Supporting Information

From 1,2-difunctionalisation to cyanide-transfer cascades – Pd-catalysed cyanosulfenylation of internal (oligo)alkynes

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1) General Experimental

All solvents were dried and stored over molecular sieves under argon atmosphere unless otherwise stated. Air- and moisture-sensitive reactions were carried out in oven-dried or flame-dried glassware, septum-capped under atmospheric pressure of argon. Commercially available compounds were used without further purification unless otherwise stated.

Proton (\(^1\)H), carbon (\(^{13}\)C) and fluorine (\(^{19}\)F) NMR spectra were recorded on a Bruker AV300, Bruker AVIII400, Bruker AVIIIHD500 or Bruker AVII600 instrument using the residual signals from CHCl\(_3\), \(\delta = 7.26\) ppm and \(\delta = 77.16\) ppm, as internal reference for \(^1\)H and \(^{13}\)C chemical shifts, respectively. Additionally, tetramethylsilane (TMS; \(\delta = 0.00\) ppm; 0.03%) was added to NMR samples. The following abbreviations were used for \(^1\)H and \(^{13}\)C NMR chemical shifts: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet/quintet, m = multiplet and combinations thereof. GC-HRMS mass spectrometry was carried out on an Agilent 6890 gas chromatograph coupled to a JMS-T100GC (GCAccuTOF, JEOL, Japan) time of flight mass spectrometer in electron ionization (EI) mode. ESI-HRMS mass spectrometry was carried out on an FTICR instrument. EI-HRSM mass spectrometry was carried out on JOEL AccuTOF GC JMS-T100GC instrument. IR spectra were recorded on an ATR spectrometer Tensor 27 from Bruker. Melting Points were recorded with a Büchi SMP-20 and Büchi M-560 melting point meter and are uncorrected. Semi-preparative HPLC were conducted using an Agilent 1260 Infinity system with an Agilent Pursuit XR5 C18 column (250 x 10 mm) or an Agilent Polaris 5 C8-A column (250 x 10 mm) with CH\(_3\)CN/H\(_2\)O (isocratic or gradient) as eluent mixture.
2) General Procedures

General Procedure (GP 1) for the preparation of propargylic ethers 11

A solution of SM1 (1.00 equiv., 0.14 - 0.36 M), PPh₃ (1.10 - 1.50 equiv.) and the corresponding propargylic alcohol (1.00 - 1.50 equiv.) in dry toluene or THF was cooled to 0 °C. DIAD (1.10 – 1.50 equiv., 0.27 - 0.59 M) in dry toluene or THF was added dropwise to the stirred solution. After completion, the reaction mixture was warmed to RT and stirred overnight. The solvent was removed under reduced pressure and silica gel column chromatography gave the desired products.

Carried out in accordance to a reported procedure.¹

General Procedure (GP 2) for the preparation of propargylic ethers 11²

To a mixture of SM2, PdCl₂(PPh₃)₄, CuI, NEt₃, Phl derivative in triethylamine (and DMF) was added the corresponding iodobenzene derivative. After stirring for 24 h at RT the mixture was quenched with water, extracted with diethyl ether, washed with brine and dried over Na₂SO₄. The solvent was removed and the crude product was purified by silica gel column chromatography.

General Procedure (GP 3) for the preparation of thiocyanatobenzenes 1

Following a modified reported procedure\textsuperscript{3} 3,5-bis(trifluoromethyl)phenyl(cyano)iodoniumtriflate\textsuperscript{4} (X-CN, 2.00 equiv.) was weighed into a sealable tube and a solution of the thioether (1.00 equiv.) in a mixture of CH\textsubscript{3}CN/THF (1:1) was added and the tube was capped. The (often) resulting brown solution was heated to 60 °C and stirred for 12 h. After cooling, the solvent was removed and the product was obtained after silica gel column chromatography.

**General Procedure (GP 3, alternative B) for the preparation of aromatic thiocyanates**

\[
\begin{align*}
\text{MeS} & \quad \text{R} \\
\begin{array}{c}
\text{(1)} \\
\text{X-CN, CH}_3\text{CN/THF} \\
\text{RT, 30 min}
\end{array} & \quad \rightarrow \\
\text{SCN} & \quad \text{R}
\end{align*}
\]

To a stirred solution of the thioether (1.00 equiv.) in a mixture of CH\textsubscript{3}CN/THF (1:1, 0.35 mM) was smoothly added 3,5-bis(trifluoromethyl)phenyl(cyano)iodoniumtriflate (X-CN, 1.00 equiv.). After 10 min the reaction progress was controlled by TLC and the reaction was stopped after 30 min. The solvent was removed and the product was obtained after silica gel column chromatography.

**General Procedure (GP 4) for the preparation of alkyne substituted alkyl bromides 13.1 from alkyl dibromides\textsuperscript{5}**

\[
\begin{align*}
\begin{array}{c}
\text{R} \\
\text{n-Buli, THF, -78 °C}
\end{array} & \quad \rightarrow \\
\begin{array}{c}
\text{R} \\
\text{DMPU, -78 °C}
\end{array} & \quad \rightarrow \\
\begin{array}{c}
\text{R} \\
\text{Br}
\end{array} & \quad \text{n-Br}
\end{align*}
\]

To a stirred solution of the alkyne (1.0 equiv.) in THF (0.2 M) was added n-butyllithium (2.5 M solution in THF, 1.1 equiv) slowly at −78 °C. The clear solution was allowed to warm to ambient temperature over 0.5 hours. First DMPU (1.2 equiv.) and then the alkyl dibromide were added at −78 °C. The reaction mixture was again allowed to warm to ambient temperature over 2 h. Remaining organolithium compounds were quenched by the addition of water. The resulting mixture was extracted with diethyl ether. The combined organic layers were washed with brine and dried over Na\textsubscript{2}SO\textsubscript{4}. The solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography.

General Procedure (GP 5) for the preparation of alkyne substituted alkyl bromides 13.1 from alkyl alcohols

\[
\text{R} \text{OH} + \text{CBr}_4, \text{PPh}_3, \text{imidazole} \rightarrow \text{R} \text{Br}
\]

The alcohol (1.0 equiv.), imidazole (2.0 equiv.) and PPh\(_3\) (2.0 equiv.) were dissolved in Et\(_2\)O/CH\(_3\)CN (4:1, 0.8 M). CBr\(_4\) (1.9 equiv.) was slowly added to the stirred solution at ambient temperature. After a few seconds a colorless precipitate was formed. The mixture was stirred for 1 h, diluted with an excess of pentane and filtrated. The filter cake was washed with additional pentane. The filtrate was concentrated in vacuo and the crude product was purified by flash column chromatography (pentane).

General Procedure (GP 6) for the preparation of aliphatic thiocyanates 3 (via S\(_{N}\))

\[
\text{R} \text{Br} + \text{EtOH, KSCN} \rightarrow \text{R} \text{SCN}
\]

A solution of the bromide (1.0 equiv.) and KSCN (1.5 equiv.) in EtOH (1 M) in a capped tube as stirred for 12 h at 85 °C. The reaction mixture was cooled to ambient temperature, diluted with water and extracted with DCM. The combined organic layers were dried over Na\(_2\)SO\(_4\). After evaporation of the solvents in vacuo the crude product was purified by flash column chromatography (pentane/ EtOAc = 10:1).

General Procedure (GP 7) for the preparation of aliphatic thiocyanates 3 (via MITSUNOBU)

\[
\text{R} \text{OH} + \text{PPh}_3, \text{NH}_4\text{SCN}, \text{DIAD, CH}_3\text{CN} \rightarrow \text{R} \text{SCN}
\]

The alcohol (1.0 equiv.), PPh\(_3\) (2.0 equiv.) and NH\(_4\)SCN (2.0 equiv.) were dissolved in CH\(_3\)CN (6 mL). DIAD (2.0 equiv.) was added slowly to the solution and the reaction mixture was stirred overnight at RT. After the solvent was evaporated in vacuo, the crude product was purified by flash column chromatography to afford the pure title product.

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General Procedure (GP CAT1) for the transformation of thiocyanates

A solution of the substrate in DMF (5 ml per 100 µmol) was degassed with argon for 20 min. Afterwards, triethylamine (5.0 equiv.), bis(benzonitrile)palladium dichloride (10 mol%) and XantPhos (20 mol%) were added and the reaction mixture was degassed for another 10 min while pre-stirring for 30 min at RT in a sealable flask. Subsequently, the reaction was heated for at least 7 h (or until full consumption of starting material; control by TLC) at 100 °C. DMF was co-evaporated (4-5 times) with toluene until dryness. The residue was then purified by flash column chromatography.

General Procedure (GP CAT2) for the transformation of thiocyanates

In a flask or tube three fifth of the solvent needed for the catalysis (5 ml for 100 µmol of substrate) were added to Pd(PPh₃)₄ (5 mol%) and SPhos (20 mol%). This mixture was prestirred for 30-45 min and then transferred to a tube with stirring bar containing the substrate in the remaining two fifth of solvent. The tube was sealed and the reaction mixture was stirred at 110 °C for the respective time. After cooling, the solvent was removed under reduced pressure (co-evaporation in with PhMe in case of DMF). The residue was then purified by flash column chromatography.
General Procedure (GP CAT2, alternative B) for the transformation of thiocyanates

In a flask or tube three fifth of the solvent needed for the catalysis (5 ml for 100 µmol of substrate) were added to $\text{Pd}_2($dba)$_3$ (10 mol%) and XantPhos (20 mol%). This mixture was prestirred for 30-45 min and then transferred to a tube with stirring bar containing the substrate in the remaining two fifth of solvent. The tube was sealed and the reaction mixture was stirred at 160 °C for the respective time. After cooling, the solvent was removed under reduced pressure. The residue was then purified by flash column chromatography.

General Procedure (GP CAT3) for the transformation of thiocyanates

The substrate (1.0 equiv.) was weighed in a microwave vial and dissolved in thoroughly degassed toluene (5 mL). Then, $\text{Pd}_2($dba)$_3$ (10 mol%) and XantPhos (20 mol%) were added. The microwave vial was capped and the solution was stirred at 160 °C for 3-14 hours. The solvent was evaporated in vacuo and the product was purified by flash column chromatography.
General Procedure (GP CAT4) for the intermolecular cyanosulfenylation

\[
\begin{align*}
\text{R}^1\text{S}^-\text{CN} + \text{R}^2=\text{R}^3 & \rightarrow \overset{\text{Pd}_2(\text{dba})_3 \atop \text{XantPhos}}{\text{PhMe, 160 °C, 24 h}} \text{R}^1\text{S}^-\text{C} \equiv \text{R}^3 \\
\text{7a} & \quad \text{7b} \\
\text{8}
\end{align*}
\]

Pd$_2$(dba)$_3$ (10 mol%) and XantPhos (20 mol%). were added to a sealable flask and dissolved in thoroughly degassed PhMe. After 30 min of pre-stirring at RT the substrates 7a (1.0 equiv.) and 7b (2.0 equiv.) were added successively. The microwave vial was capped and the solution was stirred at 160 °C for 24 hours. The solvent was evaporated in vacuo and the product was purified by flash column chromatography.
3) Preparation of Starting Materials

2-(Methylthio)phenol (SM1)

Following a reported procedure\(^7\) phenol (9.40 g, 100.00 mmol, 1.00 equiv.) was dissolved in dry toluene (150 mL). To the stirred solution AlCl\(_3\) (16.00 g, 120.00 mmol, 1.20 equiv.) and dimethyl disulfide (28.30 g, 27.1 ml, 300.00 mmol, 3.00 equiv.) were added. The solution was then heated to 105 °C for 12 h. Afterwards, it was cooled to 40 °C and hydrolyzed with hydrochloric acid (10%, 100 ml). The mixture was extracted with DCM (5 x 160 ml) and the combined organic layers were washed with water, brine, dried over Na\(_2\)SO\(_4\) and concentrated under reduced pressure. Silica gel column chromatography (n-pentane:EtOAc = 20:1) gave the desired product **SM1** (10.9 g, 77.7 mmol, 77%) as pale yellow oil.

\[ R_f = 0.61 \text{ (n-pentane:EtOAc = 20:1).} \]

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 2.33 \text{ (s, 3H), 6.64 \text{ (s, 1H), 6.88 \text{ (td, } J = 7.5, 1.4 \text{ Hz, 1H), 6.99 \text{ (dd, } J = 8.2, 1.3 \text{ Hz, 1H), 7.25 \text{ (ddd, } J = 8.2, 7.3, 1.7 \text{ Hz, 1H), 7.49 \text{ (dd, } J = 7.7, 1.7 \text{ Hz, 1H).} \]

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\(^7\) EP 0318394 A2, 1989.
$^{1}$H-NMR (300 MHz, CDCl$_3$).
1-(Methylthio)-2-(2-propyn-1-yloxy)benzene (SM2)

To a solution of SM1 (750.0 mg, 5.35 mmol, 1.00 equiv.) in acetone (5 ml) was added K$_2$CO$_3$ (2.22 g, 16.06 mmol, 3.00 equiv.) followed by dropwise addition of propargyl bromide (760.0 mg, 0.49 ml, 6.38 mmol, 1.20 equiv.). The mixture was stirred overnight, filtered and the solvent was removed under reduced pressure. Silica gel column chromatography (n-pentane:EtOAc = 100:1 → 60:1) gave the desired product SM2 (336 mg, 1.15 mmol, 60%) as a colorless oil which crystallized slowly to a colorless solid. Carried out in accordance to a reported procedure.$^8$

m.p.: 36 °C.

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ = 14.8, 56.4, 75.7, 78.4, 112.3, 122.2, 125.7, 126.5, 127.8, 154.3.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3284, 2920, 2121, 1576, 1472, 1441, 1214, 1137, 1071.

C$_{10}$H$_{10}$OS calcd. for [M+H]$^+$: 179.0525, found: 179.0526 (ESI-HRMS).

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$^{1}H$-NMR (300 MHz, CDCl$_{3}$).

$^{13}C$-NMR (75 MHz, CDCl$_{3}$).
1-(Methylthio)-2-(but-3-yn-1-yl)benzene (SM3)

2-(Methylthio)benzyl bromide was synthesized according literature-known procedures starting from thiosalicylic acid.\textsuperscript{9,10}\n
Subsequently, compound SM\textsuperscript{3.3} was prepared from bromide SM\textsuperscript{3.2} (2.17 g, 10.00 mmol, 1.00 equiv.) and 1-(trimethylsilyl)propyne (1.34 g, 1.78 ml, 12.00 mmol, 1.20 equiv.) in accordance to a reported procedure.\textsuperscript{11} The crude product SM\textsuperscript{3.1} was then directly subjected to a described desilylation protocol\textsuperscript{11} to obtain SM\textsuperscript{3} (1.28 g, 7.28 mmol, 73% over two steps) as colorless oil.

\( R_f = 0.59 \) (n-pentane:EtOAc = 50:1).

\textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}): \( \delta = 1.98 \) (t, \( J = 2.6 \) Hz, 1H), 2.47 (s, 3H), 2.48 – 2.56 (m, 2H), 2.96 (t, \( J = 7.6 \) Hz, 2H), 7.10 – 7.14 (m, 1H), 7.18 – 7.24 (m, 3H).

\textsuperscript{13}C-NMR (75 MHz, CDCl\textsubscript{3}): \( \delta = 15.9, 18.8, 32.8, 68.9, 83.8, 125.0, 125.8, 127.3, 129.4, 137.2, 138.2. \)

IR (ATR) \( \tilde{\nu} \) (cm\textsuperscript{-1}) = 3058, 2920, 2863, 2116, 1588, 1467, 1435, 1067, 1043.

C\textsubscript{11}H\textsubscript{12}S calcd.: 176.0660, found: 176.0664 (GC-HRMS).

$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
Further Starting Materials

1-(Methylthio)-2-(thiocyanatomethyl)benzene (5.1b)

Procedure similar to GP7.

The alcohol SM3.1 (926 mg, 6.0 mmol, 1.0 equiv., in 2 ml of CH$_3$CN for transfer), PPh$_3$ (3.15 g, 12.0 mmol, 2.0 equiv.) and NH$_4$SCN (914 mg, 12.0 mmol, 2.0 equiv.) were dissolved in CH$_3$CN (12 mL). DEAD (2.09 g, 1.88 ml, 12.0 mmol, 2.0 equiv.) was added slowly to the solution and the reaction mixture was stirred for 9 h. After the solvent was evaporated in vacuo, the crude product was purified by flash column chromatography (n-pentane:EtOAc = 50:1→20:1) to afford the pure title product as a colorless oil (537 mg, 2.75 mmol, 46%).

R$_f$ = 0.31 (n-pentane:EtOAc = 20:1).

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ = 2.51 (s, 3H), 4.27 (s, 2H), 7.19 (ddd, $J$ = 7.8, 6.1, 2.5 Hz, 1H), 7.29 – 7.39 (m, 3H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ = 16.6, 36.8, 112.2, 125.8, 127.6, 129.7, 130.3, 132.8, 138.1.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3059, 2990, 2921, 2834, 2149, 1584, 1467, 1432, 1239, 1055, 1041, 963.

C$_9$H$_9$NS$_2$ calcd.: 195.0176, found: 195.0180 (GC-HRMS).
$^{1}H$-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
According to a reported procedure\(^\text{12}\), the bromide SM3.2 (2.17 g, 10.0 mmol, 1.0 equiv.) was dissolved in DMF (80 mL). KSeCN (1.44 g, 10.0 mmol, 1.0 equiv.) was added to the solution and the reaction mixture was stirred for 2 h. Then, Et\(_2\)O (20 ml) and water (20 ml) were added and the mixture was stirred for a short time. After transfer to a separation funnel, the organic layer was separated and the aqueous layer was extracted with Et\(_2\)O (3 x 50 ml). The combined organic phases were washed with water and brine and dried over Na\(_2\)SO\(_4\). After filtration, the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (n-pentane:EtOAc = 50:1→10:1) to afford the pure title product as a colorless solid (2.01 g, 8.30 mmol, 83%).

\[ \text{m.p.: 85 °C.} \]
\[ R_f = 0.28 \text{ (n-pentane:EtOAc = 20:1).} \]
\[^1\text{H-NMR} \text{(300 MHz, CDCl}\text{_3}): \delta = 2.52 \text{ (s, 3H), 4.35 (s, 2H), 7.12 − 7.22 (m, 1H), 7.28 − 7.37 (m, 3H).} \]
\[^{13}\text{C-NMR} \text{(75 MHz, CDCl}\text{_3):} \delta = 16.5, 31.7, 102.6, 125.8, 127.4, 129.4, 129.8, 134.4, 137.7. \]
\[^\text{IR (ATR)} \nu (\text{cm}^{-1}) = 3057, 2967, 2916, 2852, 2150, 1577, 1466, 1426, 1201, 1036. \]
\[^\text{C}_9\text{H}_9\text{NSSe} \text{ calcd.: 242.9621, found: 242.9626 (GC-HRMS).} \]

$^{1}H$-NMR (300 MHz, CDCl$_3$).

$^{13}C$-NMR (75 MHz, CDCl$_3$).
2-(2-{Prop-1-yn-1-yl}phenyl)ethan-1-ol (5.1e)

Similar to the synthesis of 11s, 2-(iodophenyl)ethan-1-ol (5.20 g, 21.0 mmol, 1.00 equiv.), PdCl$_2$(PPh$_3$)$_2$ (295 mg, 2 mol%) and Cul (160 mg, 4 mol%) were dissolved in triethylamine (60 ml). Afterwards, propyne (22.0 ml, 22.0 mmol, 1.0 M in THF, 1.05 equiv.) was added via syringe. After stirring overnight, saturated NH$_4$Cl solution was added and the mixture was extracted with Et$_2$O (3 x 100 ml). The combined organic phases were washed with brine, dried over Na$_2$SO$_4$, filtrated and evaporated. Silica gel column chromatography (n-pentane:EtOAc = 10:1 → 4:1) gave the desired product 5.1e (3.28 g, 20.5 mmol, 98%) as a brown oil.

R$_f$ = 0.31 (n-pentane:EtOAc = 4:1).

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ = 1.84 (s, 1H), 2.06 (s, 3H), 3.03 (t, $J$=6.8, 2H), 3.86 (t, $J$=6.7, 2H), 7.10 – 7.23 (m, 3H), 7.39 (dt, $J$=7.2, 1.2, 1H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ = 4.3, 37.8, 62.8, 78.1, 89.5, 123.8, 126.3, 127.6, 129.4, 132.4, 140.0.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3328, 3063, 3023, 2949, 2921, 2876, 1482, 1441, 1040.

