, NMe₉₂), 2.89 (d, J = 4.9 Hz, 3H, NMe₉₁), 2.59 (s, 6H, ArMe₉₂), 2.58 (s, 6H, ArMe₉₁).

**¹³C NMR (151 MHz, CDCl₃):** δ 154.5, 152.9, 144.5 (2C), 122.2 (2C), 118.7, 110.3, 27.7, 22.1 (2C).

**IR (neat) νmax:** 3346, 2946, 2155, 1727, 1525, 1459, 1300, 1239, 1158 cm⁻¹.

**HRMS (ESI⁺):** exact mass calculated for [M+Na]⁺ (C₁₁H₁₂N₂O₂SNa) m/z 259.0512, found m/z 259.0512.

Mp: 140–142 °C.
(2-thiocyanatoethyl)benzene (2o)

a) Following the general procedure using (2-(methylsulfinyl)ethyl)benzene 1o (33.7 mg, 0.20 mmol, 1.0 equiv.), trifluoromethanesulfonic anhydride (34 µL, 0.20 mmol, 1.0 equiv.), trimethylsilyl cyanide (25 µL, 0.20 mmol, 1.0 equiv.) and CH₂Cl₂ (1.0 mL). Analysis of the crude §H NMR showed quantitative formation of phenethyl trifluoromethanesulfonate (homobenzyl triflate) using mesitylene as internal standard, (2-thiocyanatoethyl)benzene 2o was not detected.

b) Following the general procedure using (2-(benzylsulfinyl)ethyl)benzene 1o’ (23.8 mg, 0.20 mmol, 1.0 equiv.), trifluoromethanesulfonic anhydride (34 µL, 0.20 mmol, 1.0 equiv.), trimethylsilyl cyanide (25 µL, 0.20 mmol, 1.0 equiv.) and CH₂Cl₂ (1.0 mL). Analysis of the crude §H NMR showed the formation of (2-thiocyanatoethyl)benzene 2o in 51% NMR yield using mesitylene as internal standard.

c) Following the general procedure using (sulfinylbis(ethane-2,1-diyld))dibenzene 1o” (51.7 mg, 0.20 mmol, 1.0 equiv.), trifluoromethanesulfonic anhydride (34 µL, 0.20 mmol, 1.0 equiv.), trimethylsilyl cyanide (25 µL, 0.20 mmol, 1.0 equiv.) and CH₂Cl₂ (2.0 mL). The title compound was obtained (28.6 mg, 88%) as a colourless oil. Spectroscopic data was consistent with the literature.²²

¹H NMR (600 MHz, CDCl₃): δ 7.39 – 7.32 (m, 2H), 7.32 – 7.27 (m, 1H), 7.26 – 7.19 (m, 2H), 3.22 – 3.16 (m, 2H), 3.15 – 3.08 (m, 2H).

¹³C NMR (151 MHz, CDCl₃): δ 137.8, 129.0 (2C), 128.8 (2C), 127.4, 112.2, 36.2, 35.3.
3-(2-thiocyanatophenyl)propyl trifluoromethanesulfonate (2p)

Following the general procedure using thiochromane 1-oxide 1p (16.6 mg, 0.10 mmol, 1.0 equiv.), trifluoromethanesulfonic anhydride (17 µL, 0.10 mmol, 1.0 equiv.), trimethylsilyl cyanide (12.5 µL, 0.10 mmol, 1.0 equiv.) and CH₂Cl₂ (1.0 mL). The title compound was obtained (31.8 mg, 98%) as a colourless oil.

*¹H NMR (600 MHz, CDCl₃): δ 7.71 (d, J = 7.8 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.39 – 7.29 (m, 2H), 4.60 (t, J = 6.0 Hz, 2H), 3.02 – 2.94 (m, 2H), 2.20 (tt, J = 12.4, 6.1 Hz, 2H).

*¹³C NMR (151 MHz, CDCl₃): δ 141.2, 133.5, 131.1, 130.9, 129.0, 123.6, 118.8 (C-F, ¹J_C-F = 319.5 Hz), 110.5, 76.1, 29.9, 29.8.

*¹⁹F NMR (565 MHz, CDCl₃): δ -74.61.

IR (neat) ν_{max}: 2938, 2865, 2158, 1467, 1411, 1245, 1209, 1143, 1116, 1030, 930, 756 cm⁻¹.

HRMS (ESI⁺): exact mass calculated for [M+H]⁺ (C₁₁H₁₁F₃NO₃S₂) m/z 326.0127, found m/z 326.1030.