C$_{11}$H$_{12}$O calcd.: 160.0888, found: 160.0880 (GC-HRMS).
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
Following a reported procedure\textsuperscript{13} \(\text{CuCl}_2\) (135 mg, 1.00 mmol, 0.2 equiv.), 2-oxazolidinone (2.18 g, 25.00 mmol, 5.0 equiv.) and \(\text{Na}_2\text{CO}_3\) (1.06 g, 10.00 mmol, 2.0 equiv.) were weighed in a three-necked round bottom flask. The reaction vessel was purged with oxygen gas (balloon) for 15 min. Afterwards, a solution of pyridine (0.81 ml, 10.00 mmol, 2.0 equiv.) in dry toluene (25 ml) was added via a syringe. The oxidative atmosphere was maintained by connection of a balloon filled with oxygen gas via syringe with needle. The mixture was heated to 70 °C, followed by the dropwise addition (over 4 h) of pent-4-yn-1-yl 4-methylbenzenesulfonate \textsuperscript{14} (1.19 g, 5.00 mmol, 1.0 equiv.) in dry toluene (25 ml). Upon completion, the reaction mixture was allowed to stir for another 4 h at 70 °C. The mixture was cooled to RT, filtrated (flask rinsed with toluene) and the filtrate evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (\(n\)-pentane:EtOAc = 4:1\(\rightarrow\)2:1\(\rightarrow\)1:2) to obtain the product (467 mg, 1.44 mmol, 29%) as colorless oil.

\(R_f = 0.09\) (\(n\)-pentane:EtOAc = 2:1).

\textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}): \(\delta = 1.81 – 1.92\ (m, 2\ H), 2.39\ (t, J = 6.9\ Hz, 2\ H), 2.45\ (s, 3\ H), 3.80 – 3.88\ (m, 2\ H), 4.14\ (t, J = 6.1\ Hz, 2\ H), 4.37 – 4.46\ (m, 2\ H), 7.33 – 7.42\ (m, 2\ H), 7.76 – 7.82\ (m, 2\ H).

\textsuperscript{13}C-NMR (75 MHz, CDCl\textsubscript{3}): \(\delta = 14.7, 21.5, 27.9, 46.8, 62.9, 68.8, 68.9, 71.1, 127.8, 129.8, 132.8, 144.8, 156.4.

\(\text{IR (ATR)}\stackrel{\nu}{\rightarrow}\ (\text{cm}^{-1}) = 2964, 2922, 2270, 1763, 1416, 1353, 1172, 1114, 921.

\(\text{C}_{13}\text{H}_{17}\text{NO}_{5}\text{S}\) calcd.: 346.0720, found: 346.0722 [M+Na]\(^+\) (ESI-HRMS).


$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-(Methylthio)-2-(but-2-yn-1-yl)oxy]benzene (11a)

Compound **11a** was synthesized according GP1.

A solution of **SM1** (1.50 g, 10.71 mmol, 1.00 equiv.), **PPh₃** (3.10 g, 11.78 mmol, 1.10 equiv.) and 2-butyn-1-ol (830.0 mg, 11.78 mmol, 1.10 equiv.) in dry toluene (30 ml) was cooled to 0 °C. **DIAD** (2.40 g, 2.33 ml, 11.78 mmol, 1.10 equiv.) in dry toluene (20 ml) was added dropwise to the stirred solution. After completion, the reaction mixture was warmed to RT and stirred overnight. The solvent was removed under reduced pressure and silica gel column chromatography (n-pentane:EtOAC = 50:1) gave the desired product (1.7 g, 9.00 mmol, 84%) as colorless oil.

**Rf** = 0.33 (n-pentane:EtOAc = 50:1).

**¹H-NMR** (300 MHz, CDCl₃): δ = 1.84 (t, J = 2.3 Hz, 3H), 2.43 (s, 3H), 4.73 (q, J = 2.3 Hz, 2H), 6.94 – 7.01 (m, 2H), 7.10 – 7.19 (m, 2H).

**¹³C-NMR** (75 MHz, CDCl₃): δ = 3.7, 14.8, 57.0, 73.9, 83.9, 112.1, 121.7, 125.7, 126.3, 127.5, 154.6.

**IR** (ATR) ν (cm⁻¹) = 2957, 2229, 1576, 1472, 1441, 1216, 999.

**C₁₁H₁₂OS** calcd.: 192.0609, found: 192.0626 (GC-HRMS).
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-(Methylthio)-2-(but-2-yn-1-yloxy)benzene (11b)

Compound 11b was synthesized according GP1.

A solution of SM1 (200.0 mg, 1.44 mmol, 1.00 equiv.), PPh₃ (568.0 mg, 2.16 mmol, 1.50 equiv.) and 4,4-dimethyl-2-pentyn-1-ol¹⁵ (162.0 mg, 1.44 mmol, 1.00 equiv.) in dry toluene (10 ml) was cooled to 0 °C. DIAD (438.0 mg, 0.44 ml, 11.78 mmol, 1.10 equiv.) in dry toluene (8 ml) was added dropwise to the stirred solution. After completion, the reaction mixture was warmed to RT and stirred overnight. The solvent was removed under reduced pressure and silica gel column chromatography (n-pentane:EtOAc = 150:1) gave the desired product (98 mg, 0.42 mmol, 29%) as colorless oil.

As 4,4-dimethyl-2-pentyn-1-ol was used without further purification after synthesis, the by-product 11b* was also formed and isolated in 14% yield (see next page).

Rᵣ = 0.21 (n-pentane:EtOAc = 50:1).

¹H-NMR (300 MHz, CDCl₃): δ = 1.19 (s, 9H), 2.42 (s, 3H), 4.74 (s, 2H), 6.93 – 7.03 (m, 2H), 7.09 – 7.20 (m, 2H).

¹³C-NMR (75 MHz, CDCl₃): δ = 14.8, 27.4, 30.7, 57.3, 73.4, 96.6, 112.7, 121.7, 125.6, 126.3, 127.6, 154.8.

IR (ATR) v ~ (cm⁻¹) = 2968, 2923, 2866, 2238, 1578, 1473, 1444, 1263, 1216.

C₁₄H₁₈OS calcd.: 234.1078, found: 234.1091 (GC-HRMS).

$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-(Methylthio)-2-(((4,4-dimethylpent-2-yn-1-yl)oxy)methoxy)benzene (11b*)

\[
\begin{align*}
\text{IR (ATR) } & \tilde{\nu} (\text{cm}^{-1}) = 3063, 2968, 2867, 2238, 1578, 1474, 1443, 1218, 1064. \\
\text{C}_{15}\text{H}_{20}\text{O}_{2}\text{S} & \quad \text{calcd.: 264.1184, found: 264.1199 (GC-HRMS).}
\end{align*}
\]

\[\text{R}_f = 0.37 \ (n\text{-pentane:EtoAc} = 50:1).\]

\[^1\text{H-NMR} \ (300 \text{ MHz, CDCl}_3): \delta = 1.22 \ (s, 6H), 1.22 \ (s, 3H), 2.42 \ (s, 3H), 4.36 \ (s, 2H), 5.37 \ (s, 2H), 6.95 - 7.07 \ (m, 1H), 7.07 - 7.20 \ (m, 3H).\]

\[^{13}\text{C-NMR} \ (75 \text{ MHz, CDCl}_3): \delta = 14.6, 27.4, 30.8, 55.8, 73.3, 91.5, 95.8, 114.5, 122.6, 125.7, 125.9, 128.1, 153.9.\]
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-(Methylthio)-2-((3-cyclopropylprop-2-yn-1-yl)oxy)benzene (11c)

Compound 11c was synthesized according GP1.

A solution of SM1 (810.0 mg, 5.77 mmol, 1.00 equiv.), PPh₃ (2.30 g, 8.66 mmol, 1.50 equiv.) and 3-cyclopropyl-2-propyn-1-ol¹⁶ (555.0 mg, 5.77 mmol, 1.00 equiv.) in dry THF (40 ml) was cooled to 0 °C. DIAD (1.80 g, 1.70 ml, 8.66 mmol, 1.50 equiv.) in dry THF (32 ml) was added dropwise to the stirred solution. After completion, the reaction mixture was warmed to RT and stirred overnight. The solvent was removed under reduced pressure and silica gel column chromatography (n-pentane:EtOAc = 50:1) gave the desired product (541 mg, 2.48 mmol, 43%) as a colorless oil.

Rᵣ = 0.39 (n-pentane:EtOAc = 50:1).

¹H-NMR (300 MHz, CDCl₃): δ = 0.64 – 0.71 (m, 2H), 0.71 – 0.79 (m, 2H), 1.19 – 1.30 (m, 1H), 2.42 (s, 3H), 4.72 (d, J = 2.0 Hz, 2H), 6.98 (ddd, J = 8.0, 6.6, 1.3 Hz, 2H), 7.10 – 7.19 (m, 2H).

¹³C-NMR (75 MHz, CDCl₃): δ = -0.6, 8.1, 14.7, 57.0, 70.0, 91.4, 112.2, 121.7, 125.6, 126.2, 127.5, 154.6.

IR (ATR) v (cm⁻¹) = 3012, 2925, 2864, 2236, 2157, 1581, 1474, 1226, 1059.

C₁₂H₁₄O₅ calcd.: 218.0765, found: 218.0755 (GC-HRMS).

$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-(Methylthio)-2-((6,6-dimethylhepta-2,4-diyln-1-yl)oxy)benzene (11d)

![Chemical Structure](image)

Compound 11d was synthesized according GP1.

A solution of SM1 (300.0 mg, 2.16 mmol, 1.00 equiv.), PPh₃ (852 mg, 3.24 mmol, 1.50 equiv.) and 6,6-dimethyl-2,4-heptadiyn-1-ol¹⁷ (442 mg, 3.24 mmol, 1.50 equiv.) in dry toluene (15 ml) was cooled to 0 °C. DIAD (657 mg, 0.66 ml, 3.24 mmol, 1.50 equiv.) in dry toluene (12 ml) was added dropwise to the stirred solution. After completion, the reaction mixture was warmed to RT and stirred overnight. The solvent was removed under reduced pressure and silica gel column chromatography (n-pentane:EtOAc = 50:1) gave the desired product (457 mg, 1.77 mmol, 82%) as a colorless oil.

\[ R_f = 0.29 \text{ (n-pentane:EtOAc = 50:1).} \]

¹H-NMR (300 MHz, CDCl₃): \( \delta = 1.21 \text{ (s, 9H), 2.39 (s, 3H), 4.79 (s, 2H), 6.91 \text{–} 7.01 \text{ (m, 2H), 7.09 \text{–} 7.17 \text{ (m, 2H).} \]

¹³C-NMR (75 MHz, CDCl₃): \( \delta = 14.6, 27.8, 30.2, 56.7, 63.1, 71.2, 72.1, 89.3, 112.0, 122.0, 125.7, 126.3, 127.6, 154.2. \]

IR (ATR) \( \tilde{\nu} (\text{cm}^{-1}) = 2970, 2921, 2865, 2251, 1774, 1577, 1472, 1444, 1213, 1008. \]

C₁₆H₁₈O₁ calcd.: 258.1078, found: 258.1091 (GC-HRMS).

$\textbf{1H-NMR (300 MHz, CDCl}_3\text{).}$

$\textbf{13C-NMR (75 MHz, CDCl}_3\text{).}$
1-(Methylthio)-2-((3-phenylprop-2-yn-1-yl)oxy)benzene (11e)

![Chemical Structure](image.png)

Compound 11e was synthesized according GP1.

A solution of SM1 (100.0 mg, 0.72 mmol, 1.00 equiv.), PPh₃ (284.0 mg, 1.08 mmol, 1.50 equiv.) and 3-phenyl-2-propyn-1-ol (96.0 mg, 0.72 mmol, 1.00 equiv.) in dry toluene (5 ml) was cooled to 0 °C. DIAD (219 mg, 0.22 ml, 1.08 mmol, 1.50 equiv.) in dry toluene (4 ml) was added dropwise to the stirred solution. After completion, the reaction mixture was warmed to RT and stirred overnight. The solvent was removed under reduced pressure and silica gel column chromatography (n-pentane:EtOAc = 50:1) gave the desired product (73 mg, 0.29 mmol, 40%) as colorless oil which crystallized slowly to a colorless solid.

m.p.: 43 °C.

Rᶠ = 0.19 (n-pentane:EtOAc = 50:1).

¹H-NMR (300 MHz, CDCl₃): δ = 2.45 (s, 3H), 5.00 (s, 2H), 7.00 (td, J = 7.4, 1.4 Hz, 1H), 7.08 (dd, J = 8.1, 1.5 Hz, 1H), 7.13 – 7.22 (m, 2H), 7.26 – 7.34 (m, 3H), 7.39 – 7.46 (m, 2H).

¹³C-NMR (75 MHz, CDCl₃): δ = 14.9, 57.3, 83.8, 87.4, 112.5, 122.1, 122.3, 125.8, 126.5, 127.8, 128.3, 128.6, 131.8, 154.6.

IR (ATR) ν (cm⁻¹) = 3059, 2918, 2237, 1575, 1472, 1441, 1214, 1014.

C₁₆H₁₄OS calcd.: 254.0765, found: 254.0775 (GC-HRMS).
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-(Methylthio)-2-((3-(2-naphthyl)prop-2-yn-1-yl)oxy)benzene (11f)

![Chemical Structure Image]

Compound 11f was synthesized according GP2.

To a mixture of SM2 (200.0 mg, 1.12 mmol, 1.00 equiv.), PdCl$_2$(PPh$_3$)$_2$ (24.0 mg, 34.2 µmol, 0.03 equiv.) and Cul (14.0 mg, 73.5 µmol, 0.06 equiv.) in dry triethylamine (8 ml) and dry DMF (2 ml) was added 2-iodonaphthalene (343.0 mg, 1.35 mmol, 1.20 equiv.). After stirring for 24 h at RT the mixture was quenched with sat. NH$_4$Cl-solution, diluted with water, extracted with diethyl ether (3 x 15 ml), washed with brine and dried over Na$_2$SO$_4$. The solvent was removed and the crude product was purified by silica gel column chromatography ($n$-pentane:EtOAc = 60:1) which afforded an off-colorless solid (149 mg, 0.49 mmol, 44%).

m.p.: 84 °C.

$R_f = 0.25$ ($n$-pentane:EtOAc = 50:1).

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 2.40$ (s, 3H), 5.00 (s, 2H), 6.95 – 7.01 (m, 1H), 7.04 – 7.20 (m, 3H), 7.38 – 7.46 (m, 3H), 7.66 – 7.77 (m, 3H), 7.90 (d, $J = 1.6$ Hz, 1H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 14.7$, 57.2, 84.1, 87.6, 112.3, 119.4, 122.0, 125.7, 126.2, 126.4, 126.7, 127.6, 127.7, 127.8, 128.2, 131.7, 132.7, 132.8, 154.5.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3052, 2992, 2920, 2856, 2235, 1593, 1499, 1475, 1379, 1227, 1071, 1016.

C$_{20}$H$_{16}$OS calcd.: 304.0922, found: 304.0900 (GC-HRMS).
$^{1}$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-(Methylthio)-2-((3-(4-fluorophenyl)prop-2-yn-1-yl)oxy)benzene (11g)

Compound 11g was synthesized according GP2.

To a mixture of SM2 (100.0 mg, 0.56 mmol, 1.00 equiv.), PdCl\(_2\)(PPh\(_3\))\(_2\) (12.0 mg, 17.1 µmol, 0.03 equiv.) and CuI (7.0 mg, 36.8 µmol, 0.06 equiv.) in dry triethylamine (4 ml) was added 4-fluoroiodobenzene (149.0 mg, 0.67 mmol, 1.20 equiv.). After stirring for 24 h at RT the mixture was quenched with water, extracted with diethyl ether (3 x 15 ml), washed with brine and dried over Na\(_2\)SO\(_4\). The solvent was removed and the crude product was purified by silica gel column chromatography (n-pentane:EtOAc = 100:1) which afforded an off-colorless solid (93 mg, 0.34 mmol, 61%).

m.p.: 67 °C.

\( R_f = 0.19 \) (n-pentane:EtOAc = 50:1).

\(^1\text{H}-\text{NMR}\) (300 MHz, CDCl\(_3\)): \( \delta = 2.44\) (s, 3H), 4.98 (s, 2H), 6.92 – 7.09 (m, 4H), 7.12 – 7.22 (m, 2H), 7.36 – 7.44 (m, 2H).

\(^{13}\text{C}-\text{NMR}\) (75 MHz, CDCl\(_3\)): \( \delta = 14.8, 57.2, 83.6\) (d, \( J = 1.5\) Hz), 86.3, 112.4, 115.6 (d, \( J = 22.1\) Hz), 118.4 (d, \( J = 3.6\) Hz), 122.1, 125.8, 126.40, 127.8, 133.8 (d, \( J = 8.5\) Hz), 154.5, 162.7 (d, \( J = 250.0\) Hz).

\(^{19}\text{F}-\text{NMR}\) (283 MHz, CDCl\(_3\)): \( \delta = -110.73\)

\( \text{IR (ATR) } \tilde{v} \text{ (cm}^{-1}\text{)} = 3056, 2853, 2231, 1503, 1476, 1226, 1018.\)

\( \text{C}_{16}\text{H}_{13}\text{FOS} \quad \text{calcd.: 272.0671, found: 272.0671 (GC-HRMS).} \)
$^{1}H$-NMR (300 MHz, CDCl$_3$).

$^{13}C$-NMR (75 MHz, CDCl$_3$).
$^{19}$F-NMR (283 MHz, CDCl$_3$).
1-(Methylthio)-2-((3-(4-chlorophenyl)prop-2-yn-1-yl)oxy)benzene (11h)

Compound 11h was synthesized according GP2.

To a mixture of SM2 (200.0 mg, 1.12 mmol, 1.00 equiv.), PdCl\(_2\)(PPh\(_3\))\(_2\) (24.0 mg, 34.2 µmol, 0.03 equiv.) and Cul (14.0 mg, 73.5 µmol, 0.06 equiv.) in dry triethylamine (8 ml) and dry DMF (2 ml) was added 1-chloro-4-iodobenzene (322.0 mg, 1.35 mmol, 1.20 equiv.). After stirring for 24 h at RT the mixture was quenched with sat. NH\(_4\)Cl-solution, diluted with water, extracted with diethyl ether (3 x 15 ml), washed with brine and dried over Na\(_2\)SO\(_4\). The solvent was removed and the crude product was purified by silica gel column chromatography (n-pentane:EtOAc = 60:1) which afforded a colorless solid (215 mg, 0.74 mmol, 67%).

**m.p.:** 72 °C.

R\(_f\) = 0.16 (n-pentane:EtOAc = 50:1).

\(^1\)H-NMR (300 MHz, CDCl\(_3\)): \(\delta = 2.44 \text{ (s, 3H)}, 4.98 \text{ (s, 2H)}, 6.96 - 7.07 \text{ (m, 2H)}, 7.11 - 7.21 \text{ (m, 2H)}, 7.23 - 7.29 \text{ (m, 2H)}, 7.30 - 7.37 \text{ (m, 2H)}.\)

\(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): \(\delta = 14.8, 57.2, 84.8, 86.2, 112.4, 120.7, 122.1, 125.7, 126.4, 127.8, 128.6, 133.0, 134.7, 154.5.\)

IR (ATR) \(\tilde{\nu} \text{ (cm}^{-1}) = 3061, 2918, 2860, 2238, 1575, 1471, 1441, 1214, 1013.\)

C\(_{16}\)H\(_{13}\)ClO\(_3\)S calcd.: 288.0376, found: 288.0399 (GC-HRMS).
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-(Methylthio)-2-((3-(o-tolyl)prop-2-yn-1-yl)oxy)benzene (11i)

Compound 11i was synthesized according GP2.

To a mixture of SM2 (200.0 mg, 1.12 mmol, 1.00 equiv.), PdCl₂(PPh₃)₂ (24.0 mg, 34.2 µmol, 0.03 equiv.) and Cul (14.0 mg, 73.5 µmol, 0.06 equiv.) in dry triethylamine (8 ml) and dry DMF (2 ml) was added 2-iodotoluene (295.0 mg, 0.17 ml, 1.35 mmol, 1.20 equiv.). After stirring for 24 h at RT the mixture was quenched with water, extracted with diethyl ether (3 x 15 ml), washed with brine and dried over Na₂SO₄. The solvent was removed and the crude product was purified by silica gel column chromatography (n-pentane:EtOAc = 60:1) which afforded a colorless solid (151 mg, 0.56 mmol, 50%).

m.p.: 58 °C.

Rᵣ = 0.19 (n-pentane:EtOAc = 50:1).

¹H-NMR (300 MHz, CDCl₃):  δ = 2.35 (s, 3H), 2.44 (s, 3H), 5.04 (s, 2H), 6.96 – 7.03 (m, 1H), 7.06 – 7.23 (m, 6H), 7.35 – 7.40 (m, 1H).

¹³C-NMR (75 MHz, CDCl₃):  δ = 14.9, 20.6, 57.3, 86.4, 87.6, 112.6, 122.0, 122.1, 125.4, 125.7, 126.5, 127.7, 128.6, 129.4, 132.1, 140.5, 154.6.

IR (ATR)  ν (cm⁻¹) = 3061, 2976, 2919, 2236, 1573, 1471, 1441, 1214, 1011.

C₁₇H₁₆OS  calcd.: 268.0922, found: 268.0937 (GC-HRMS).
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-(Methylthio)-2-[(3-<m-tolyl)prop-2-yn-1-yl]oxy]benzene (11j)

Compound 11j was synthesized according GP2.

To a mixture of SM2 (200.0 mg, 1.12 mmol, 1.00 equiv.), PdCl₂(PPh₃)₂ (24.0 mg, 34.2 µmol, 0.03 equiv.) and Cul (14.0 mg, 73.5 µmol, 0.06 equiv.) in dry triethylamine (8 ml) and dry DMF (2 ml) was added 3-iodotoluene (295.0 mg, 0.17 ml, 1.35 mmol, 1.20 equiv.). After stirring for 24 h at RT the mixture was quenched with water, extracted with diethyl ether (3 x 15 ml), washed with brine and dried over Na₂SO₄. The solvent was removed and the crude product was purified by silica gel column chromatography (n-pentane:EtOAc = 60:1) which afforded an orange oil (199 mg, 0.74 mmol, 66%).

Rᵣ = 0.16 (n-pentane:EtOAc = 50:1).

¹H-NMR (300 MHz, CDCl₃): δ = 2.30 (d, J = 0.7 Hz, 3H), 2.44 (s, 3H), 4.99 (s, 2H), 7.00 (td, J = 7.4, 1.5 Hz, 1H), 7.05 – 7.25 (m, 7H).

¹³C-NMR (75 MHz, CDCl₃): δ = 14.9, 21.1, 57.3, 83.5, 87.5, 112.5, 122.0, 122.1, 125.8, 126.5, 127.7, 128.1, 128.8, 129.5, 132.3, 137.9, 154.6.

IR (ATR) ν (cm⁻¹) = 3059, 2918, 2860, 2229, 1576, 1472, 1441, 1214, 999.

C₁₇H₁₆OS calcd.: 268.0922, found: 268.0942 (GC-HRMS).
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-(Methylthio)-2-[(3-(p-toly1)prop-2-yn-1-yl)oxy]benzene (11k)

Compound 11h was synthesized according GP2.

To a mixture of SM2 (200.0 mg, 1.12 mmol, 1.00 equiv.), PdCl$_2$(PPh$_3$)$_2$ (24.0 mg, 34.2 µmol, 0.03 equiv.) and Cul (14.0 mg, 73.5 µmol, 0.06 equiv.) in dry triethylamine (8 ml) and dry DMF (2 ml) was added 4-iodotoluene (295.0 mg, 1.35 mmol, 1.20 equiv.). After stirring for 24 h at RT the mixture was quenched with water, extracted with diethyl ether (3 x 15 ml), washed with brine and dried over Na$_2$SO$_4$. The solvent was removed and the crude product was purified by silica gel column chromatography ($n$-pentane:EtOAc = 60:1) which afforded a colorless solid (130 mg, 0.48 mmol, 43%).

m.p.: 52 °C.

$R_f$ = 0.19 ($n$-pentane:EtOAc = 50:1).

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ = 2.30 (s, 3H), 2.41 (s, 3H), 4.96 (s, 2H), 6.97 (td, $J$ = 7.5, 1.5 Hz, 1H), 7.03 – 7.09 (m, 3H), 7.10 – 7.18 (m, 2H), 7.27 – 7.33 (m, 2H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ = 14.7, 21.4, 57.3, 83.1, 87.4, 112.4, 119.1, 121.9, 125.7, 126.3, 127.7, 128.9, 131.6, 138.7, 154.5.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 2920, 2865, 2225, 1603, 1509, 1377, 1220, 1023.

C$_{17}$H$_{16}$OS calcd.: 268.0922, found: 268.0947 (GC-HRMS).
$^1$H-NMR (300 MHz, CDCl$_3$).

$^1$H-NMR (300 MHz, CDCl$_3$).
1-(Methylthio)-2-((2-methylallyl)oxy)benzene (11l)

According to a reported procedure\textsuperscript{18}, a suspension of SM1 (562.0 mg, 4.0 mmol, 1.0 equiv.) and K\textsubscript{2}CO\textsubscript{3} (1.11 g, 8.0 mmol, 2.0 equiv.) in DMF (20 ml) was treated with 3-bromo-2-methyl-1-propene (648.0 mg, 0.49 ml, 4.8 mmol, 1.2 equiv.). The mixture was stirred at RT for 18 h. It was then quenched with H\textsubscript{2}O, extracted with Et\textsubscript{2}O (3 x 50 ml), washed with brine and dried over Na\textsubscript{2}SO\textsubscript{4}. The solvent was evaporated \textit{in vacuo} to obtain the product as a pale yellow oil (777 mg, 4.33 mmol, quant.) which was used without further purification.

R\textsubscript{f} = 0.61 (\textit{n}-pentane:EtOAc = 20:1).

\textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}): \( \delta = 1.85 \) (dd, \( J=1.6, 0.8, 3\)H), 2.42 (s, 3H), 4.50 (q, \( J=1.1, 0.6, 2\)H), 4.99 (p, \( J=1.3, 1\)H), 5.15 (dq, \( J=1.6, 0.8, 1\)H), 6.81 (dd, \( J=8.0, 1.3, 1\)H), 6.95 (td, \( J=7.6, 1.3, 1\)H), 7.06 – 7.19 (m, 2H).

\textsuperscript{13}C-NMR (75 MHz, CDCl\textsubscript{3}): \( \delta = 14.5, 19.4, 72.0, 111.4, 112.5, 121.3, 125.6, 125.8, 127.5, 140.6, 155.2. \)

IR (ATR) \( \nu \) (cm\textsuperscript{-1}) = 3068, 2979, 2919, 2860, 1674, 1577, 1471, 1441, 1075, 1008.

C\textsubscript{11}H\textsubscript{14}OS \( \text{calcd.: 194.0765, found: 194.0773 (GC-HRMS).} \)

\[ ^1H-NMR \ (300\ MHz, CDCl_3) \].
1-(Methylthio)-2-(cinnamyoxy)benzene (11m)

Following a reported procedure, a solution of SM1 (701 mg, 5.0 mmol, 1.0 equiv.) in THF (50 ml) was cooled to 0 °C and treated with NaH (400 mg of 60% dispersion, 10.0 mmol, 2.0 equiv.). After 30 min of stirring, cinnamyl bromide (1.97 g, 10.0 mmol, 2.0 equiv.) in THF (20 ml) followed by TBAI (277.0 mg, 0.75 mmol, 0.15 equiv.) were added, the reaction was warmed to RT and stirred overnight. It was then quenched with sat. NH₄Cl solution at 0 °C, diluted with H₂O, extracted with Et₂O (3 x 50 ml), washed with brine and dried over Na₂SO₄. The solvent was evaporated in vacuo to obtain an isomeric mixture after flash column chromatography (n-pentane:EtOAc = 50:1) as a colorless oil (1.04 g). This was used without further purification.

1-(Methylthio)-2-(pent-3-yn-1-yl)benzene (11n)

A solution of SM3 (530.0 mg, 3.00 mmol, 1.00 equiv.) in dry THF (6 ml) was cooled to -78 °C. Then, n-butyllithium was added dropwise over 30 min to the stirred solution. After completion, the reaction mixture was stirred for 1 h at -78 °C. Afterwards, methyl iodide (426.0 mg, 3.00 mmol, 190.0 µl, 1.00 equiv.) was added, the mixture warmed to RT and stirred overnight. It was then quenched with sat. NH₄Cl solution, extracted with Et₂O (3 x 40 ml), washed with brine and dried over Na₂SO₄. The solvent was removed under reduced pressure and silica gel column chromatography (n-pentane:EtOAc = 80:1) gave the desired product (505 mg, 2.65 mmol, 88%) as colorless oil.

Carried out in accordance to a reported procedure.²⁰

Rᵣ = 0.67 (n-pentane:EtOAc = 20:1).

¹H-NMR (300 MHz, CDCl₃): δ = 1.77 (t, J = 2.5 Hz, 3H), 2.39 – 2.51 (m, 5H), 2.87 – 2.94 (m, 2H), 7.06 – 7.14 (m, 1H), 7.15 – 7.22 (m, 3H).

¹³C-NMR (75 MHz, CDCl₃): δ = 3.5, 15.8, 19.2, 33.4, 76.2, 78.5, 124.9, 125.7, 127.0, 129.2, 137.2, 138.7.

IR (ATR) ν (cm⁻¹) = 3058, 2917, 2856, 1588, 1467, 1436, 1042.

C₁₂H₁₄S calcd.: 190.0816, found: 190.0819 (GC-HRMS).

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$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-(Methylthio)-2-(but-2-yn-1-yl)benzene (11o)

Propyne (5.52 mmol, 1 M in THF, 1.20 equiv.) in additional dry THF (40 ml) was treated with n-butyllithium at -78 °C. The reaction was kept at this temperature and stirred for further 2 h. A solution of 2-methylthio benzylbromide SM3.2 (4.60 mmol, 1.00 g, 1.00 equiv.) in dry THF (10 ml) was added and the reaction mixture warmed to RT and quenched after 24 h with brine, diluted with water, extracted with Et₂O (3 x 50 ml) and dried over Na₂SO₄. After evaporation, the residue was purified by silica gel column chromatography (n-pentane:EtOAc = 100:1) to obtain the product as colorless oil (490 mg, 2.78 mmol, 60%).

Carried out in accordance to a reported procedure.¹¹

\[ R_f = 0.52 \ (n\text{-pentane}:\text{EtOAc} = 50:1). \]

\(^1\text{H-NMR} \ (300 \text{ MHz, CDCl}_3): \delta = 1.86 \ (t, J = 2.6 \text{ Hz, 3H}), 2.45 \ (s, 3H), 3.59 \ (q, J = 2.6, 2H), 7.11 - 7.29 \ (m, 3H), 7.52 \ (m, 1H). \]

\(^{13}\text{C-NMR} \ (75 \text{ MHz, CDCl}_3): \delta = 3.6, 15.8, 23.2, 75.9, 78.5, 125.1, 125.6, 127.2, 128.3, 135.5, 136.7. \]

\( \text{IR (ATR)} \ \tilde{\nu} \ (\text{cm}^{-1}) = 3056, 2913, 2865, 1581, 1436, 1419, 1269, 1038, 963. \)

\( \text{C}_{11}\text{H}_{12}\text{S} \quad \text{calcd.: } 176.0660, \text{found: } 176.0657 \) (GC-HRMS).
1-(Methylthio)-2-((pent-3-yn-1-yl)oxy)benzene (11p)
Compound 11p was synthesized according GP1.

A solution of SM1 (350.0 mg, 2.50 mmol, 1.00 equiv.), PPh₃ (980.0 mg, 3.75 mmol, 1.50 equiv.) and 3-pentyn-1-ol (315.0 mg, 0.35 ml, 3.75 mmol, 1.50 equiv.) in dry toluene (15 ml) was cooled to 0 °C. DIAD (760 mg, 0.74 ml, 3.75 mmol, 1.50 equiv.) in dry toluene (12 ml) was added dropwise to the stirred solution. After completion, the reaction mixture was warmed to RT and stirred overnight. The solvent was removed under reduced pressure and silica gel column chromatography (n-pentane:EtOAc = 50:1) gave the desired product (490 mg, 2.40 mmol, 96%) as a colorless solid.

m.p.: 69 °C.

Rᵣ = 0.70 (n-pentane:EtOAc = 50:1).

¹H-NMR (300 MHz, CDCl₃): δ = 1.79 (t, J = 2.6 Hz, 3H), 2.42 (s, 3H), 2.68 (tq, J = 7.5, 2.6 Hz, 2H), 4.11 (t, J = 7.4 Hz, 2H), 6.84 (dd, J = 8.1, 1.3 Hz, 1H), 6.95 (td, J = 7.6, 1.3 Hz, 1H), 7.08 – 7.19 (m, 2H).

¹³C-NMR (75 MHz, CDCl₃): δ = 3.1, 14.3, 19.3, 66.9, 74.4, 111.2, 121.1, 125.5, 126.0, 126.9, 154.9.

IR (ATR) ν (cm⁻¹) = 3064, 2916, 2878, 2848, 1575, 1440, 1235, 1073, 1023.

C₁₂H₁₄OS calcd.: 206.0765, found: 206.0781 (GC-HRMS).
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-(Methylthio)-2-((2-iodobenzyl)oxy)benzene (11.1q)

According to a reported procedure\textsuperscript{21}, a solution of SM1 (1.68 g, 12.0 mmol, 1.2 equiv.) in DMF (20 ml) was treated with K\textsubscript{2}CO\textsubscript{3} (4.15 g, 30.0 mmol, 3.0 equiv.). After 10 min of stirring, 1-(bromomethyl)-2-iodobenzene (2.97 g, 10.0 mmol, 1.0 equiv.) was added and the reaction was stirred overnight. It was then quenched with H\textsubscript{2}O, extracted with Et\textsubscript{2}O (3 x 100 ml), washed with brine and dried over Na\textsubscript{2}SO\textsubscript{4}. The solvent was evaporated \textit{in vacuo} to obtain the product as a colorless solid (3.55 g, 9.96 mmol, quant.) which was used without further purification.

\textbf{m.p.:} 73 °C.

\textbf{R}\textsubscript{f} = 0.53 \textit{(n-pentane:EtOAc = 20:1)}.

\textbf{\textsuperscript{1}H-NMR} (300 MHz, CDCl\textsubscript{3}): \(\delta = 2.45 \text{ (s, 3H)}, 5.09 \text{ (s, 2H)}, 6.86 \text{ (dd, } J=8.1, 1.3, 1\text{H}), 6.99 \text{ (tdd, } J=7.6, 5.7, 1.5, 2\text{H}), 7.06 - 7.20 \text{ (m, 2H)}, 7.37 \text{ (td, } J=7.6, 1.3, 1\text{H}), 7.61 - 7.67 \text{ (m, 1H)}, 7.83 \text{ (dd, } J=7.9, 1.2, 1\text{H)}.

\textbf{\textsuperscript{13}C-NMR} (75 MHz, CDCl\textsubscript{3}): \(\delta = 14.5, 74.1, 96.2, 111.7, 121.7, 125.6, 125.8, 127.6, 128.1, 128.4, 129.2, 138.9, 154.7, 162.4\).

\textbf{IR} (ATR) \(\tilde{\nu} \text{ (cm}^{-1}) = 3056, 2911, 2849, 1669, 1570, 1473, 1434, 1237, 1038, 1002.

\textbf{C}_{14}\textbf{H}_{13}\textbf{I}_{3}\textbf{OS} \quad \text{calcd.:} \ 355.9732, \ \text{found:} \ 355.9754 \ \text{(GC-HRMS)}.

1-(Methylthio)-2-((2-(prop-1-yn-1-yl)benzyl)oxy)benzene (11.2q)

Similar to the synthesis of 11s, compound 11.1q (1.78 g, 5.0 mmol, 1.00 equiv.), PdCl₂(PPh₃)₂ (71 mg, 2 mol%) and Cul (39 mg, 4 mol%) were dissolved in triethylamine (15 ml). Afterwards, propyne (5.0 ml, 5.0 mmol, 1.0 M in THF) was added via syringe. After stirring overnight, saturated NH₄Cl solution was added and the mixture was extracted with Et₂O. The combined organic phases were washed with brine, dried over Na₂SO₄, filtrated and evaporated. Silica gel column chromatography (n-pentane:EtOAc = 50:1 → 20:1) gave the desired product 11.2q (990 mg, 3.69 mmol, 74%) as off-colorless oil.

Rᵣ = 0.47 (n-pentane:EtOAc = 50:1).

¹H-NMR (300 MHz, CDCl₃): δ = 2.07 (s, 3H), 2.43 (s, 3H), 5.31 (s, 2H), 6.87 (dd, J=8.1, 1.3, 1H), 6.94 (td, J=7.6, 1.3, 1H), 7.08 (ddd, J=8.0, 7.4, 1.7, 1H), 7.18 (ddd, J=14.6, 7.5, 1.6, 2H), 7.29 (td, J=7.6, 1.5, 1H), 7.40 (dd, J=7.5, 1.5, 1H), 7.61 (dq, J=7.7, 0.8, 1H).

¹³C-NMR (75 MHz, CDCl₃): δ = 4.4, 14.6, 68.5, 76.9, 91.3, 111.7, 121.4, 121.6, 125.6, 125.9, 126.5, 127.1, 127.5, 127.9, 131.8, 138.5, 155.2.

IR (ATR) ν (cm⁻¹) = 3062, 2917, 2851, 1576, 1473, 1440, 1229, 1073, 1032.

C₁₇H₁₆OS calcd.: 268.0922, found: 268.0903 (GC-HRMS).
$^{1}H$-NMR (300 MHz, CDCl$_3$).

$^{13}C$-NMR (75 MHz, CDCl$_3$).
Compound 11r was synthesized according GP1.

A solution of SM1 (701.0 mg, 5.00 mmol, 1.00 equiv.), PPh₃ (1.97 g, 7.50 mmol, 1.50 equiv.) and alcohol 5.1e (962.0 mg, 6.00 mmol, 1.20 equiv.) in dry toluene (30 ml) was cooled to 0 °C. DIAD (1.52 g, 1.50 ml, 7.50 mmol, 1.50 equiv.) in dry toluene (24 ml) was added dropwise to the stirred solution. After completion, the reaction mixture was warmed to RT and stirred overnight. The solvent was removed under reduced pressure and silica gel column chromatography (n-pentane:EtOAc = 50:1) gave the desired product (714 mg, 2.53 mmol, 51%) as a pale yellow oil.

Rᵣ = 0.47 (n-pentane:EtOAc = 20:1).

¹H-NMR (300 MHz, CDCl₃): δ = 2.08 (s, 3H), 2.40 (s, 3H), 3.32 (t, J=7.3, 2H), 4.26 (t, J=7.3, 2H), 6.82 – 7.02 (m, 3H), 7.05 – 7.19 (m, 3H), 7.31 – 7.42 (m, 2H).

¹³C-NMR (75 MHz, CDCl₃): δ = 4.5, 14.6, 34.4, 68.4, 78.1, 89.6, 111.2, 121.1, 123.8, 125.7, 126.0, 126.4, 127.3, 127.7, 129.9, 132.2, 139.5, 155.5.

IR (ATR) ν (cm⁻¹) = 3062, 3022, 2920, 2861, 1575, 1470, 1436, 1235, 1071, 1015.

C₁₈H₁₈O₅S calcd.: 282.1078, found: 282.1053 (GC-HRMS).
$^1$H-NMR (300 MHz, CDCl₃).

$^{13}$C-NMR (75 MHz, CDCl₃).
1-(Methylthio)-2-(prop-1-yn-1-yl)benzene (11s)

According to a reported procedure22 2-iodothioanisole (1.25 g, 5.0 mmol, 1.00 equiv.), PdCl$_2$(PPh$_3$)$_2$ (71 mg, 2 mol%) and CuI (39 mg, 4 mol%) were dissolved in triethylamine (15 ml). The reaction was stirred at RT and propyne (5.0 ml, 5.0 mmol, 1.0 M in THF) was added via syringe. After 5.5 h, saturated NH$_4$Cl solution was added and the mixture was extracted with Et$_2$O. The combined organic phases were washed with brine, dried over Na$_2$SO$_4$, filtrated and evaporated. Silica gel column chromatography ($n$-pentane:EtOAc = 80:1) gave the desired product 11s (723 mg, 4.46 mmol, 89%) as pale orange solid.

m.p.: 30 °C.

$R_f$ = 0.51 ($n$-pentane:EtOAc = 50:1).

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ = 2.13 (s, 3H), 2.46 (s, 3H), 7.04 (td, $J$ = 7.5, 1.3 Hz, 1H), 7.11 (dd, $J$ = 8.0, 1.2 Hz, 1H), 7.20 – 7.27 (m, 1H), 7.35 (dd, $J$ = 7.6, 1.5 Hz, 1H).

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3055, 2982, 2915, 2846, 2230, 1580, 1462, 1431, 1275, 1073, 1035.

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ = 4.6, 15.0, 77.2, 92.6, 122.0, 123.8, 124.1, 128.0, 132.2, 141.0.

$C_{10}H_{10}S$ calcd.: 162.0503, found: 162.0509 (GC-HRMS).

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$^{1}H$-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-(Methylthio)-2-((but-3-yn-1-yl)oxy)benzene (11t)

A solution of SM1 (500.0 mg, 3.57 mmol, 1.00 equiv.), PPh₃ (940.0 mg, 3.57 mmol, 1.00 equiv.) and 3-butyln-1-ol (250.0 mg, 0.27 ml, 3.57 mmol, 1.00 equiv.) in dry toluene (10 ml) was cooled to 0 °C. DEAD (630 mg, 0.57 ml, 3.57 mmol, 1.00 equiv.) in dry toluene (2 ml) was added to the stirred solution. After completion, the reaction mixture was warmed to RT and stirred for 17 h. The solvent was removed under reduced pressure and silica gel column chromatography (n-pentane:EtOAc = 40:1) gave the desired product (200 mg, 1.04 mmol, 29%) as colorless solid.

Carried out in accordance to a reported procedure.¹

m.p.: 71 °C.

Rₕ = 0.35 (n-pentane:EtOAc = 50:1).