2.3. One-pot transformations

hex-1-yn-1-yl(naphthalen-2-yl)sulfane (3)

A solution of 2-(methylsulfinyl)naphthalene 1h (28.5 mg, 0.15 mmol, 1.0 equiv.) in CH₂Cl₂ (1.5 mL, 0.1 M) was cooled −78 °C. Trifluoromethanesulfonic anhydride (25 µL, 0.15 mmol, 1.0 equiv.) was added and the mixture was stirred for 5 minutes at this temperature. After this time, trimethylsilyl cyanide (19 µL, 0.15 mmol, 1.0 equiv.) was added and the resulting mixture was
allowed to warm to ambient temperature (23 °C) over the course of 2 h. In a separate flame-dried Schlenk tube, a solution of 1-hexyne (103 µL, 0.90 mmol, 6.0 equiv.) in THF (4.5 mL) was cooled to −78 °C and n-BuLi (1.6 M in hexane, 0.56 mL, 0.90 mmol, 6.0 equiv.) was added dropwise. This solution was stirred for 30 minutes at −78 °C then warmed to 0 °C. The volatiles of the reaction mixture containing the crude thiocyanate were removed in vacuo and the flask containing the crude material was placed under argon in an ice bath. The solution of lithium alkynylide in THF was transferred using a syringe and the reaction was allowed to warm to ambient temperature (23 °C) and stirred for 15 h. A saturated aqueous solution of ammonium chloride (4 mL) was added and the reaction mixture was extracted with ethyl acetate (2 × 5 mL). The combined organic phases were dried over anhydrous magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude residue was purified by flash column chromatography (SiO₂, heptane/ethyl acetate) affording the product (28.9 mg, 80%) as a yellowish oil.

**1H NMR (600 MHz, CDCl₃):** δ 7.88 (d, J = 1.6 Hz, 1H), 7.80 (t, J = 7.8 Hz, 2H), 7.76 (d, J = 8.0 Hz, 1H), 7.51 – 7.42 (m, 3H), 2.52 (t, J = 7.1 Hz, 2H), 1.68 – 1.62 (m, 2H), 1.57 – 1.49 (m, 2H), 0.98 (t, J = 7.3 Hz, 3H).

**13C NMR (151 MHz, CDCl₃):** δ 133.9, 132.0, 131.3, 128.8, 128.0, 127.2, 126.9, 125.9, 124.1, 124.0, 100.5, 64.8, 30.9, 22.2, 20.2, 13.8.

**IR (neat) νmax:** 3053, 2928, 2865, 1588, 1501, 1457, 1134, 1067, 944, 849, 809, 742 cm⁻¹.

This compound was not detected using ESI ionization. **LRMS (EI⁺):** mass calculated for [M]⁺ (C₁₆H₁₆S) m/z 240.1, found m/z 240.1. Fragmentation pattern: 242.1 (5), 241.1 (18), 240.1 (100), 197.1 (44), 160.1 (36), 153.1 (52), 152.1 (36).
hex-1-yn-1-yl(naphthalen-2-yl)sulfane (4)

\[
\begin{align*}
\text{O} & \quad \text{Tf}_2\text{O (1.0 equiv.),} \\
& \quad \text{CH}_2\text{Cl}_2, -78 \degree \text{C, 5 min} \\
& \quad \text{then TMSCN (1.0 equiv.),} \\
& \quad -78 \degree \text{C to rt, 2 h} \\
& \quad \text{then TMSCF}_3 \ (5 \text{ equiv.)} \\
& \quad \text{TBAF in (1M in THF, 5 equiv)} \\
& \quad \text{DCM/THF, 0 \degree \text{C to rt, 15 h}}
\end{align*}
\]

A solution of 2-(methylsulfinyl)naphthalene 1h (28.5 mg, 0.15 mmol, 1.0 equiv.) in CH$_2$Cl$_2$ (1.5 mL, 0.1 M) was cooled $-78 \degree$C. Trifluoromethanesulfonic anhydride (25 µL, 0.15 mmol, 1.0 equiv.) was added and the mixture was stirred for 5 minutes at this temperature. After this time, trimethylsilyl cyanide (19 µL, 0.15 mmol, 1.0 equiv.) was added and the resulting mixture was allowed to warm to ambient temperature (23 °C) over the course of 2 h. The reaction was placed in an ice bath and (trifluoromethyl)trimethylsilane (111 µL, 0.75 mmol, 5.0 equiv.) was added followed by a dropwise addition of a solution of TBAF (1 M in THF, 0.75 mL, 0.75 mmol, 5.0 equiv.). The reaction was allowed to warm to ambient temperature (23 °C) and stirred for 15 h. A saturated aqueous solution of ammonium chloride (1 mL) was added and the reaction mixture was extracted with ethyl acetate (2 × 2 mL). The combined organic phases were dried over anhydrous magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude residue was purified by flash column chromatography (SiO$_2$, heptane/ethyl acetate) affording the product (16.8 mg, 49%) as a colourless oil. Spectroscopic data was consistent with the literature.\textsuperscript{23}