¹H-NMR (300 MHz, CDCl₃): δ = 2.04 (t, J = 2.7 Hz, 1H), 2.43 (s, 3H), 2.74 (td, J = 7.2, 2.7 Hz, 2H), 4.16 (t, J = 7.2 Hz, 2H), 6.84 (dd, J = 8.0, 1.3 Hz, 1H), 6.97 (td, J = 7.6, 1.3 Hz, 1H), 7.09 – 7.19 (m, 2H).

¹³C-NMR (75 MHz, CDCl₃): δ = 14.7, 19.5, 66.7, 70.0, 80.2, 111.6, 121.7, 125.8, 126.3, 127.5, 155.1.

IR (ATR) ν (cm⁻¹) = 3275, 3062, 2955, 1577, 1439, 1237, 1023.

C₁₁H₁₂OS       calcd.: 192.0609, found: 192.0624 (GC-HRMS).
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-(Methylthio)-2-((3-bromoprop-2-yn-1-yl)oxy)benzene (11u)

![Chemical Structure]

A solution of **SM1** (457.0 mg, 3.26 mmol, 1.00 equiv.) and 3-bromoprop-2-yn-1-yl 4-methylbenzenesulfonate\(^{23}\) (1.13 g, 3.91 mmol, 1.20 equiv.) in dry DMF (35 ml) was treated with potassium carbonate (8.15 mmol, 1.13 g, 2.5 equiv.). After stirring overnight, the solvent was removed under reduced pressure via co-evaporation with toluene. The crude mixture was purified by silica gel column chromatography (**n-pentane**:EtOAc = 80:1) to afford the title compound (596 mg, 2.32 mmol, 71%) as off-white solid.

Carried out in accordance to a reported procedure.\(^{24}\)

**m.p.: 64 °C.**

**R**\(_f\) = 0.33 (**n-pentane**:*EtOAc* = 50:1).

\(^1\)H-NMR (300 MHz, CDCl\(_3\)): δ = 2.43 (s, 3H), 4.79 (s, 2H), 6.93 – 7.04 (m, 2H), 7.12 – 7.20 (m, 2H).

\(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): δ = 14.8, 47.9, 57.3, 74.9, 112.2, 122.2, 125.8, 126.5, 127.8, 154.3.

**IR** (ATR) \(\tilde{\nu}\) (cm\(^{-1}\)) = 3062, 2988, 2921, 2211, 1575, 1473, 1438, 1215, 1073, 1035.

**C**\(_{10}\)H\(_8\)BrO\(_5\)** calcld.: 257.9537, found: 257.9558 (GC-HRMS).

\(^{23}\) CA2141376 A1.

H-NMR (300 MHz, CDCl$_3$).

$^{1}$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-(Methylthio)-2-((3-(3-pyridyl)prop-2-yn-1-yl)oxy)benzene (11v)

![Chemical Structure](attachment:image)

Compound 11r was synthesized according GP2.

To a mixture of SM2 (100.0 mg, 0.56 mmol, 1.00 equiv.), PdCl\(_2\)(PPh\(_3\))\(_2\) (12.0 mg, 17.1 µmol, 0.03 equiv.) and Cul (7.0 mg, 36.8 µmol, 0.06 equiv.) in dry triethylamine (4 ml) was added 3-iodopyridine (138.0 mg, 0.67 mmol, 1.20 equiv.). After stirring for 24 h at RT the mixture was quenched with water, extracted with diethyl ether (3 x 15 ml), washed with brine and dried over Na\(_2\)SO\(_4\). The solvent was removed and the crude product was purified by silica gel column chromatography (n-pentane:EtOAc = 20:1) which afforded a pale yellow solid (104 mg, 0.41 mmol, 73%).

\[\text{m.p.: } 49 \degree \text{C.} \]
\[\text{R}_f = 0.06 \text{ (n-pentane:EtOAc = 10:1).} \]
\[\text{^1H-NMR } (300 \text{ MHz, CDCl}_3): \delta = 2.45 \text{ (s, 2H), 5.01 (s, 2H), 6.99 – 7.08 (m, 2H), 7.13 – 7.25 (m, 3H), 7.70 (dt, } J = 7.9, 1.9 \text{ Hz, 1H), 8.53 (dd, } J = 4.9, 1.7 \text{ Hz, 1H), 8.66 (dd, } J = 2.2, 0.9 \text{ Hz, 1H).} \]
\[\text{^13C-NMR } (75 \text{ MHz, CDCl}_3): \delta = 14.8, 57.1, 84.0, 87.3, 112.4, 119.4, 122.3, 122.9, 125.7, 126.4, 127.9, 138.7, 149.0, 152.4, 154.4. \]
\[\text{IR (ATR) } \tilde{\nu} \text{ (cm}^{-1}) = 3060, 2919, 2861, 2241, 1576, 1472, 1441, 1214, 1012. \]
\[\text{C}_{15}\text{H}_{13}\text{NO}_2 \text{ calcd.: } 255.0718, \text{ found: } 255.0717 \text{ (GC-HRMS).} \]
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-(Methylthio)-2-((3-(4-methoxyphenyl)prop-2-yn-1-yl)oxy)benzene (11w)

Compound 11w was synthesized according GP2.

To a mixture of SM2 (200.0 mg, 1.12 mmol, 1.00 equiv.), PdCl$_2$(PPh$_3$)$_2$ (24.0 mg, 34.2 µmol, 0.03 equiv.) and Cul (14.0 mg, 73.5 µmol, 0.06 equiv.) in dry triethylamine (8 ml) was added 4-iodoanisole (316.0 mg, 1.35 mmol, 1.20 equiv.). After stirring for 24 h at RT the mixture was quenched with water, extracted with diethyl ether (3 x 15 ml), washed with brine and dried over Na$_2$SO$_4$. The solvent was removed and the crude product was purified by silica gel column chromatography (n-pentane:EtOAc = 60:1) which afforded an off-white solid (181 mg, 0.64 mmol, 57%).

**m.p.:** 73 °C.

**R**$_f$ = 0.40 (n-pentane:EtOAc = 10:1).

**$^1$H-NMR** (300 MHz, CDCl$_3$): $\delta$ = 2.44 (s, 3H), 3.80 (s, 3H), 4.98 (s, 2H), 6.79 – 6.84 (m, 2H), 7.00 (td, $J$ = 7.4, 1.4 Hz, 1H), 7.08 (dd, $J$ = 8.1, 1.4 Hz, 1H), 7.13 – 7.21 (m, 2H), 7.33 – 7.39 (m, 2H).

**$^{13}$C-NMR** (75 MHz, CDCl$_3$): $\delta$ = 14.9, 55.3, 57.4, 82.5, 87.4, 112.5, 113.9, 114.4, 122.0, 125.8, 126.5, 127.7, 133.3, 154.7, 159.9.

**IR** (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3003, 2927, 2910, 2840, 2226, 1601, 1507, 1437, 1224, 1073, 1025.

C$_{17}$H$_{16}$O$_2$S  calcd.: 284.0871, found: 284.0882 (GC-HRMS).
$^{1}$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-(Methylthio)-2-[(3-(4-nitrophenyl)prop-2-yn-1-yl)oxy]benzene (11x)

\[
\begin{array}{c}
\text{S} \\
\text{O} \\
\text{NO}_2
\end{array}
\]

Compound **11x** was synthesized according GP2.

To a mixture of **SM2** (200.0 mg, 1.12 mmol, 1.00 equiv.), PdCl\(_2\)(PPh\(_3\))\(_2\) (24.0 mg, 34.2 µmol, 0.03 equiv.) and CuI (14.0 mg, 73.5 µmol, 0.06 equiv.) in dry triethylamine (8 ml) was added 1-iodo-4-nitrobenzene (337.0 mg, 1.35 mmol, 1.20 equiv.). After stirring for 24 h at RT the mixture was quenched with water, extracted with diethyl ether (3 x 15 ml), washed with brine and dried over Na\(_2\)SO\(_4\). The solvent was removed and the crude product was purified by silica gel column chromatography (n-pentane:EtOAc = 60:1) which afforded a yellow oil (309 mg, 1.03 mmol, 92%).

\(R_f = 0.34\) (n-pentane:EtOAc = 10:1).

\(^1\)H-NMR (300 MHz, CDCl\(_3\)): \(\delta = 2.45\) (s, 3H), 5.02 (s, 2H), 7.00 – 7.07 (m, 2H), 7.13 – 7.23 (m, 2H), 7.52 – 7.59 (m, 2H), 8.13 – 8.19 (m, 2H).

\(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): \(\delta = 14.7, 57.1, 85.4, 89.2, 112.4, 122.4, 123.5, 125.7, 126.3, 128.0, 129.0, 132.5, 147.3, 154.3\).

IR (ATR) \(\tilde{\nu}\) (cm\(^{-1}\)) = 3066, 2921, 2853, 2246, 1592, 1516, 1340, 1214, 1016.

\(\text{C}_{16}\text{H}_{13}\text{NO}_3\text{S}\) calcd.: 322.0508, found: 322.0511 [M+Na]\(^+\) (ESI-HRMS).
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-(Methylthio)-2-((4-((p-tolyl)but-3-yn-1-yl)oxy)benzene (11y)

A mixture of 4-iodotoluene (377.0 mg, 1.73 mmol, 1.00 equiv.), PdCl\(_2\)(PPh\(_3\))\(_2\) (24.3 mg, 34.6 µmol, 0.02 equiv.) and Cul (5.0 mg, 26.0 µmol, 0.015 equiv.) in dry triethylamine (8 ml) was stirred for 30 min. Then, 11t (220.0 mg, 1.15 mmol, 0.66 equiv.) in dry triethylamine/DMF (1:1, 4 ml) was added dropwise. After stirring for 24 h at RT the mixture was quenched with water, extracted with diethyl ether, washed with brine and dried over Na\(_2\)SO\(_4\). The solvent was removed and the crude product was purified by silica gel column chromatography (n-pentane:EtOAc = 70:1→50:1) which afforded a white solid (205 mg, 0.73 mmol, 63%).

Carried out in accordance to a reported procedure.\(^2\)

\(\text{m.p.}: 82 ^\circ \text{C}.\)

\(R_f = 0.38 \ (n\text{-pentane}:\text{EtOAc} = 50:1).\)

\(^1\text{H-NMR} \ (300 \text{ MHz, CDCl}_3): \delta =2.33 \ (s, 3H), 2.44 \ (s, 3H), 2.95 \ (t, J = 7.3 \text{ Hz}, 2H), 4.24 \ (t, J = 7.3 \text{ Hz}, 2H), 6.86 – 7.00 \ (m, 2H), 7.06 – 7.20 \ (m, 4H), 7.31 \ (d, J = 8.1 \text{ Hz}, 2H).\)

\(^{13}\text{C-NMR} \ (75 \text{ MHz, CDCl}_3): \delta = 14.8, 20.4, 21.4, 67.0, 82.2, 84.8, 111.7, 120.3, 121.6, 125.9, 126.6, 127.5, 129.0, 131.5, 137.9, 155.4.\)

\(\text{IR} \ (\text{ATR}) \ \tilde{\nu} \ (\text{cm}^{-1}) = 3019, 2918, 2887, 2224, 1576, 1463, 1236, 1021.\)

\(\text{C}_{18}\text{H}_{18}\text{OS} \ \text{calcd.: 282.1078, found: 282.1080 (GC-HRMS).}\)
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1,6-Bis(2-(methylthio)phenoxy)hexa-2,4-diyne (11z)

To a mixture of SM2 (430.0 mg, 2.42 mmol, 1.00 equiv.), PdCl$_2$(PPh$_3$)$_2$ (34.0 mg, 48.4 µmol, 0.04 equiv.) and Cul (23.0 mg, 0.12 mmol, 0.10 equiv.) in dry triethylamine (5 ml) and dry DMF (4 ml) was added iodine (610 mg, 2.44 mmol, 1.01 equiv.) at RT. After stirring for 2.5 h the reaction was quenched with NH$_4$Cl-solution, extracted with diethyl ether (3 x 50 ml), washed with brine and dried over Na$_2$SO$_4$. The solvent was removed and the crude product was purified by silica gel column (n-pentane:EtOAc = 60:1→10:1) which afforded a colorless solid (261 mg, 0.74 mmol, 61%). Carried out in accordance to a reported procedure.$^{2a}$

m.p.: 106 °C.

R$_f$ = 0.19 (n-pentane:EtOAc = 20:1).

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ = 2.40 (s, 6H), 4.80 (s, 4H), 6.91 (dd, $J$ = 8.0, 1.3 Hz, 2H), 6.99 (td, $J$ = 7.6, 1.3 Hz, 2H), 7.08 – 7.19 (m, 4H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ = 14.7, 56.7, 71.2, 74.5, 112.3, 122.4, 125.8, 126.4, 127.8, 154.1.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3106, 2920, 2855, 2165, 1573, 1474, 1438, 1366, 1221, 1012.

C$_{20}$H$_{18}$O$_2$S$_2$ calcd.: 377.0640, found: 377.0641 [M+Na]$^+$ (ESI-HRMS).
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).

S79
1-(Methylthio)-2-[[3-[(1,1-dimethylethyl)dimethylsilyl]-2-propyn-1-yl]oxy]benzene (15a)

![Chemical structure](image)

Compound 15a was synthesized according GP1.

A solution of SM1 (300.0 mg, 2.16 mmol, 1.00 equiv.), PPh₃ (852 mg, 3.24 mmol, 1.50 equiv.) and 3-[(1,1-Dimethylethyl)dimethylsilyl]-2-propyn-1-ol[25] (552 mg, 3.24 mmol, 1.50 equiv.) in dry toluene (15 ml) was cooled to 0 °C. DIAD (657 mg, 0.66 ml, 3.24 mmol, 1.50 equiv.) in dry toluene (12 ml) was added dropwise to the stirred solution. After completion, the reaction mixture was warmed to RT and stirred overnight. The solvent was removed under reduced pressure and silica gel column chromatography (n-pentane:EtOAc = 50:1) gave the desired product (524 mg, 1.79 mmol, 83%) as colorless oil.

\[ R_f = 0.33 \] (n-pentane:EtOAc = 50:1).

\[^1H\text{-NMR} (300 \text{ MHz, CDCl}_3):\delta = 0.00 \text{ (s, 6H), 0.80 \text{ (s, 9H), 2.34 \text{ (s, 3H), 4.69 \text{ (s, 2H), 6.86 - 6.96 \text{ (m, 2H), 7.04 \text{ (ddd, } J = 8.1, 7.3, 1.7 \text{ Hz, 1H), 7.09 \text{ (dd, } J = 7.6, 1.7 \text{ Hz, 1H).}}} \]

\[^{13}C\text{-NMR} (75 \text{ MHz, CDCl}_3):\delta = -4.9, 14.8, 16.4, 25.9, 57.3, 91.2, 100.6, 112.8, 121.9, 125.6, 126.4, 127.7, 154.5.\]

\[ \text{IR (ATR) } \tilde{\nu} (\text{cm}^{-1}) = 2953, 2928, 2856, 2178, 1775, 1578, 1471, 1443, 1250, 1216, 1029.\]

\[ C_{16}H_{24}OSSi \quad \text{calcd.:} \quad 292.1317, \text{ found:} \quad 292.1327 \text{ (GC-HRMS).} \]

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$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
According to a reported procedure\textsuperscript{26} \(n\text{-}\)butyllithium (1.65 ml, 2.64 mmol, 1.05 equiv., 1.6 M in hexane) was added dropwise over a period of 10 min to a solution of ethynyl\((\text{phenyl})\text{sulfane}\)\textsuperscript{27} (355 mg, 2.64 mmol, 1.05 equiv.) in dry THF (62 ml) at -25 °C. The solution was stirred for 2 h at -40 °C. Afterwards, compound \(5.1b\) (491 mg, 2.51 mmol, 1.00 equiv.) was dissolved in dry THF (31 ml) and was added dropwise within a period of 1.5 h. The mixture was then stirred for 1 h. After warming to RT, the reaction was quenched with sat. \(\text{NH}_4\text{Cl}\) solution and diluted with water. The mixture was extracted with \(\text{Et}_2\text{O}\) (3 \times 50 ml). The combined organic layers were washed with brine, dried over \(\text{Na}_2\text{SO}_4\) and the solvent was removed \textit{in vacuo}. The crude product was purified by flash column chromatography (\(n\)-pentane:EtOAc = 100:1) to afford a yellow oil (243 mg, 0.82 mmol, 33\%)

\(R_F = 0.57\) \((n\text{-}\text{pentane}:\text{EtOAc} = 20:1)\).

\(^1\text{H-NMR}\) (300 MHz, CDCl\(_3\)): \(\delta = 2.48\) (s, 3H), 4.10 (s, 2H), 7.05 – 7.31 (m, 9H).

\(^{13}\text{C-NMR}\) (75 MHz, CDCl\(_3\)): \(\delta = 16.5, 39.7, 83.8, 92.2, 125.2, 125.7, 126.4, 127.0, 129.0, 130.4, 133.7, 134.6, 137.8\).

\(\text{IR\ (ATR)}\ \tilde{\nu}\ (\text{cm}^{-1}) = 3055, 2984, 2917, 1579, 1470, 1433, 1228, 1068, 960\).

\(\text{C}_{16}\text{H}_{14}\text{S}_3\) \hspace{1cm} \text{calcd.: 302.0258, found: 302.0238 (GC-HRMS)}.


$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
According to a reported procedure\textsuperscript{26} n-butyllithium (2.63 ml, 4.20 mmol, 1.05 equiv., 1.6 M in hexane) was added dropwise over a period of 10 min to a solution of (tert-butyldimethylsilyl)acetylene (562 mg, 0.75 ml, 4.20 mmol, 1.05 equiv.) in dry THF (100 ml) at -25 °C. The solution was stirred for 2 h at -40 °C. Afterwards, compound 5.1d (969 mg, 4.00 mmol, 1.00 equiv.) was dissolved in dry THF (50 ml) and was added dropwise within a period of 1.5 h. The mixture was then stirred for 1 h. After warming to RT, the reaction was quenched with sat. NH\textsubscript{4}Cl solution and diluted with water. The mixture was extracted with Et\textsubscript{2}O (1 x 50 ml, 2 x 100 ml). The combined organic layers were washed with brine, dried over Na\textsubscript{2}SO\textsubscript{4} and the solvent was removed \textit{in vacuo}. The crude product was purified by flash column chromatography (\textit{n}-pentane:EtOAc = 100:1) to afford a yellow oil (1.19 g, 3.35 mmol, 84%)

\( R_f = 0.74 \) (\textit{n}-pentane:EtOAc = 20:1).

\textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}): \( \delta = 0.00 \) (s, 6H), 0.83 (s, 9H), 2.39 (s, 3H), 4.02 (s, 2H), 6.96 – 7.04 (m, 1H), 7.12 – 7.18 (m, 3H).

\textsuperscript{13}C-NMR (75 MHz, CDCl\textsubscript{3}): \( \delta = -4.6, 16.2, 16.7, 26.0, 31.4, 87.1, 107.5, 125.0, 126.7, 128.3, 129.9, 135.8, 137.4. \)

\textbf{IR (ATR)} \( \bar{\nu} \) (cm\textsuperscript{-1}) = 2926, 2886, 2852, 2078, 1584, 1464, 1433, 1251, 1187.

\textbf{C\textsubscript{16}H\textsubscript{24}SSeSi} calcd.: 356.0533, found: 356.0543 (GC-HRMS).
$^{1}H$-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
Following a reported procedure\textsuperscript{28}, n-butyllithium (1.50 ml, 3.75 mmol, 1.10 equiv., 2.5 M in hexane) was added dropwise over a period of 30 min to a solution of SM3 (600 mg, 3.40 mmol, 1.00 equiv.) in THF (6 ml) and DMPU (0.75 ml) at -78 °C. The mixture was then allowed to stir 1h at ambient temperature. After this time, it was recooled to -78 °C and (5-iodopent-1-yn-1-yl)benzene\textsuperscript{31} (1.02 g, 3.75 mmol, 1.10 equiv.) was added via syringe. The temperature was kept at -78 °C for one further hour. The mixture was then warmed to RT and stirred overnight. After quenching with sat. NH\textsubscript{4}Cl solution, the mixture was extracted with Et\textsubscript{2}O (3 x 50 ml). The combined organic layers were washed with brine, dried over Na\textsubscript{2}SO\textsubscript{4} and the solvent was removed \textit{in vacuo}. The crude product was purified by flash column chromatography (n-pentane:EtOAc = 100:1) to afford a colorless oil (862 mg, 2.71 mmol, 80%).

\textit{R}_{f} = 0.60 \ (n\text{-}pentane:EtOAc = 20:1).

\textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}): \(\delta = 1.76 \ (p, J = 7.0 \ Hz, 2H), 2.32 \ (tt, J = 6.9, 2.4 \ Hz, 2H), 2.45 \ (s, 3H), 2.46 - 2.53 \ (m, 4H), 2.92 \ (t, J = 7.5 \ Hz, 2H), 7.07 - 7.15 \ (m, 1H), 7.17 - 7.31 \ (m, 6H), 7.37 - 7.43 \ (m, 2H).

\textsuperscript{13}C-NMR (75 MHz, CDCl\textsubscript{3}): \(\delta = 15.8, 18.0, 18.5, 19.2, 28.2, 33.3, 79.9, 80.1, 81.0, 89.5, 123.9, 124.8, 125.6, 127.0, 127.5, 128.1, 129.4, 131.5, 137.2, 138.6.

\textbf{IR} (ATR) \(\tilde{\nu} \ (\text{cm}^{-1}) = 3056, 2924, 2862, 2838, 1593, 1434, 1335, 1066, 1042.

\textbf{C}_{22}\textbf{H}_{22}\textbf{S} \quad \text{calcd.: 318.1442, found: 318.1473} \ (\text{GC-HRMS}).
H-NMR (300 MHz, CDCl₃).

13C-NMR (75 MHz, CDCl₃).
1-(Methylthio)-2-(deca-3,8-diyn-1-yl)benzene (19b)

Following a reported procedure,\textsuperscript{25} \( n \)-butyllithium (0.66 ml, 1.65 mmol, 1.10 equiv., 2.5 M in hexane) was added dropwise over a period of 30 min to a solution of SM3 (265 mg, 1.50 mmol, 1.00 equiv.) in THF (3.3 ml) and DMPU (0.33 ml) at -78 °C. The mixture was then allowed to stir 1 h at ambient temperature. After this time, it was recooled to -78 °C and 6-iodohex-2-yn\textsuperscript{31} (344 mg, 1.65 mmol, 1.10 equiv.) was added via syringe. The temperature was kept at -78 °C for one further hour. The mixture was then warmed to RT and stirred for 6 h. After quenching with sat. NH\textsubscript{4}Cl solution, the mixture was extracted with Et\textsubscript{2}O (3 x 50 ml). The combined organic layers were washed with brine, dried over Na\textsubscript{2}SO\textsubscript{4} and the solvent was removed \textit{in vacuo}. The crude product was purified by flash column chromatography (\( n \)-pentane:EtOAc = 100:1) to afford a colorless oil (300 mg, 1.17 mmol, 78%).

\( {R_f} = 0.36 \) (\( n \)-pentane:EtOAc = 50:1).

\textbf{\( ^1\text{H-NMR} \)} (300 MHz, CDCl\textsubscript{3}): \( \delta = 1.58 – 1.69 \) (m, 2H), 1.78 (t, \( J = 2.6 \) Hz, 3H), 2.14 – 2.30 (m, 4H), 2.46 (s, 3H), 2.43 – 2.51 (m, 2H), 2.91 (t, \( J = 7.6 \) Hz, 2H), 7.07 – 7.13 (m, 1H), 7.17 – 7.22 (m, 3H).

\textbf{\( ^{13}\text{C-NMR} \)} (75 MHz, CDCl\textsubscript{3}): \( \delta = 3.5, 15.9, 17.9, 18.0, 19.2, 28.5, 33.4, 75.9, 78.5, 79.9, 80.1, 124.9, 125.7, 127.1, 129.4, 137.2, 138.7.\)

\textbf{\( \text{IR (ATR)} \)} \( \tilde{\nu} \) (cm\textsuperscript{-1}) = 3058, 2916, 2859, 1588, 1435, 1336, 1043, 863.

\( \text{C}_{17}\text{H}_{20}\text{S} \) calcd.: 256.1286, found: 256.1274 (GC-HRMS).
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
Following a reported procedure,\textsuperscript{25} n-butyllithium (0.66 ml, 1.65 mmol, 1.10 equiv., 2.5 M in hexane) was added dropwise over a period of 30 min to a solution of SM3 (265 mg, 1.50 mmol, 1.00 equiv.) in THF (3.3 ml) and DMPU (0.33 ml) at -78 °C. The mixture was then allowed to stir 1 h at ambient temperature. After this time, it was recooled to -78 °C and 11-iodoundeca-2,7-diyne (344 mg, 1.65 mmol, 1.10 equiv., from 6-iodohex-2-yn and tert-butylidemethyl(pent-4-yn-1-yloxy)silane, according the literature\textsuperscript{25,29,31}) was added via syringe. The temperature was kept at -78 °C for one further hour. The mixture was then warmed to RT and stirred for 6 h. After quenching with sat. NH\textsubscript{4}Cl solution, the mixture was extracted with Et\textsubscript{2}O (3 x 50 ml). The combined organic layers were washed with brine, dried over Na\textsubscript{2}SO\textsubscript{4} and the solvent was removed in vacuo. The crude product was purified by flash column chromatography (n-pentane:EtOAc = 100:1) to afford a colorless oil (300 mg, 1.17 mmol, 78%).

\textbf{R}_{t} = 0.34 \ (n\text{-}pentane:EtOAc = 50:1).

\textbf{\textsuperscript{1}H-NMR} (600 MHz, CDCl\textsubscript{3}): \delta = 1.64 (dp, \textit{J} = 9.0, 7.0 Hz, 4H), 1.78 (t, \textit{J} = 2.5 Hz, 3H), 2.20 – 2.28 (m, 8H), 2.46 (s, 3H), 2.44 – 2.51 (m, 2H), 2.91 (dd, \textit{J} = 7.9, 7.3 Hz, 2H), 7.11 (ddd, \textit{J} = 7.6, 5.8, 2.7 Hz, 1H), 7.18 – 7.22 (m, 3H).

\textbf{\textsuperscript{13}C-NMR} (151 MHz, CDCl\textsubscript{3}): \delta = 3.5, 15.9, 17.9, 17.9, 17.9, 18.0, 19.2, 28.5, 28.5, 33.4, 76.0, 78.4, 79.8, 79.9, 80.0, 80.1, 124.9, 125.7, 127.1, 129.4, 137.2, 138.7.

\textbf{IR \ (ATR) } \tilde{\nu} \ (\text{cm}^{-1}) = 3058, 2920, 2850, 1587, 1436, 1335, 1043, 963.

\textbf{C_{22}H_{26}S} \ \ \ \ \text{calcd.}: \ 322.17497, \ \text{found}: \ 322.17499 \ (GC\text{-}HRMS).

$^{1}$H-NMR (600 MHz, CDCl$_3$).

$^{13}$C-NMR (151 MHz, CDCl$_3$).
1-(Methylthio)-2-(((4-(2-methylallyl)oxy)but-2-yn-1-yl)oxy)benzene (19e)

\[
\text{SM1} \quad (350 \text{ mg, 2.50 mmol, 1.0 equiv.}), \text{ PPh}_3 \quad (980 \text{ mg, 3.75 mmol, 1.5 equiv.}) \text{ and 4-(2-methylallyloxy)-2-butyn-1-ol}^{30} \quad (530 \text{ mg, 3.75 mmol, 1.5 equiv.}) \text{ were dissolved in toluene (17 ml) and cooled to 0 °C. To this solution DIAD} \quad (0.74 \text{ ml, 760 mg, 3.75 mmol, 1.5 equiv.}) \text{ in toluene (15 ml) was added dropwise. Afterwards, the mixture was warmed to RT and stirred overnight. The solvent was evaporated and the crude product purified by flash column chromatography (}n\text{-pentane:EtOAc = 50:1)} \text{ to afford a colorless oil (520 mg, 1.98 mmol, 80%).}
\]

\[R_f = 0.27 \quad (n\text{-pentane:EtOAc = 50:1}).\]

\[^{1}H\text{-NMR (300 MHz, CDCl}_3]: \delta = 1.71 \text{ (t, } J = 1.3 \text{ Hz, 3H), 2.41 \text{ (s, 3H), 3.90 – 3.91 (m, 2H), 4.14 \text{ (t, } J = 1.8 \text{ Hz, 2H), 4.89 \text{ (ddq, } J = 2.1, 1.5, 0.8 \text{ Hz, 1H), 4.93 \text{ (dq, } J = 2.2, 1.1 \text{ Hz, 1H), 6.98 \text{ (ddd, } J = 8.1, 6.3, 1.3 \text{ Hz, 2H), 7.09 – 7.19 (m, 2H).}}\]

\[^{13}C\text{-NMR (75 MHz, CDCl}_3]: \delta = 14.7, 19.4, 56.5, 57.0, 73.4, 80.9, 83.6, 112.2, 112.9, 121.9, 125.6, 126.3, 127.6, 141.2, 154.3.\]

\[\text{IR (ATR) } \tilde{\nu} \text{ (cm}^{-1}) = 3068, 2977, 2918, 2852, 1577, 1471, 1443, 1356, 1217, 1129, 1073, 1004.\]

\[C_{15}H_{18}O_{2}S \quad \text{calcd.: 262.1028, found: 262.10465 (GC-HRMS).}\]

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\( ^1H\text{-NMR (300 MHz, CDCl}_3 \).} \\
\( ^{13}C\text{-NMR (75 MHz, CDCl}_3 \).}
(Z)-4-(2-(Methylthio)phenoxy)but-2-en-1-ol (19.1f)

![Chemical Structure](image)

Compound 19.1f was synthesized according GP1. A solution of SM1 (1.40 g, 10.00 mmol, 1.00 equiv.), PPh₃ (2.62 g, 10.00 mmol, 1.00 equiv.) and (Z)-but-2-ene-1,4-diol (882.0 mg, 10.00 mmol, 1.00 equiv.) in dry toluene (60 ml) was cooled to 0 °C. DIAD (2.02 g, 1.96 ml, 10.00 mmol, 1.00 equiv.) in dry toluene (48 ml) was added dropwise to the stirred solution. After completion, the reaction mixture was warmed to RT and stirred for 48 h. The solvent was removed under reduced pressure and silica gel column chromatography (n-pentane:EtOAc = 4:1→2:1) gave the desired product (827 mg, 3.93 mmol, 39%) as a colorless oil.

Rf = 0.17 (n-pentane:EtOAc = 4:1).

\(^1\)H-NMR (300 MHz, CDCl₃): \(\delta = 2.42\) (s, 3H), 4.22 – 4.33 (m, 2H), 4.68 (d, \(J=4.5\), 2H), 5.84 – 5.92 (m, 2H), 6.83 (dd, \(J=8.1, 1.3, 1H\)), 6.97 (td, \(J=7.6, 1.3, 1H\)), 7.08 – 7.20 (m, 2H).

\(^13\)C-NMR (75 MHz, CDCl₃): \(\delta = 14.6, 58.8, 64.5, 111.6, 121.6, 125.7, 126.1, 126.8, 127.4, 133.0, 155.0\).

IR (ATR) \(\nu\) (cm\(^{-1}\)) = 3314, 3061, 3024, 2980, 2923, 2870, 1713, 1576, 1470, 1440, 1226, 1011.

\(\text{C}_{11}\text{H}_{14}\text{O}_{2}\text{S}\)

$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
Following a reported procedure\textsuperscript{31}, a solution of 19.1f (483 mg, 2.3 mmol, 1.0 equiv.) in DMF (12 ml) was cooled to 0 °C and treated with NaH (148 mg of 60% dispersion, 3.7 mmol, 1.61 equiv.). After 30 min of stirring, 3-bromo-2-methyl-1-propene (378.0 mg, 0.29 ml, 2.8 mmol, 1.22 equiv.) in DMF (14 ml) followed by TBAI (130.0 mg, 0.35 mmol, 0.15 equiv.) were added, the reaction was warmed to RT and stirred overnight. It was then quenched with H\textsubscript{2}O at 0 °C, extracted with Et\textsubscript{2}O (3 x 50 ml), washed with brine and dried over Na\textsubscript{2}SO\textsubscript{4}. The solvent was evaporated \textit{in vacuo} to obtain the product after flash column chromatography (n-pentane:EtOAc = 40:1 \rightarrow 20:1) as a colorless oil (1.42 mmol, 375 mg, 62%).

\[ R_f = 0.35 \text{ (n-pentane:EtOAc = 20:1)}. \]

\textsuperscript{1}H\textsuperscript{NMR} (300 MHz, CDCl\textsubscript{3}): \( \delta = 1.68 - 1.79 \) (m, 3H), 2.42 (s, 3H), 3.84 – 3.96 (m, 2H), 4.11 (dt, \( J = 5.6, 1.1 \), 2H), 4.70 (dd, \( J = 5.6, 1.2 \), 2H), 4.90 (dd, \( J = 2.1 \), 1.5, 0.7, 1H), 4.97 (dd, \( J = 2.2 \), 1.1, 1H), 5.69 – 5.97 (m, 2H), 6.82 (dd, \( J = 8.1, 1.3 \), 1H), 6.96 (td, \( J = 7.6, 1.3 \), 1H), 7.07 – 7.19 (m, 2H).

\textsuperscript{13}C\textsuperscript{NMR} (75 MHz, CDCl\textsubscript{3}): \( \delta = 14.6, 19.5, 64.9, 65.8, 74.3, 111.6, 112.3, 121.5, 125.7, 126.0, 127.5, 127.8, 129.9, 142.0, 155.1 \).

\textbf{IR (ATR)} \( \nu \text{ (cm}^{-1}) = 3067, 3025, 2976, 2918, 2854, 1577, 1470, 1442, 1228, 1075, 1009 \).

\textbf{C}_{15}\textbf{H}_{20}\textbf{O}_{2}\textbf{S} \quad \text{calcd.: 264.1184, found: 264.1207 (GC-HRMS).}

$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
Synthesis of Thiocyanates 4

1-(But-2-yn-1-ol)-2-thiocyanatobenzene (1a)

[Chemical structure image]

Thiocyanate 1a was synthesized from compound 11a (1.6 g, 8.32 mmol) according GP 3. A mixture of CH₃CN/THF (1:1, 32 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (n-pentane:EtOAc = 60:1) to obtain the product (887 mg, 4.32 mmol, 52%) as colorless solid.

m.p.: 43 °C.

Rₖ = 0.67 (n-pentane:EtOAc = 20:1).

¹H-NMR (300 MHz, CDCl₃): δ = 1.85 (t, J = 2.4 Hz, 3H), 4.76 (q, J = 2.4 Hz, 2H), 7.04 – 7.10 (m, 2H), 7.32 – 7.39 (m, 1H), 7.58 (dd, J = 8.2, 1.6 Hz, 1H).

¹³C-NMR (75 MHz, CDCl₃): δ = 3.7, 57.5, 73.0, 85.0, 110.4, 113.2, 113.9, 122.6, 129.7, 130.2, 154.6.

IR (ATR) ν (cm⁻¹) = 3066, 2967, 2159, 1579, 1473, 1447, 1224, 1143, 1060.

$\text{H-NMR (300 MHz, CDCl}_3\text{).}$

$\text{C-NMR (75 MHz, CDCl}_3\text{).}$
Thiocyanate 1b was synthesized from compound 11b (105 mg, 448 µmol) according GP 3. A mixture of CH$_3$CN/THF (1:1, 2.0 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (n-pentane:EtOAc = 100:1) to obtain the product (52 mg, 212 µmol, 47%) as colorless oil.

$R_f = 0.34$ (n-pentane:EtOAc = 50:1).

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 1.19$ (s, 9H), 4.76 (s, 2H), 7.03 – 7.12 (m, 2H), 7.34 (ddd, $J = 8.4, 7.5, 1.6$ Hz, 1H), 7.55 – 7.59 (m, 1H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 27.5, 30.6, 57.8, 72.4, 97.7, 110.4, 113.6, 114.2, 122.6, 129.4, 130.0, 154.7$.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 2969, 2929, 2869, 2239, 2158, 1582, 1475, 1227, 1066.

C$_{14}$H$_{15}$NO$_S$ calcd.: 268.0767, found: 268.0769 [M+Na]$^+$ (ESI-HRMS).
$^{13}$C-NMR (75 MHz, CDCl$_3$).

$^1$H-NMR (300 MHz, CDCl$_3$).
1-((3-Cyclopropyl-2-yn-1-yl)oxy)-2-thiocyanatobenzene (1c)

Thiocyanate 1c was synthesized from compound 11c (211 mg, 0.97 mmol) according GP 3. A mixture of CH₃CN/THF (1:1, 5.6 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (n-pentane:EtOAc = 60:1) to obtain the product (24 mg, 104 µmol, 11%) as colorless oil.

Rᵣ = 0.48 (n-pentane:EtOAc = 50:1).

¹H-NMR (300 MHz, CDCl₃): δ = 0.66 – 0.71 (m, 2H), 0.75 – 0.82 (m, 2H), 1.22 – 1.29 (m, 1H), 4.75 (d, J = 1.9 Hz, 2H), 7.08 (td, J = 7.6, 1.2 Hz, 2H), 7.34 – 7.37 (m, 1H), 7.57 – 7.59 (m, 1H).

¹³C-NMR (75 MHz, CDCl₃): δ = -0.8, 8.1, 57.5, 68.8, 92.4, 110.3, 113.1, 113.8, 122.4, 129.4, 129.9, 154.4.

IR (ATR) v (cm⁻¹) = 3012, 2925, 2864, 2236, 2157, 1581, 1474, 1226, 1059.

C₁₃H₁₁NO₅ calcd.: 229.0561, found: 229.0563 (GC-HRMS).
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-((6,6-Dimethylhepta-2,4-diyn-1-yl)oxy)-2-thiocyanatobenzene (1d)

Thiocyanate 1d was synthesized from compound 11d (200 mg, 774 μmol) according GP 3. A mixture of CH₃CN/THF (1:1, 4.4 ml) was used as solvent. After evaporation, the crude mixture was redissolved in a small amount of DCM and added to a silica gel column. After elution (n-pentane:EtOAc = 60:1) the product was obtained as a colorless solid (116 mg, 431 μmol, 56%).

**m.p.:** 49 °C

**Rᵣ = 0.18** (n-pentane:EtOAc = 50:1).

**¹H-NMR** (300 MHz, CDCl₃): δ = 1.24 (s, 9H), 4.85 (s, 2H), 7.05 – 7.13 (m, 2H), 7.37 (ddd, J = 8.1, 7.6, 1.6 Hz, 1H), 7.59 (dd, J = 7.8, 1.6 Hz, 1H).

**¹³C-NMR** (75 MHz, CDCl₃): δ = 28.0, 30.3, 57.4, 62.8, 69.9, 73.2, 90.2, 110.3, 113.0, 114.0, 123.0, 129.9, 130.3, 154.4.

**IR** (ATR) v (cm⁻¹) = 2972, 2931, 2868, 2246, 2158, 1580, 1474, 1449, 1284, 1222, 1165.

C₁₆H₁₅NOS  calcd.: 269.0874, found: 269.0895 (GC-HRMS).
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-((3-Phenylprop-2-yn-1-yl)oxy)-2-thiocyanatobenzene (1e)

Thiocyanate 1e was synthesized from compound 11e (201 mg, 790 μmol) according GP 3. A mixture of CH₃CN/THF (1:1, 4.6 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (n-pentane:EtOAc = 100:1) to obtain the product (107 mg, 403 μmol, 51%) as pale yellow solid.

m.p.: 39 °C.

Rf = 0.13 (n-pentane:EtOAc = 50:1).

¹H-NMR (300 MHz, CDCl₃): δ = 5.02 (s, 2H), 7.06 – 7.12 (m, 1H), 7.18 (dd, J = 8.3, 1.2 Hz, 1H), 7.26 – 7.45 (m, 6H), 7.60 (dd, J = 7.9, 1.6 Hz, 1H).

¹³C-NMR (75 MHz, CDCl₃): δ = 57.8, 82.6, 88.3, 110.4, 113.4, 114.1, 121.8, 122.9, 128.3, 128.9, 129.8, 130.2, 131.8, 154.6.

IR (ATR) ν (cm⁻¹) = 3063, 2921, 2866, 2238, 2157, 1580, 1474, 1446, 1223, 1062.

C₁₆H₁₁NO₅ calcd.: 288.0454, found: 288.0455 [M+Na]⁺ (ESI-HRMS).
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-(3-(2-Naphthyl)prop-2-yn-1-yl)oxy)-2-thiocyanatobenzene (1f)

Thiocyanate 1f was synthesized from compound 11f (143 mg, 469 µmol) according GP 3. A mixture of CH$_3$CN/THF (1:1, 2.8 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (n-pentane:EtOAc = 100:1) to obtain the product (62 mg, 196 µmol, 42%) as colorless solid.

**m.p.:** 55 °C.

R$_f$ = 0.12 (n-pentane:EtOAc = 50:1).

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ = 5.03 (s, 2H), 7.07 (td, J = 7.7, 1.3 Hz, 1H), 7.18 (dd, J = 8.3, 1.3 Hz, 1H), 7.37 (ddd, J = 8.3, 7.5, 1.6 Hz, 1H), 7.41 – 7.50 (m, 3H), 7.59 (dd, J = 7.9, 1.5 Hz, 1H), 7.71 – 7.81 (m, 3H), 7.93 (d, J = 1.4 Hz, 1H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ = 57.8, 82.8, 88.6, 110.3, 113.3, 114.1, 119.0, 122.8, 126.6, 127.0, 127.7, 128.0, 128.1, 129.8, 130.2, 132.0, 132.7, 133.0, 154.6.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3062, 2963, 2925, 2226, 2148, 1580, 1499, 1474, 1295, 1223, 1014.