\textsuperscript{1}H NMR (600 MHz, CDCl$_3$): δ 8.21 (d, $J = 1.0$ Hz, 1H), 7.91 – 7.82 (m, 3H), 7.67 (dd, $J = 8.6$, 1.5 Hz, 1H), 7.62 – 7.54 (m, 2H).

\textsuperscript{13}C NMR (151 MHz, CDCl$_3$): δ 137.0, 133.9, 133.4, 131.8, 129.7 (CF, $^1$J$_{CF} = 308.5$ Hz), 129.2, 128.2, 127.9, 127.8, 127.0, 121.5 (CF, $^3$J$_{CF} = 1.8$ Hz).

\textsuperscript{19}F NMR (565 MHz, CDCl$_3$): δ -42.49.
naphthalene-2-sulfonyl cyanide (5)

A solution of 2-(methylsulfinyl)naphthalene 1h (47.6 mg, 0.25 mmol, 1.0 equiv.) in CH₂Cl₂ (2.5 mL, 0.1 M) was cooled –78 °C. Trifluoromethanesulfonic anhydride (44 µL, 0.25 mmol, 1.0 equiv.) was added and the mixture was stirred for 5 minutes at this temperature. After this time, trimethylsilyl cyanide (31 µL, 0.25 mmol, 1.0 equiv.) was added and the resulting mixture was allowed to warm to ambient temperature (23 °C) over the course of 2 h. In a separate round bottom flask, a solution of trifluoroacetic anhydride (TFAA, 0.35 mL, 2.5 mmol, 10 equiv.) in CH₂Cl₂ (2.5 mL) was cooled to 0 °C and treated dropwise with hydrogen peroxide (30 wt.% in H₂O, 0.25 mL, 2.5 mmol, 10 equiv.).²⁴ The mixture was stirred for 45 minutes at 0 °C then, the crude thiocyanate solution in DCM was transferred from the other flask using a syringe. The round bottom flask was closed with a glass lid and placed in a sand bath (40 °C). The reaction mixture was stirred at this temperature for 16 h, when water (5 mL) was added. The reaction was extracted with DCM (2 x 5 mL) and the combined organic phases were dried over anhydrous magnesium sulfate. Filtration and evaporation of the solvent removed under reduced pressure afforded a crude residue which was purified by flash column chromatography (SiO₂, heptane/ethyl acetate) affording the product (32.9 mg, 61%) as colourless crystals.

¹H NMR (400 MHz, CDCl₃): δ 8.69 (d, J = 1.5 Hz, 1H), 8.14 (d, J = 8.8 Hz, 1H), 8.09 (d, J = 8.2 Hz, 1H), 8.04 – 7.96 (m, 2H), 7.85 – 7.79 (m, 1H), 7.78 – 7.72 (m, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 136.8, 134.0, 132.5, 132.1, 131.5, 131.1, 130.2, 128.9, 128.5, 122.0, 114.3.

IR (neat) νmax: 3065, 2927, 2183, 1377, 1176, 674 cm⁻¹.

This compound was not detected using ESI ionization. LRMS (EI⁺): mass calculated for [M]⁺ (C₁₁H₇NO₅S) m/z 217.0, found m/z 217.0. Fragmentation pattern: 218.0 (10), 217.0 (79), 153.1 (63), 128.1 (16), 127.1 (100), 126.1 (33).
$M_p$: 48–50 °C.
3. NMR Spectra

methyl 3-methoxy-4-(methylsulfinyl)-2-naphthoate (1l) – $^1$H NMR (400 MHz)

methyl 3-methoxy-4-(methylsulfinyl)-2-naphthoate (1l) – $^{13}$C NMR (101 MHz)
1-methyl-4-thiocyanatobenzene (2a) – $^1$H NMR (400 MHz)

1-methyl-4-thiocyanatobenzene (2a) – $^{13}$C NMR (101 MHz)
1-methyl-2-thiocyanatobenzene (2b) – $^1$H NMR (600 MHz)

1-methyl-2-thiocyanatobenzene (2b) – $^{13}$C NMR (151 MHz)
1,3,5-trimethyl-2-thiocyanatobenzene (2c) – $^1$H NMR (600 MHz)

1,3,5-trimethyl-2-thiocyanatobenzene (2c) – $^{13}$C NMR (151 MHz)
1-bromo-4-thiocyanatobenzene (2d) – $^1$H NMR (500 MHz)

$^1$H NMR spectrum of 1-bromo-4-thiocyanatobenzene (2d) showing peaks at various ppm values.