C$_{20}$H$_{13}$NOS calcd.: 315.0718, found: 315.0722 (GC-HRMS).
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-[(3-(4-Fluorophenyl)prop-2-yn-1-yl)oxy]-2-thiocyanatobenzene (1g)

Thiocyanate 1g was synthesized from compound 11g (85 mg, 312 µmol) according GP 3. A mixture of CH₃CN/THF (1:1, 1.6 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (n-pentane:EtOAc = 100:1) to obtain the product (43 mg, 152 µmol, 49%) as colorless solid.

m.p.: 92 °C.

Rf = 0.08 (n-pentane:EtOAc = 50:1).

¹H-NMR (300 MHz, CDCl₃): δ = 5.00 (s, 2H), 7.00 (t, J = 8.7 Hz, 2H), 7.06 – 7.12 (m, 1H), 7.15 (dd, J = 8.3, 1.2 Hz, 1H), 7.35 – 7.44 (m, 3H), 7.60 (dd, J = 7.9, 1.6 Hz, 1H).

¹³C-NMR (75 MHz, CDCl₃): δ = 57.7, 82.3, 82.4, 87.2, 110.3, 113.3, 114.1, 115.5, 115.8, 117.9, 117.9, 122.9, 129.9, 130.3, 133.7, 133.9, 154.6, 161.2, 164.5.

¹⁹F-NMR (283 MHz, CDCl₃): δ = -110.07

IR (ATR) ν (cm⁻¹) = 3101, 3068, 2932, 2242, 2150, 1580, 1502, 1472, 1449, 1278, 1212, 1009.

$^{1}H$-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
$^{19}$F-NMR (283 MHz, CDCl$_3$).
1-((3-(4-Chlorophenyl)prop-2-yn-1-yl)oxy)-2-thiocyanatobenzene (1h)

Thiocyanate 1h was synthesized from compound 11h (165 mg, 571 µmol) according GP 3. A mixture of CH₃CN/THF (1:1, 3.2 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (n-pentane:EtOAc = 100:1) to obtain the product (87 mg, 290 µmol, 51%) as yellow solid.

m.p.: 53 °C.
Rᵣ = 0.17 (n-pentane:EtOAc = 50:1).

¹H-NMR (300 MHz, CDCl₃): δ = 5.00 (s, 2H), 7.05 – 7.11 (m, 1H), 7.14 (dd, J = 8.3, 1.2 Hz, 1H), 7.23 – 7.41 (m, 5H), 7.58 (dd, J = 7.9, 1.6 Hz, 1H).

¹³C-NMR (75 MHz, CDCl₃): δ = 57.6, 83.6, 87.0, 113.2, 114.0, 120.2, 122.9, 128.6, 129.9, 130.3, 133.0, 135.0, 154.5.

IR (ATR) v (cm⁻¹) = 3083, 3057, 2923, 2856, 2254, 2154, 1578, 1476, 1443, 1382, 1290, 1240, 1012.

C₁₆H₁₀ClNO₂S calcd.: 322.0064, found: 322.0065 [M+Na]⁺ (ESI-HRMS).
$^{1}H$-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-((3-o-Tolyl)prop-2-yn-1-yl)oxy)-2-thiocyanatobenzene (1i)

![Chemical Structure](image)

Thiocyanate 1i was synthesized from compound 11i (119 mg, 444 µmol) according GP 3. A mixture of CH$_3$CN/THF (1:1, 2.4 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (n-pentane:EtOAc = 100:1) to obtain the product (54 mg, 193 µmol, 43%) as pale yellow oil.

$R_f = 0.13$ (n-pentane:EtOAc = 50:1).

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 2.34$ (s, 3H), 5.06 (s, 2H), 7.04 – 7.26 (m, 5H), 7.33 – 7.41 (m, 2H), 7.59 (dd, $J = 7.9$, 1.6 Hz, 1H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 20.5$, 57.8, 86.3, 87.3, 110.3, 113.5, 114.2, 121.6, 122.8, 125.5, 128.9, 129.5, 129.7, 130.1, 132.1, 140.5, 154.5.

IR (ATR) $\tilde{v}$ (cm$^{-1}$) = 3063, 2917, 2869, 2232, 2157, 1580, 1475, 1449, 1222, 1007.

C$_{17}$H$_{13}$NOS     calcd.: 302.0610, found: 302.0612 [M+Na]$^+$ (ESI-HRMS).
$\text{H-NMR (300 MHz, CDCl$_3$).}$

$\text{\textsuperscript{13}C-NMR (75 MHz, CDCl$_3$).}$
1-((3-(m-Tolyl)prop-2-yn-1-yl)oxy)-2-thiocyanatobenzene (1j)

Thiocyanate 1j was synthesized from compound 11j (164 mg, 611 µmol) according GP 3. A mixture of CH₃CN/THF (1:1, 3.2 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (n-pentane:EtOAc = 100:1) to obtain the product (74 mg, 265 µmol, 43%) as pale yellow oil.

Rᵣ = 0.21 (n-pentane:EtOAc = 50:1).

¹H-NMR (300 MHz, CDCl₃): δ = 2.30 (d, J = 0.7 Hz, 3H), 4.99 (s, 2H), 7.03 – 7.26 (m, 6H), 7.36 (ddd, J = 8.2, 7.4, 1.5 Hz, 1H), 7.58 (dd, J = 7.9, 1.6 Hz, 1H).

¹³C-NMR (75 MHz, CDCl₃): δ = 21.1, 57.7, 82.2, 88.4, 110.3, 113.3, 114.0, 121.5, 122.8, 128.2, 128.8, 129.7, 129.8, 130.2, 132.3, 138.0, 154.5.

IR (ATR) ν (cm⁻¹) = 3063, 2920, 2863, 2230, 2157, 1580, 1475, 1447, 1281, 1223, 1061.

$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-((3-((p-Tolyl)prop-2-yn-1-yl)oxy)-2-thiocyanatobenzene (1k)

Thiocyanate 1k was synthesized from compound 11k (118 mg, 440 µmol) according GP 3. A mixture of CH₃CN/THF (1:1, 2.4 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (n-pentane:EtOAc = 100:1) to obtain the product (30 mg, 107 µmol, 24%) as off-white solid.

m.p.: 74 °C.
Rₙ = 0.21 (n-pentane:EtOAc = 50:1).

¹H-NMR (300 MHz, CDCl₃): δ = 2.34 (s, 3H), 5.00 (s, 2H), 7.05 – 7.20 (m, 4H), 7.28 – 7.42 (m, 3H), 7.59 (dd, J = 7.9, 1.6 Hz, 1H).

¹³C-NMR (75 MHz, CDCl₃): δ = 21.5, 57.8, 76.6, 77.0, 77.4, 81.9, 88.4, 110.4, 113.4, 114.1, 118.7, 122.8, 129.1, 129.7, 130.2, 131.7, 139.2, 154.6.

IR (ATR) ν (cm⁻¹) = 3032, 2919, 2856, 2224, 2158, 1577, 1475, 1443, 1374, 1230, 1008.

$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
Compound 1I was synthesized according GP3 (alternative B) from substrate 11l (2.0 mmol, 389.0 mg). The desired product was obtained after flash column chromatography (n-pentane:EtOAc = 50:1) as a colorless oil (0.68 mmol, 140.0 mg, 34%).

$R_f = 0.40$ (n-pentane:EtOAc = 20:1).

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 1.80 – 1.91$ (m, 3H), 4.53 (p, $J=0.8$, 2H), 4.99 – 5.06 (m, 1H), 5.12 (dd, $J=1.5$, 0.9, 1H), 6.92 (dd, $J=8.2$, 1.2, 1H), 7.04 (td, $J=7.6$, 1.1, 1H), 7.33 (ddd, $J=8.3$, 7.6, 1.7, 1H), 7.57 (dd, $J=7.8$, 1.6, 1H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 19.3, 72.6, 110.4, 112.6, 113.4, 113.6, 122.1, 129.7, 130.3, 139.7, 155.4$.

IR (ATR) $\tilde{v}$ (cm$^{-1}$) = 3075, 2977, 2940, 2864, 2158, 1740, 1582, 1476, 1446, 1235, 1062, 1002.

C$_{11}$H$_{11}$NOS          calcd.: 205.0561, found: 205.0582 (GC-HRMS).
$^{1}H$-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-(Cinnamyloxy)-2-thiocyanatobenzene (1m)

Compound 1m was synthesized according GP3 (alternative B) from substrate 11m (3.86 mmol, 990.0 mg, isomeric mixture). The desired product was obtained after flash column chromatography (n-pentane:EtOAc = 30:1) as a yellow oil (1.26 mmol, 338.0 mg, 33%).

Rf = 0.43 (n-pentane:EtOAc = 10:1).

\(^1\)H-NMR (300 MHz, CDCl\(_3\)): δ = 4.78 (dd, J=5.7, 1.5, 2H), 6.38 (dt, J=16.1, 5.8, 1H), 6.75 (dt, J=16.1, 1.7, 1H), 6.97 (dd, J=8.3, 1.2, 1H), 7.03 (td, J=7.7, 1.2, 1H), 7.22 – 7.29 (m, 1H), 7.33 (m, 3H), 7.39 – 7.44 (m, 2H), 7.57 (dd, J=7.9, 1.6, 1H).

\(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): δ = 69.7, 110.4, 112.8, 113.7, 122.3, 123.0, 126.6 (2 C), 128.1, 128.6 (2 C), 129.7, 130.3, 133.7, 136.0, 155.4.

IR (ATR) \(\nu\) (cm\(^{-1}\)) = 3059, 3027, 2926, 2866, 2156, 1580, 1475, 1447, 1240, 964.

C\(_{16}\)H\(_{13}\)NOS calcd.: 290.0610 [M+Na\(^+\)], found: 290.0613 [M+Na\(^+\)] (ESI-HRMS).
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-(Pent-3-yn-1-yl)-2-thiocyanatobenzene (1n)

Thiocyanate 1n was synthesized from compound 11n (94 mg, 367 µmol) according GP 3. A mixture of CH$_3$CN/THF (1:1, 2.2 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography ($n$-pentane:EtOAc = 60:1) to obtain the product (36 mg, 134 µmol, 37%) as colorless oil.

$R_f = 0.43$ ($n$-pentane:EtOAc = 20:1).

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta =$ 1.75 (t, $J = 2.5$ Hz, 3H), 2.46 (tq, $J = 7.4$, 2.5 Hz, 2H), 2.97 (t, $J = 7.3$ Hz, 2H), 7.27 – 7.42 (m, 3H), 7.65 – 7.70 (m, 1H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta =$ 3.4, 20.0, 33.2, 111.0, 123.9, 128.3, 130.2, 130.7, 132.5, 141.8.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3062, 2917, 2853, 2155, 1469, 1440, 1039.

C$_{12}$H$_{11}$NS calcd.: 200.0539, found: 200.0549 [M-H$^-$] (GC-HRMS).
S126
1-(But-2-yn-1-yl)-2-thiocyanatobenzene (1o)

![Structure](image)

Thiocyanate 1o was synthesized from compound 11o (177 mg, 1.0 mmol) according GP 3. A mixture of CH₃CN/THF (1:1, 5.8 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (n-pentane:EtOAc = 100:1) to obtain the product (13 mg, 69 µmol, 7%) as colorless oil.

Rᵣ = 0.36 (n-pentane:EtOAc = 50:1).

¹H-NMR (300 MHz, CDCl₃): δ = 1.85 (t, J = 2.6 Hz, 3H), 3.67 (q, J = 2.6 Hz, 2H), 7.29 – 7.36 (m, 1H), 7.42 (td, J = 7.5, 1.4 Hz, 1H), 7.56 – 7.60 (m, 1H), 7.64 – 7.69 (m, 1H).

¹³C-NMR (75 MHz, CDCl₃): δ = 3.5, 24.1, 74.6, 80.0, 110.4, 123.3, 128.5, 130.2, 130.4, 132.5, 138.9.

IR (ATR) ν (cm⁻¹) = 3063, 2917, 2878, 2853, 2812, 2152, 1579, 1467, 1416, 1322, 1029.

C₁₁H₉NS calcd.: 187.0456, found: 187.0445 (GC-HRMS).
$^{1}$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).

1-{$($Pent-3-yn-1-yl)oxy$}$-2-thiocyanatobenzene (1p)
Thiocyanate 1p was synthesized from compound 11p (260 mg, 1.26 mmol) according GP 3. A mixture of CH$_3$CN/THF (1:1, 7.2 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography ($n$-pentane:EtOAc = 60:1) to obtain the product (157 mg, 720 µmol, 57%) as colorless solid.

m.p.: 59 °C.

$R_f = 0.46$ ($n$-pentane:EtOAc = 20:1).

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 1.79$ (t, $J = 2.6$ Hz, 3H), 2.65 (tq, $J = 7.1$, 2.5 Hz, 2H), 4.12 (t, $J = 7.1$ Hz, 2H), 6.92 (dd, $J = 8.3$, 1.2 Hz, 1H), 6.99 – 7.07 (m, 1H), 7.33 (ddd, $J = 8.2$, 7.4, 1.5 Hz, 1H), 7.54 (dd, $J = 7.9$, 1.6 Hz, 1H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 2.7$, 18.8, 66.9, 73.5, 77.0, 109.6, 111.8, 112.9, 121.5, 128.8, 129.5, 154.5.

IR (ATR) $\tilde{v}$ (cm$^{-1}$) = 3084, 2948, 2922, 2881, 2159, 1581, 1481, 1447, 1244, 1062, 1026.

C$_{12}$H$_{11}$NO$_S$ calcd.: 217.0561, found: 217.0572 (GC-HRMS).
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-((2-{Prop-1-yn-1-yl}benzoyl)oxy)-2-thiocyanatobenzene (1q)

Compound 1q was synthesized according GP3 (alternative B) from substrate 11q (2.1 mmol, 564.0 mg). The desired product was obtained after flash column chromatography (n-pentane:EtOAc = 20:1) as a colorless solid (1.29 mmol, 359.0 mg, 61%).

\[ \text{m.p.: } 80\ \degree\text{C.} \]

\[ R_f = 0.28 (\text{n-pentane:EtOAc = 20:1}). \]

\(^1\text{H-NMR}\ (300\ \text{MHz, CDCl}_3): \delta = 2.07\ (s, 3H), 5.33\ (s, 2H), 6.99\ (dd, \; J=8.3, 1.2, 1H), 7.01 – 7.08\ (m, 1H), 7.21 – 7.36\ (m, 3H), 7.43\ (dd, \; J=7.5, 1.6, 1H), 7.47 – 7.51\ (m, 1H), 7.58\ (dd, \; J=7.9, 1.6, 1H). \]

\(^{13}\text{C-NMR}\ (75\ \text{MHz, CDCl}_3): \delta = 4.5, 69.3, 76.8, 91.6, 110.5, 113.0, 113.8, 122.3, 122.3, 126.9, 127.8, 128.0, 129.7, 130.3, 132.2, 137.2, 155.5. \]

\(^\text{IR\ (ATR)}\ \tilde{\nu}\ (\text{cm}^{-1}) = 3097, 3063, 2911, 2850, 2155, 1850, 1480, 1441, 1245, 1022. \]

\(\text{C}_{17}\text{H}_{13}\text{NOS} \quad \text{calcd.}: \quad 279.0718, \text{found: } 279.0729\ \text{(GC-HRMS)}. \)
$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-(2-(Prop-1-yn-1-yl)phenethoxy)-2-thiocyanatobenzene (1r)

Compound 1r was synthesized according GP3 (alternative B, 1.1 equiv. of X-CN) from substrate 11r (2.5 mmol, 711.0 mg). The desired product was obtained after flash column chromatography (n-pentane:EtOAc = 20:1) as a colorless oil (0.84 mmol, 247.0 mg, 34%).

Rf = 0.26 (n-pentane:EtOAc = 20:1).

1H-NMR (300 MHz, CDCl3): δ = 2.08 (s, 3H), 3.29 (t, J=6.9, 2H), 4.29 (t, J=6.9, 2H), 6.93 (dd, J=8.2, 1.2, 1H), 7.00 (td, J=7.7, 1.3, 1H), 7.17 (td, J=7.4, 1.8, 1H), 7.21 – 7.32 (m, 3H), 7.40 (dd, J=7.4, 1.7, 1H), 7.53 (dd, J=7.9, 1.6, 1H).

13C-NMR (75 MHz, CDCl3): δ = 4.5, 34.2, 68.8, 78.0, 89.8, 110.6, 112.2, 113.6, 122.0, 123.8, 126.6, 127.8, 129.4, 129.8, 130.1, 132.4, 139.0, 155.5.

IR (ATR) v (cm⁻¹) = 3065, 3024, 3923, 2882, 2853, 2157, 1582, 1474, 1284, 1244, 1060, 1012.

C₁₈H₁₅NOS calcd.: 293.0874, found: 293.0849 (GC-HRMS).
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-(Methylthio)-2-(prop-1-yn-1-yl)benzene (1s)

Thiocyanate 1s was synthesized from compound 11s (170 mg, 1.05 mmol) according GP 3. A mixture of CH$_3$CN/THF (1:1, 6.0 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography ($n$-pentane:EtOAc = 60:1) to obtain the product (71 mg, 410 µmol, 39%) as yellow oil.

$R_f = 0.65$ ($n$-pentane:EtOAc = 50:1).

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 2.13$ (s, 3H), 7.25 – 7.31 (m, 1H), 7.35 (td, $J = 7.7$, 1.8 Hz, 1H), 7.43 (dd, $J =$ 7.5, 1.8 Hz, 1H), 7.59 – 7.64 (m, 1H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 4.5$, 75.6, 95.5, 110.0, 123.3, 127.6, 127.6, 128.3, 129.1, 132.7.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3063, 2917, 2848, 2157, 1466, 1434, 1062, 1029.

C$_{10}$H$_7$NS calcd.: 173.0299, found: 173.0305 (GC-HRMS).
$^{1}H$-NMR (300 MHz, CDCl$_3$).

$^{13}C$-NMR (75 MHz, CDCl$_3$).
1-((3-Bromoprop-2-yn-1-yl)oxy)-2-thiocyanatobenzene (1u)

Thiocyanate 1u was synthesized from compound 11u (155 mg, 0.60 mmol) according GP 3. A mixture of CH$_3$CN/THF (1:1, 3.4 ml) was used as solvent. The reaction mixture was directly added to a silica gel column. After elution (n-pentane:EtOAc = 20:1), the product was obtained as colorless solid (86 mg, 0.32 mmol, 53%).

m.p.: 50 °C.

R$_f$ = 0.16 (n-pentane:EtOAc = 50:1).

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ = 4.81 (s, 2H), 7.03 – 7.13 (m, 2H), 7.37 (ddd, $J$ = 8.3, 7.6, 1.6 Hz, 1H), 7.58 (dd, $J$ = 7.9, 1.5 Hz, 1H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ = 49.1, 57.6, 73.8, 110.1, 113.0, 113.9, 123.0, 129.9, 130.3, 154.2.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3283, 3096, 3067, 2928, 2231, 1580, 1501, 1475, 1365, 1289, 1241, 1064, 996.

C$_{10}$H$_6$BrNO$_S$ calcd.: 268.9333, found: 268.9347 (GC-HRMS).

S137
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-((3-(4-Nitrophenyl)prop-2-yn-1-yl)oxy)-2-thiocyanatobenzene (1x)

Thiocyanate 1x was synthesized from compound 11x (264 mg, 882 µmol) according GP 3. A mixture of CH₃CN/THF (1:1, 5.2 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (n-pentane:EtOAc = 20:1) to obtain the product (156 mg, 502 µmol, 57%) as off-white/beige solid.

m.p.: 97 °C.

Rf = 0.46 (n-pentane:EtOAc = 4:1).

¹H-NMR (300 MHz, CDCl₃): δ = 5.07 (s, 2H), 7.09 – 7.18 (m, 2H), 7.41 (ddd, J = 8.3, 7.4, 1.6 Hz, 1H), 7.55 – 7.60 (m, 2H), 7.62 (dd, J = 7.8, 1.5 Hz, 1H), 8.15 – 8.21 (m, 2H).

¹³C-NMR (75 MHz, CDCl₃): δ = 57.4, 86.1, 87.7, 110.2, 113.2, 114.2, 123.2, 123.6, 128.5, 130.3, 130.4, 132.6, 147.5, 154.5.

IR (ATR) ν (cm⁻¹) = 3106, 3070, 2934, 2839, 2156, 1585, 1515, 1472, 1446, 1337, 1063, 1011.

$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-((4-(p-Tolyl)but-3-yn-1-yl)oxy)-2-thiocyanatobenzene (1y)

Thiocyanate 1y was synthesized from compound 11y (186 mg, 0.66 mmol) according GP 3. A mixture of CH$_3$CN/THF (1:2, 6.0 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (n-pentane:EtOAc = 50:1) to obtain the product (44 mg, 150 µmol, 23%) as colorless solid.

m.p.: 63 °C.

R$_f$ = 0.16 (n-pentane:EtOAc = 50:1).

$^1$H-NMR (300 MHz, CDCl$_3$): δ = 2.34 (s, 3H), 2.94 (t, $J$ = 7.0 Hz, 2H), 4.26 (t, $J$ = 7.0 Hz, 2H), 6.97 (dd, $J$ = 8.2, 1.3 Hz, 1H), 7.02 – 7.14 (m, 3H), 7.27 – 7.40 (m, 3H), 7.57 (dd, $J$ = 7.9, 1.6 Hz, 1H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): δ = 20.4, 21.4, 67.4, 82.5, 84.1, 110.5, 112.6, 113.9, 120.1, 122.5, 129.0, 129.6, 130.3, 131.5, 138.1, 155.3.

IR (ATR) v (cm$^{-1}$) = 3097, 3067, 2953, 2921, 2162, 1583, 1482, 1385, 1288, 1251, 1062, 1038, 1019.

C$_{18}$H$_{15}$NO$_2$ calcd.: 293.0874, found: 293.0903 (GC-HRMS).
$^{1}H$-NMR (300 MHz, CDCl$_3$).

$^{13}C$-NMR (75 MHz, CDCl$_3$).
**1,6-Bis(2-thiocyanatophenoxy)hexa-2,4-diyn (1z)**

![Chemical Structure](image)

Thiocyanate 1v was synthesized from compound 11z (261 mg, 736 µmol) according GP 3. A mixture of CH₃CN/THF (1:1, 4.2 ml) as solvent and 3.0 equiv. of X-CN were used for the reaction. After evaporation, the crude mixture was redissolved in a small amount of DCM and added to a silica gel column. After elution (n-pentane:EtOAc = 100:1) the product (122 mg, 324 µmol, 44%) was obtained as colorless solid.

**m.p.:** 128 °C.
**R_f:** 0.29 (n-pentane:EtOAc = 4:1).

**¹H-NMR** (300 MHz, CDCl₃): δ = 4.87 (s, 4H), 7.03 (dd, J = 8.3, 1.2 Hz, 2H), 7.07 – 7.14 (m, 2H), 7.38 (ddd, J = 8.3, 7.5, 1.6 Hz, 2H), 7.59 (dd, J = 7.8, 1.6 Hz, 2H).

**¹³C-NMR** (75 MHz, CDCl₃): δ = 57.1, 71.7, 73.9, 110.1, 114.0, 123.3, 130.2, 130.5, 154.2.

**IR (ATR)** ν (cm⁻¹) = 3061, 2926, 2854, 2155, 1577, 1471, 1447, 1284, 1215, 1061, 1011.

**C₂₀H₁₂N₂O₂S₂** calcd.: 399.0232, found: 399.0233 [M+Na]+ (ESI-HRMS).
$^{1}{H}$-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-[(3-[(1,1-Dimethylethyl)dimethylsilyl]-2-propyn-1-yl]oxy]-2-thiocyanatobenzene (5a)

Thiocyanate 5a was synthesized from compound 15a (200 mg, 684 μmol) according GP 3. A mixture of CH₃CN/THF (1:1, 4.0 ml) was used as solvent. After evaporation, the crude mixture was redissolved in a small amount of DCM and added to a silica gel column. After elution (n-pentane:EtOAc = 60:1) the product was obtained as a pale yellow oil (122 mg, 402 μmol, 59%).

Rₛ = 0.27 (n-pentane:EtOAc = 50:1).

¹H-NMR (300 MHz, CDCl₃): δ = 0.09 (s, 6H), 0.88 (s, 9H), 4.80 (s, 2H), 7.05 – 7.13 (m, 2H), 7.35 (ddd, J = 8.3, 7.4, 1.6 Hz, 1H), 7.58 (dd, J = 7.9, 1.6 Hz, 1H).

¹³C-NMR (75 MHz, CDCl₃): δ = -4.9, 16.4, 25.9, 57.8, 92.8, 99.3, 110.4, 113.7, 114.3, 122.9, 129.6, 130.0, 154.4.

IR (ATR) ν (cm⁻¹) = 3069, 2953, 2930, 2857, 2159, 1582, 1475, 1282, 1250, 1225, 1028.

$^{1}H$-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-(((Phenylthio)ethynyl)thio)methyl)-2-thiocyanatobenzene (5b)

3,5-Bis(trifluoromethyl)phenyl(cyano)iodoniumtriflate (X-CN, 340 mg, 0.66 mmol, 1.00 equiv.) was weighed into a sealable tube and a solution of the compound 15b (201 mg, 0.66 mmol, 1.00 equiv.) in a mixture of CH$_3$CN/THF (1.9 ml/1.9 ml) was added and the tube capped. The solution was stirred for 20 min at RT. The solvent was removed and the crude mixture redissolved in DCM for adsorption on silica gel. The product was purified via flash column chromatography (n-pentane:EtOAc = 60:1) to afford a yellow oil (41 mg, 0.13 mmol, 20%).

$R_f = 0.31$ (n-pentane:EtOAc = 20:1).

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 2.48$ (s, 3H), 4.10 (s, 2H), 7.05 – 7.31 (m, 9H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 16.5, 39.7, 83.8, 92.2, 125.2, 125.7, 126.4, 127.0, 128.6, 129.0, 130.4, 133.7, 134.6, 137.8$.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3058, 2929, 2848, 2153, 1578, 1472, 1435, 1198, 1025.

C$_{16}$H$_{11}$NS$_3$ calcd.: 335.9946, found: 335.9949 [M+Na]$^+$ (ESI-HRMS).
$^{1}H$-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
2-Thiocyanatobenzenethiol (15.1c)

Following a reported procedure⁴ 1,2-benzenedithiol (142 mg, 1.00 mmol, 1.00 equiv.) was dissolved in THF (10 ml). To this solution DBU (160 mg, 157 µl, 1.05 mmol, 1.05 equiv.) and then CDBX⁴ (287 mg, 1.00 mmol, 1.00 equiv.) were added to the open flask. The mixture was stirred for 5 min at RT, quenched with aq. citric acid (5%, 20 ml) and extracted with EtOAc (3 x 20 ml). The combined organic layers were dried over Na₂SO₄, filtrated and the solvent was removed in vacuo. The product was purified via flash column chromatography (DCM) to afford a light pink solid (113 mg, 0.68 mmol, 68%).

m.p.: 126 °C.

Rf = 0.10 (n-pentane:EtOAc = 20:1).

¹H-NMR (300 MHz, CDCl₃): δ = 7.13 – 7.19 (m, 2H), 7.20 – 7.28 (m, 2H), 8.90 (s, 1H).

¹³C-NMR (75 MHz, CDCl₃): δ = 121.8 (2C), 126.1 (3C), 134.6, 172.4.

IR (ATR) ν (cm⁻¹) = 3174, 3049, 1697, 1547, 1430, 1231.

C₇H₅NS₂ calcd.: 166.9863, found: 166.9890 (GC-HRMS).
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
According a reported procedure compound 15.1c (50 mg, 0.30 mmol, 1.00 equiv.) was dissolved in dry THF (4 ml) and TMG (38 mg, 42 µl, 0.33 mmol, 1.10 equiv.) was added. The Me-EBX reagent (95 mg, 0.33 mmol, 1.10 equiv.) was added after 5 min of stirring and 15 min later, the mixture was quenched with water and showed then a blue color. The mixture was extracted with Et2O, dried over Na2SO4 and evaporated under reduced pressure. Flash column chromatography (n-pentane/1% NEt3) furnished the desired product as a pale yellow oil (21 mg, 0.10 mmol, 34%).

Rf = 0.23 (n-pentane:EtOAc = 50:1).

\[ ^1H\text{-NMR} \] (300 MHz, CDCl3): \[ \delta = 2.11 \text{ (s, 3H)}, 7.28 – 7.35 \text{ (m, 1H)}, 7.43 – 7.49 \text{ (m, 1H)}, 7.66 \text{ (dd, } J = 7.9, 1.3 \text{ Hz, 1H)}, 7.77 \text{ (dd, } J = 7.9, 1.4 \text{ Hz, 1H}).

\[ ^{13}C\text{-NMR} \] (75 MHz, CDCl3): \[ \delta = 5.3, 62.5, 96.8, 109.5, 122.1, 128.3, 129.2, 131.1, 133.1, 137.2. \]

\[ \text{IR (ATR) } \tilde{\nu} \text{ (cm}^{-1} \text{) = 3059, 2955, 2915, 2844, 2201, 2156, 1727, 1568, 1438, 1263, 1028.} \]

C\text{10H7NS2} \quad \text{calcd.: 205.0020, found: 204.9995 (GC-HRMS).}
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
3,5-Bis(trifluoromethyl)phenyl(cyano)iodoniumtriflate (X-CN, 541 mg, 1.05 mmol, 1.00 equiv.) was weighed into a sealable tube and a solution of the compound 15d (375 mg, 1.05 mmol, 1.00 equiv.) in a mixture of CH$_3$CN/THF (3.0 ml/3.0 ml) was added and the tube capped. The solution was stirred for 30 min at RT and then filtered through a short plug of silica. The reaction flask was rinsed with DCM and the plug was washed 4 times with the later eluent. The crude mixture was adsorbed on silica gel. The product was purified via flash column chromatography ($n$-pentane:EtOAc = 60:1) to afford an orange oil (122 mg, 0.33 mmol, 31%).

$\text{R}_f = 0.50$ ($n$-pentane:EtOAc = 20:1).

$^1\text{H-NMR}$ (300 MHz, CDCl$_3$): $\delta = 0.00$ (s, 6H), 0.81 (s, 9H), 4.07 (s, 2H), 7.24 – 7.34 (m, 3H), 7.60 – 7.68 (m, 1H).

$^{13}\text{C-NMR}$ (75 MHz, CDCl$_3$): $\delta = -4.7$, 16.6, 25.9, 29.9, 84.7, 109.2, 110.3, 123.9, 129.4, 130.2, 131.5, 133.4, 139.2.

$\text{IR}$ (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 2951, 2928, 2890, 2855, 2155, 2078, 1466, 1361, 1253, 1182.

C$_{16}$H$_{21}$NSeSi calcd.: 309.9625, found: 309.9649 [M-TBS] (GC-HRMS).
$^{1}H$-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).

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1-(9-Phenylnona-3,8-diyln-1-yl)-2-thiocyanatobenzene (9a)

Thiocyanate 9a was synthesized from compound 19a (105 mg, 330 µmol) according GP 3. A mixture of CH\textsubscript{3}CN/THF (1:1, 2.0 ml) was used as solvent. After evaporation, the crude mixture was redissolved in a small amount of DCM and added to a silica gel column. After elution (n-pentane:EtOAc = 50:1) the product was obtained as a colorless oil (44 mg, 133 µmol, 40%).

\[ R_f = 0.36 \text{ (n-pentane:EtOAc = 20:1).} \]

\[ ^1H-NMR \text{ (300 MHz, CDCl}_3\text{): } \delta = 1.74 \text{ (p, } J = 7.0 \text{ Hz, 2H), 2.30 (tt, } J = 7.0, 2.3 \text{ Hz, 2H), 2.44 (t, } J = 7.0 \text{ Hz, 2H), 2.50 (tt, } J = 7.3, 2.4 \text{ Hz, 2H), 2.99 (t, } J = 7.2 \text{ Hz, 2H), 7.24 \text{ – 7.43 m, 8H), 7.68 (dd, } J = 7.8, 1.4 \text{ Hz, 1H).} \]

\[ ^13C-NMR \text{ (75 MHz, CDCl}_3\text{): } \delta = 18.0, 18.5, 20.0, 27.9, 33.2, 78.9, 81.1, 81.2, 89.2, 111.0, 123.8, 123.9, 127.6, 128.2, 128.4, 130.3, 130.9, 131.5, 132.6, 141.8. \]

\[ IR \text{ (ATR) } \tilde{\nu} \text{ (cm}^{-1} \text{) } = 3058, 2937, 2866, 2838, 2155, 1596, 1482, 1436, 1337, 1033. \]

\[ C_{22}H_{19}NS \]  

calcd.: 329.1238, found: 329.1233 (GC-HRMS).
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-(Deca-3,8-diyn-1-yl)-2-thiocyanatobenzene (9b)

Thiocyanate 9b was synthesized from compound 19b (94 mg, 367 µmol) according GP 3. A mixture of CH₃CN/THF (1:1, 2.2 ml) was used as solvent. After evaporation, the crude mixture was redissolved in a small amount of DCM and added to a silica gel column. After elution (n-pentane:EtOAc = 60:1) the product was obtained as a colorless oil (36 mg, 134 µmol, 37%).

Rᵣ = 0.34 (n-pentane:EtOAc = 50:1).

¹H-NMR (300 MHz, CDCl₃): δ = 1.55 – 1.66 (m, 2H), 1.78 (t, J = 2.5 Hz, 2H), 2.15 (tt, J = 7.0, 2.6 Hz, 2H), 2.22 (tt, J = 6.9, 2.3 Hz, 2H), 2.49 (tt, J = 7.2, 2.3 Hz, 2H), 2.98 (t, J = 7.2 Hz, 2H), 7.28 – 7.43 (m, 3H), 7.68 (ddd, J = 7.7, 1.5, 0.7 Hz, 1H).

¹³C-NMR (75 MHz, CDCl₃): δ = 3.4, 17.8, 17.8, 20.0, 28.2, 33.2, 76.0, 78.2, 78.6, 81.4, 111.0, 123.9, 128.3, 130.2, 130.9, 132.5, 141.8.

IR (ATR) ν (cm⁻¹) = 3061, 2939, 2913, 2862, 2844, 2156, 1472, 1437, 1338, 1035.

C₁₇H₁₇NS calcd.: 266.1003, found: 266.1012 (GC-HRMS).
$^{1}H$-NMR (300 MHz, CDCl$_3$).

$^{13}C$-NMR (75 MHz, CDCl$_3$).
1-{Pentadeca-3,8,13-triyn-1-yl}-2-thiocyanatobenzene (9d)

Thiocyanate 9d was synthesized from compound 19d (258 mg, 0.80 mmol) according GP 3. A mixture of CH$_3$CN/THF (1:2, 4.6 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (n-pentane:EtOAc = 50:1) to obtain the product (37 mg, 135 μmol, 8%) as colorless oil.

R$_f$ = 0.21 (n-pentane:EtOAc = 50:1).

$^1$H-NMR (500 MHz, CDCl$_3$): δ = 1.63 (dp, $J$ = 21.1, 7.0 Hz, 4H), 1.78 (t, $J$ = 2.6 Hz, 3H), 2.14 – 2.29 (m, 8H), 2.49 (tt, $J$ = 7.1, 2.4 Hz, 2H), 2.98 (t, $J$ = 7.2 Hz, 2H), 7.30 – 7.42 (m, 3H), 7.69 (dd, $J$ = 7.8, 1.3 Hz, 1H).

$^{13}$C-NMR (126 MHz, CDCl$_3$): δ = 3.4, 17.8, 17.8, 17.8, 17.9, 20.0, 28.2, 28.5, 33.2, 75.9, 78.3, 78.6, 79.6, 79.9, 81.3, 111.0, 123.9, 128.3, 130.2, 130.9, 132.5, 141.8.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3061, 2937, 2862, 2841, 2156, 1472, 1435, 1337, 1036.

C$_{22}$H$_{23}$NS calcd.: 333.1546, found: 333.1529 (EI-HRMS).
$^{1}$H-NMR (500 MHz, CDCl$_3$).

$^{13}$C-NMR (126 MHz, CDCl$_3$).
Thiocyanate 9e was synthesized from compound 19e (424 mg, 1.62 mmol) according GP 3. A mixture of CH₃CN/THF (1:2, 9.0 ml) was used as solvent. After evaporation, the crude mixture was purified by silica gel column chromatography (n-pentane:EtOAc = 40:1 → 20:1) to obtain the product (37 mg, 135 µmol, 8%) as colorless oil.

Rᵣ = 0.23 (n-pentane:EtOAc = 20:1).

¹H-NMR (300 MHz, CDCl₃): δ = 1.72 (t, J = 1.3 Hz, 3H), 3.88 – 3.92 (m, 2H), 4.15 (t, J = 1.8 Hz, 2H), 4.85 (t, J = 1.8 Hz, 2H), 4.88 – 4.96 (m, 2H), 7.05 – 7.13 (m, 2H), 7.36 (ddd, J = 8.4, 7.4, 1.6 Hz, 1H), 7.59 (dd, J = 8.1, 1.5 Hz, 1H).

¹³C-NMR (75 MHz, CDCl₃): δ = 19.4, 57.0, 57.1, 73.7, 79.8, 84.7, 110.2, 113.1, 113.2, 114.1, 122.9, 129.8, 130.2, 141.2, 154.4.

IR (ATR) ν (cm⁻¹) = 3072, 2923, 2855, 2158, 1582, 1474, 1448, 1360, 1287, 1228, 1130, 1068, 998.

C₁₅H₁₅NO₂S calcd.: 273.0818, found: 273.0820 (EI-HRMS).
\( ^1H\)-NMR (300 MHz, CDCl\(_3\)).

\( ^{13}C\)-NMR (75 MHz, CDCl\(_3\)).
Compound 9f was synthesized according GP3 (alternative B) from substrate 19.2f (1.3 mmol, 341.0 mg). The desired product was obtained after flash column chromatography (n-pentane:EtOAc = 20:1) as a colorless oil (0.10 mmol, 27.6 mg, 8%).

\[
R_f = 0.45 \ (n\text{-}pentane:EtOAc = 10:1).
\]

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 1.75 \ (s, 4H), 3.91 \ (s, 2H), 4.06 - 4.15 \ (m, 2H), 4.69 - 4.84 \ (m, 2H), 4.95 \ (ddd, J=23.1, 2.2, 1.3, 2H), 5.79 - 5.92 \ (m, 2H), 6.93 \ (dd, J=8.3, 1.1, 1H), 7.04 \ (td, J=7.6, 1.2, 1H), 7.30 - 7.37 \ (m, 1H), 7.57 \ (dd, J=7.9, 1.6, 1H).

\(^{13}\)C-NMR (101 MHz, CDCl\(_3\)): \(\delta = 19.5, 65.4, 65.8, 74.4, 110.4, 112.5, 112.6, 113.7, 122.3, 126.7, 129.8, 130.3, 130.6, 141.9, 155.3.

IR (ATR) \(\tilde{\nu} \ (cm^{-1}) = 3074, 3030, 2972, 2918, 2853, 2158, 1582, 1476, 1446, 1297, 1281, 1060, 997.

\(\text{C}_{15}\text{H}_{17}\text{NO}_2\text{S} \quad \text{calcd.:} \ 275.0980, \text{found:} \ 275.0985 \ (\text{GC-HRMS}).

Compound 9f was synthesized to do a cascade reaction with an alkene-alkene system. Unfortunately, the isolation of the desired product was not possible. The GC-MS showed only traces of a new peak with the right mass.
$^{1}H$-NMR (400 MHz, CDCl$_3$).

$^{13}C$-NMR (101 MHz, CDCl$_3$).
1-(2-Bromoethyl)-2-(pent-1-yn-1-yl)benzene (13.1e)

2-(2-(Pent-1-yn-1-yl)phenyl)ethan-1-ol\textsuperscript{133} (339 mg, 1.80 mmol) was converted via the aforementioned general procedure (GP 5) to afford the title compound 13.1d as a slightly yellow oil (382 mg, 1.52 mmol, 85 %).

R\textsubscript{f} = 0.61 (n-pentane).

\textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}): \( \delta = 7.42-7.37 \) (m, 1H), 7.24-7.15 (m, 3H), 3.65-3.58 (m, 2H), 3.31 (t, \( J = 7.9 \) Hz, 2H), 2.43 (t, \( J = 7.0 \) Hz, 2H), 1.66 (s, \( J = 7.3 \) Hz, 2H), 1.07 (t, \( J = 7.3 \) Hz, 3H).

\textsuperscript{13}C-NMR (75 MHz, CDCl\textsubscript{3}): \( \delta = 140.5, 132.4, 129.3, 127.7, 126.9, 123.7, 94.7, 78.6, 38.5, 31.9, 22.3, 21.5, 13.6. \)

IR (ATR) \( \bar{\nu} \) (cm\textsuperscript{-1}) = 3065, 3022, 2963, 2932, 2870, 2232, 1484, 1448, 1214, 1040.

C\textsubscript{13}H\textsubscript{15}Br calcd.: 250.0357, found: 250.0364 (GC-HRMS).

$^{1}H$-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
(6-Thiocyanato-hex-1-yn-1-yl)benzene (3a)

(6-Bromohex-1-yn-1-yl)benzene (550 mg, 2.32 mmol, prepared via GP 5) was converted via the aforementioned general procedure (GP 6) to afford the title compound 3a as a colorless oil (437 mg, 2.03 mmol, 87%).

R_f = 0.50 (n-pentane:EtOAc = 10:1).

^1H-NMR (300 MHz, CDCl_3): δ = 7.43-7.36 (m, 2H), 7.33-7.24 (m, 3H), 3.02 (t, J = 7.2 Hz, 2H), 2.49 (t, J = 6.9 Hz, 2H), 2.09-1.97 (m, 2H), 1.83-1.70 (m, 2H).