1-bromo-4-thiocyanatobenzene (2d) – $^{13}$C NMR (126 MHz)

$^{13}$C NMR spectrum of 1-bromo-4-thiocyanatobenzene (2d) showing peaks at various ppm values.
1-chloro-2-thiocyanatobenzene (2e) – \textsuperscript{1}H NMR (600 MHz)

1-chloro-2-thiocyanatobenzene (2e) – \textsuperscript{13}C NMR (151 MHz)
1,3-dichloro-2-thiocyano-benzene (2f) – $^1$H NMR (600 MHz)

1,3-dichloro-2-thiocyano-benzene (2f) – $^{13}$C NMR (151 MHz)
1,3-difluoro-2-thiocyanatobenzene (2g) – ^1^H NMR (600 MHz)

1,3-difluoro-2-thiocyanatobenzene (2g) – ^1^C NMR (151 MHz)
1,3-difluoro-2-thiocyanatobenzene (2g) – $^{19}$F NMR (565 MHz)

2-thiocyanatonaphthalene (2h) – $^1$H NMR (600 MHz)
2-thiocyanatonaphthalene (2h) – $^{13}$C NMR (151 MHz)

1-methoxy-2-thiocyanatobenzene (2i) – $^1$H NMR (600 MHz)
1-methoxy-2-thiocyanatobenzene (2i) – $^{13}$C NMR (151 MHz)

1,3-dimethoxy-2-thiocyanatobenzene (2j) – $^1$H NMR (400 MHz)
1,3-dimethoxy-2-thiocyanatobenzene (2j) – $^{13}$C NMR (101 MHz)

1-nitro-3-thiocyanatobenzene (2k) – $^1$H NMR (600 MHz)
1-nitro-3-thiocyanatobenzene (2k) – $^{13}$C NMR (151 MHz)

![1-nitro-3-thiocyanatobenzene spectrum](image)

methyl 3-methoxy-4-thiocyanato-2-naphthoate (2l) – $^1$H NMR (400 MHz)

![methyl 3-methoxy-4-thiocyanato-2-naphthoate spectrum](image)
methyl 3-methoxy-4-thiocyanato-2-naphthoate (2l) – $^{13}$C NMR (101 MHz)

1-thiocyanatoctane (2m) – $^1$H NMR (600 MHz)
1-thiocyanatoctane (2m) – $^{13}$C NMR (151 MHz)

3,5-dimethyl-4-thiocyanatophenyl methylcarbamate (2n) – $^1$H NMR (600 MHz)
3,5-dimethyl-4-thiocyanatophenyl methylcarbamate (2n) – $^{13}$C NMR (151 MHz)

(2-thiocyanatoethyl)benzene (1o) – $^1$H NMR (600 MHz)
(2-thiocyanatoethyl)benzene (1o) – $^{13}$C NMR (151 MHz)

3-(2-thiocyanatophenyl)propyl trifluoromethanesulfonate (2p) – $^1$H NMR (600 MHz)
3-(2-thiocyanatophenyl)propyl trifluoromethanesulfonate (2p) – $^{13}$C NMR (151 MHz)

3-(2-thiocyanatophenyl)propyl trifluoromethanesulfonate (2p) – $^{19}$F NMR (565 MHz)
hex-1-yn-1-yl(naphthalen-2-yl)sulfane (3) – $^1$H NMR (600 MHz)

hex-1-yn-1-yl(naphthalen-2-yl)sulfane (3) – $^{13}$C NMR (151 MHz)
naphthalen-2-yl(trifluoromethyl)sulfane (4) – $^1$H NMR (600 MHz)

naphthalen-2-yl(trifluoromethyl)sulfane (4) – $^{13}$C NMR (151 MHz)
naphthalen-2-yl(trifluoromethyl)sulfane (4) – $^{19}$F NMR (565 MHz)

naphthalene-2-sulfonyl cyanide (5) – $^1$H NMR (400 MHz)
naphthalene-2-sulfonyl cyanide (S) – $^{13}$C NMR (101 MHz)
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