^13C-NMR (75 MHz, CDCl_3): δ = 131.5, 128.2, 127.8, 123.5, 112.1, 88.6, 81.6, 33.6, 29.0, 26.8, 18.8.

IR (ATR) ν (cm⁻¹) = 3078, 3056, 2941, 2863, 2230, 2153, 1598, 1489, 1439.

C_{13}H_{13}NS  calcd.: 215.0769, found: 215.0771 (GC-HRMS).
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
2,2-Dimethyl-8-thiocyanatooct-3-yne (3b)

8-Bromo-2,2-dimethyloct-3-yne (prepared via GP 4, used crude) was converted via the aforementioned general procedure (GP 6) to afford the title compound 3b as a colorless oil (19 mg, 0.10 mmol, 10% over two steps).

Rf = 0.31 (n-pentane:EtOAc = 50:1).

1H-NMR (300 MHz, CDCl3): δ = 1.20 (s, 9H), 1.57 – 1.69 (m, 2H), 1.89 – 2.01 (m, 2H), 2.22 (t, J = 6.8 Hz, 2H), 2.97 – 3.03 (m, 2H).

13C-NMR (75 MHz, CDCl3): δ = 18.0, 27.0, 27.3, 28.8, 31.2, 33.6, 77.0, 90.1, 112.1.

IR (ATR) ʋ (cm⁻¹) = 2967, 2866, 2154, 1454, 1362, 1265, 1205, 1064.

$^{1}$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
9-Thiocyano-7-nonen-4-yn (3c)

9-Bromonon-4-yn (450 mg, 2.22 mmol, prepared via GP 4) was converted via the aforementioned general procedure (GP 6) to afford the title compound 3c as a colorless oil (301 mg, 1.66 mmol, 75%).

\( R_f = 0.62 \) (n-pentane:EtOAc = 10:1).

\(^1\text{H-NMR}\) (300 MHz, CDCl\(_3\)): \( \delta = 2.99 \text{ (t, J = 7.3 Hz, 1H)}, 2.23 \text{ (tt, J = 6.8, 2.4 Hz, 1H)}, 2.12 \text{ (tt, J = 7.0, 2.3 Hz, 1H)}, 2.03-1.89 \text{ (m, 1H)}, 1.70-1.59 \text{ (m, 1H)}, 1.51 \text{ (s, J = 7.0 Hz, 1H)}, 0.97 \text{ (t, J = 7.4 Hz, 2H)}.\)

\(^{13}\text{C-NMR}\) (75 MHz, CDCl\(_3\)): \( \delta = 112.2, 81.3, 78.8, 33.7, 28.9, 27.1, 22.4, 20.7, 18.1, 13.5. \)

\( \text{IR (ATR) } \tilde{\nu} \text{ (cm}^{-1}) = 2960, 2934, 2869, 2154, 1455, 1435, 1335. \)

C\(_{10}\)H\(_{15}\)NS \hspace{1em} \text{calcd.: 181.0925, found: 181.0918 (GC-HRMS).}
$^{1}H$-NMR (300 MHz, CDCl$_3$).

$^{13}C$-NMR (75 MHz, CDCl$_3$).
According to a reported procedure\textsuperscript{34}, to a solution of 2-(2-iodophenyl)ethan-1-ol (993 mg, 4.0 mmol, 1.2 equiv.), PdCl\(_2\)(PPh\(_3\))\(_2\) (85 mg, 3 mol%) and Cul (38 mg, 5 mol%) in degassed triethylamine (20 ml) and degassed THF (30 mol) was added a solution of 1-ethynlnaphthalene (7321 mg, 4.8 mmol, 1.2 equiv.) in degassed THF (10 ml). Afterwards, propyne (10.0 ml, 10.0 mmol, 1.0 M in THF, 1.00 equiv.) was added via syringe. After stirring overnight, the reaction mixture was diluted with EtOAc (60 ml) and washed with brine (3 x 60 ml). The organic phase was washed with brine, dried over Na\(_2\)SO\(_4\), filtrated and evaporated. Silica gel column chromatography (n-pentane:EtOAc = 10:1→4:1) gave the desired product 13d (1.08 g, 3.97 mmol, quant.) as brownish solid.

m.p.: 68 °C.

R\(_f\) = 0.27 (n-pentane:EtOAc = 4:1).

\(^1\)H-NMR (300 MHz, CDCl\(_3\)): \(\delta = 1.58\) (s, 1H), 3.23 (t, \(J=6.7\), 2H), 4.01 (t, \(J=6.7\), 2H), 7.22 – 7.34 (m, 3H), 7.44 (dd, \(J=8.3\), 7.1, 1H), 7.49 – 7.62 (m, 2H), 7.63 – 7.68 (m, 1H), 7.75 (dd, \(J=7.1\), 1.2, 1H), 7.80 – 7.89 (m, 2H), 8.41 (ddt, \(J=8.3\), 1.4, 0.8, 1H).

\(^13\)C-NMR (75 MHz, CDCl\(_3\)): \(\delta = 38.2, 62.9, 91.4, 92.7, 120.9, 123.2, 125.3, 126.1, 126.4, 126.6, 126.9, 128.3, 128.6, 128.8, 129.8, 130.5, 132.6, 133.1, 133.2, 140.3.

IR (ATR) \(\tilde{\nu}\) (cm\(^{-1}\)) = 3216, 3052, 2941, 2861, 1578, 1445, 1385, 1031.

C\(_{20}\)H\(_{16}\)O \hspace{1cm} calcd.: 272.1201, found: 272.1224 (GC-HRMS).

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$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
Alcohol **13d** (415 mg, 1.52 mmol) was converted via the aforementioned general procedure (GP 7) to afford the title compound **3d** as a colorless oil (391.0 mg, 1.25 mmol, 82%).

\[ R_f = 0.19 \ (n\text{-}pentane:EtOAc = 20:1). \]

**H-NMR** (300 MHz, CDCl₃): \( \delta = 3.28 – 3.37 \) (m, 2H), \( 3.39 – 3.50 \) (m, 2H), \( 7.29 – 7.35 \) (m, 3H), \( 7.46 \) (dd, \( J=8.3, 7.2 \) (1H), \( 7.53 \) (ddd, \( J=8.2, 6.8, 1.3 \) (1H), \( 7.61 \) (ddd, \( J=8.3, 6.8, 1.4 \) (1H), \( 7.65 – 7.70 \) (m, 1H), \( 7.78 \) (dd, \( J=7.2, 1.2 \) (2H), 8.32 – 8.41 (m, 1H).

**C-NMR** (75 MHz, CDCl₃): \( \delta = 33.9, 35.4, 91.8, 92.2, 112.0, 120.4, 122.9, 125.3, 125.8, 126.5, 127.0, 127.4, 128.4, 128.9, 129.1, 129.6, 130.7, 132.8, 133.0, 133.2, 139.2.

**IR (ATR) \( \nu (cm^{-1}) \) = 3056, 2936, 2850, 2152, 1583, 1484, 1442, 1395.**

\( \text{C}_{21}\text{H}_{15}\text{NS} \) calcd.: 313.0925, found: 313.0917 (GC-HRMS).
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-(Pent-1-yn-1-yl)-2-(2-thiocyanatoethyl)benzene (3e)

1-(2-Bromoethyl)-2-(pent-1-yn-1-yl)benzene (13.1e, 100 mg, 0.40 mmol) was converted via the aforementioned general procedure (GP 6) to afford the title compound 3e as a colorless oil (89 mg, 0.39 mmol, 97%).

Rf = 0.62 (n-pentane:EtOAc = 10:1).

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 7.44$-$7.39$ (m, 1H), 7.30-$7.14$ (m, 3H), 3.31-$3.18$ (m, 4H), 2.45 (t, $J = 7.0$ Hz, 2H), 1.66 (s, $J = 7.3$ Hz, 2H), 1.06 (t, $J = 7.4$ Hz, 3H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 139.2$, 132.6, 129.3, 127.9, 127.2, 123.7, 112.1, 95.3, 78.4, 35.3, 33.9, 22.2, 21.5, 13.6.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3065, 3023, 2963, 2933, 2871, 2232, 2154, 1484, 1447.

C$_{14}$H$_{15}$NS calcd.: 229.0925, found: 229.0909 (GC-HRMS).
\[ ^{1}H\text{-NMR (300 MHz, } CDCl_{3}) \].

\[ ^{13}C\text{-NMR (75 MHz, } CDCl_{3}) \].
(5-Thiocyanatopent-1-yn-1-yl)benzene (3f)

(5-Bromopent-1-yn-1-yl)benzene (prepared via GP 4, used crude) was converted via the aforementioned general procedure (GP 6) to afford the title compound 3f as a pale yellow oil (1.44 g, 7.15 mmol, 40% over two steps).

\[ R_f = 0.48 \text{ (n-pentane:EtOAc = 10:1).} \]

**\(^1\)H-NMR** (300 MHz, CDCl\(_3\)): \( \delta = 2.04 - 2.16 \text{ (m, 2H)}, 2.61 \text{ (t, } J = 6.6 \text{ Hz, 2H)}, 3.11 \text{ (t, } J = 7.0 \text{ Hz, 2H)}, 7.26 - 7.32 \text{ (m, 3H)}, 7.36 - 7.42 \text{ (m, 2H)}.\)

**\(^{13}\)C-NMR** (75 MHz, CDCl\(_3\)): \( \delta = 17.6, 28.4, 32.7, 82.2, 87.0, 111.9, 123.1, 127.9, 128.2, 131.5. \)

**IR (ATR)** \( \tilde{\nu} \text{ (cm}^{-1}) = 3078, 2939, 2838, 2153, 1598, 1489, 1439, 1332, 1283, 1069. \)

\( \text{C}_{12}\text{H}_{11}\text{NS} \quad \text{calcd.: 201.0612, found: 201.0615 (GC-HRMS).} \)
$^{1}H$-NMR (300 MHz, CDCl$_3$).

$^{13}C$-NMR (75 MHz, CDCl$_3$).
(3,3-Dimethyl-5-thiocyanatopent-1-yn-1-yl)benzene (3f')

Compound 3f' was synthesized from 3,3-dimethyl-5-phenylpent-4-yn-1-ol, which was obtained in a 4-step procedure. Before reduction of the ester, the phenyl substituent was introduced by a Sonogashira reaction.

3,3-dimethyl-5-phenylpent-4-yn-1-ol (257 mg, 1.52 mmol) was converted via the aforementioned general procedure (GP 7) to afford the title compound 3f' as a yellow oil (258 mg, 1.12 mmol, 74%).

$R_f = 0.31 \ (n$-pentane:EtOAc = 20:1).

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 1.35 \ (6H), 1.92 - 2.07 \ (2H), 3.11 - 3.21 \ (2H), 7.25 - 7.31 \ (3H), 7.34 - 7.43 \ (2H)$.

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 29.1 \ (2C), 30.4, 31.8, 43.5, 82.0, 94.4, 112.2, 123.1, 127.9, 128.2 \ (2C), 131.5 \ (2C)$.

IR (ATR) $\tilde{\nu} \ (cm^{-1}) = 3058, 2972, 2932, 2869, 2154, 1598, 1483, 1446, 1315, 1242, 1199$.

$C_{14}H_{15}NS \quad$ calcd.: 229.0925, found: 299.0938 (GC-HRMS).

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$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
4-(5-Thiocyanatopent-1-yn-1-yl)benzaldehyde (3g)

4-(5-Hydroxypent-1-yn-1-yl)benzaldehyde\(^\text{36}\) (377 mg, 2.00 mmol) was converted via the aforementioned general procedure (GP 7) to afford the title compound 3g as a yellow solid (93 mg, 0.41 mmol, 20%).

\[ \text{m.p.: 41 °C.} \]
\[ \text{R}_f = 0.37 \text{ (n-pentane:EtOAc = 4:1).} \]
\[ ^1\text{H-NMR (300 MHz, CDCl}_3\text{): } \delta = 2.15 \text{ (p, } J = 6.8 \text{ Hz, 2H), 2.68 (t, } J = 6.7 \text{ Hz, 2H), 3.15 (t, } J = 7.0 \text{ Hz, 2H), 7.51 – 7.56 \text{ (m, 2H), 7.78 – 7.83 (m, 2H), 9.99 (s, 1H).} \]
\[ ^{13}\text{C-NMR (75 MHz, CDCl}_3\text{): } \delta = 17.7, 28.3, 32.7, 81.5, 91.6, 111.7, 129.4, 129.4, 132.0, 135.1, 191.3. \]
\[ \text{IR (ATR) } \tilde{\nu} \text{ (cm}^{-1}) = 3068, 2946, 2843, 2744, 2222, 2147, 1932, 1687, 1599, 1423, 1204, 1162. \]
\[ \text{C}_{13}\text{H}_{11}\text{NOS calcd.: 229.0561, found: 229.0573 (GC-HRMS).} \]

$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1-Methoxy-4-(5-thiocyanatopent-1-yn-1-yl)benzene (3h)

![Chemical Structure](image)

5-(4-Methoxyphenyl)pent-4-yn-1-ol\(^{37}\) (190 mg, 1.00 mmol) was converted via the aforementioned general procedure (GP 7) to afford the title compound 3h as a colorless oil (183 mg, 0.79 mmol, 79%).

R\(_f\) = 0.23 (n-pentane:EtOAc = 20:1).

**\(^1\)H-NMR** (300 MHz, CDCl\(_3\)): \(\delta = 2.05 - 2.15\) (m, 2H), 2.61 (t, \(J = 6.6\) Hz, 2H), 3.14 (t, \(J = 7.0\) Hz, 2H), 3.80 (s, 3H), 6.78 – 6.86 (m, 2H), 7.29 – 7.36 (m, 2H).

**\(^{13}\)C-NMR** (75 MHz, CDCl\(_3\)): \(\delta = 17.7, 28.6, 32.9, 55.2, 82.1, 85.4, 112.0, 113.9, 115.3, 132.9, 159.3\).

**IR (ATR)** \(\tilde{\nu}\) (cm\(^{-1}\)) = 3043, 3003, 2939, 2838, 2153, 1604, 1506, 1453, 1287, 1243, 1174, 1029.

C\(_{13}\)H\(_{13}\)NOS \hspace{1em} calcd.: 231.0718, found: 231.0725 (GC-HRMS).

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$^{1}H$-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
1,3,5-Trimethyl-2-(5-thiocyanatopent-1-yn-1-yl)benzene (3i)

5-Mesitylpent-4-yn-1-ol\textsuperscript{38} (405 mg, 2.00 mmol) was converted via the aforementioned general procedure (GP 7) to afford the title compound 3i as a colorless oil (332 mg, 1.36 mmol, 68%).

$R_f = 0.51$ (n-pentane:EtOAc = 20:1).

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 2.14$ (p, $J = 6.8$ Hz, 2H), 2.26 (s, 3H), 2.35 (s, 6H), 2.72 (t, $J = 6.6$ Hz, 2H), 3.17 (t, $J = 7.0$ Hz, 2H), 6.83 – 6.85 (m, 2H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 18.0$, 21.0, 21.2, 28.8, 32.9, 80.0, 94.5, 111.9, 119.9, 127.5, 137.3, 139.9.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 2917, 2854, 2154, 1609, 1475, 1435, 1341, 1283, 1031.

C$_{15}$H$_{17}$NS calcd.: 243.1082, found: 243.1100 (GC-HRMS).

$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
3-([5-Thiocyanatopent-1-yn-1-yl]pyridine (3j)

5-(Pyridin-3-yl)pent-4-yn-1-ol39 (322 mg, 2.00 mmol) was converted via the aforementioned general procedure (GP 7) to afford the title compound 3j as a yellow oil (247 mg, 1.22 mmol, 61%).

Rf = 0.09 (n-pentane:EtOAc = 4:1).

1H-NMR (300 MHz, CDCl3): δ = 2.15 (p, J = 6.8 Hz, 2H), 2.67 (t, J = 6.7 Hz, 2H), 3.14 (t, J = 7.0 Hz, 2H), 7.23 (ddd, J = 7.8, 4.9, 0.9 Hz, 1H), 7.68 (dt, J = 7.9, 1.9 Hz, 1H), 8.51 (dd, J = 4.9, 1.7 Hz, 1H), 8.63 (dd, J = 2.2, 0.9 Hz, 1H).

13C-NMR (75 MHz, CDCl3): δ = 17.6, 28.3, 32.7, 78.9, 90.7, 111.7, 120.2, 122.8, 138.4, 148.2, 152.1.

IR (ATR) ν (cm⁻¹) = 3034, 2939, 2843, 2231, 2153, 1560, 1475, 1408, 1262, 1020.


$^{1}H$-NMR (300 MHz, CDCl$_3$).

$^{13}C$-NMR (75 MHz, CDCl$_3$).
According to a reported procedure\textsuperscript{40}, to a mixture of 2-(2-hydroxyethyl)phenol (2.24 g, 16.2 mmol, 1.0 equiv.) and K$_2$CO$_3$ (3.36 g, 24.3 mmol, 1.5 equiv.) in acetone (162 ml) was added 1-(bromomethyl)-2-iodobenzene (4.81 g, 16.2 mmol, 1.0 equiv.). The reaction mixture was refluxed for 4 h. After cooling, it was diluted with H$_2$O, extracted with EtOAc (3 x 100 ml), washed with brine and dried over Na$_2$SO$_4$. The solvent was evaporated \textit{in vacuo} and the product was purified by flash column chromatography ($n$-pentane:EtOAc = 20:1 $\rightarrow$ 10:1) to afford a colorless solid (4.73 g, 13.4 mmol, 82%).

\textbf{m.p.:} 98 °C.

\textbf{R$_f$} = 0.25 ($n$-pentane:EtOAc = 4:1).

\textbf{\textsuperscript{1}H-NMR} (300 MHz, CDCl$_3$): $\delta$ = 1.69 (s, 1H), 2.98 (t, $J$=6.5, 2H), 3.87 (q, $J$=6.1, 2H), 5.04 (s, 2H), 6.88 – 6.98 (m, 2H), 6.99 – 7.06 (m, 1H), 7.16 – 7.25 (m, 2H), 7.36 (td, $J$=7.5, 1.3, 1H), 7.45 – 7.51 (m, 1H), 7.86 (dd, $J$=7.9, 1.2, 1H).

\textbf{\textsuperscript{13}C-NMR} (75 MHz, CDCl$_3$): $\delta$ = 34.1, 62.7, 74.0, 97.2, 111.8, 121.1, 127.2, 127.8, 128.4, 128.4, 129.5, 131.0, 139.1, 139.3, 156.4.

\textbf{IR (ATR) $\nu$ (cm$^{-1}$)} = 3304, 3066, 2928, 2861, 1593, 1489, 1440, 1374, 1240, 1044, 1012.

\textbf{C$_{15}$H$_{15}$IO$_2$} calcd.: 354.0117, found: 354.0100 (GC-HRMS).

S192

$^{1}H$-NMR (300 MHz, CDCl$_3$).

$^{13}C$-NMR (75 MHz, CDCl$_3$).
Similar to the synthesis of 11s, compound 13.1k (3.54 g, 10.0 mmol, 1.00 equiv.), PdCl$_2$(PPh$_3$)$_2$ (142 mg, 2 mol%) and Cul (78 mg, 4 mol%) were dissolved in triethylamine (30 ml). Afterwards, propyne (10.0 ml, 10.0 mmol, 1.0 M in THF, 1.00 equiv.) was added via syringe. After stirring overnight, saturated NH$_4$Cl solution was added and the mixture was extracted with Et$_2$O (3 x 100 ml). The combined organic phases were washed with brine, dried over Na$_2$SO$_4$, filtrated and evaporated. Silica gel column chromatography (n-pentane:EtOAc = 4:1) gave the desired product 13.2k (2.42 g, 9.09 mmol, 91%) as brownish solid.

m.p.: 75 °C.
R$_f$ = 0.09 (n-pentane:EtOAc = 10:1).

$^1$H-NMR (300 MHz, CDCl$_3$): δ = 1.75 (t, J=5.8, 1H), 2.05 (s, 3H), 2.97 (t, J=6.5, 2H), 3.86 (q, J=6.3, 2H), 5.23 (s, 2H), 6.86 – 6.97 (m, 2H), 7.14 – 7.33 (m, 4H), 7.40 – 7.49 (m, 2H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): δ = 4.4, 34.2, 62.8, 68.4, 91.2, 111.9, 120.8, 122.3, 126.9, 127.3, 127.4, 127.7, 127.9, 130.9, 132.1, 138.5, 156.8, 1 C (alkyne) covered by CDCl$_3$.

IR (ATR) ν (cm$^{-1}$) = 3343, 3067, 3032, 2920, 2874, 1592, 1492, 1445, 1379, 1241, 1041, 1016.

C$_{18}$H$_{18}$O$_2$ calcd.: 266.1307, found: 266.1286 (GC-HRMS).
$^{1}H$-NMR (300 MHz, CDCl$_3$).

$^{13}C$-NMR (75 MHz, CDCl$_3$).
1-{Prop-1-yn-1-yl}-2-{(2-(2-thiocyanatoethyl)phenoxy)methyl}benzene (3k)

Alcohol 13.2k (1.33 g, 5.00 mmol) was converted via the aforementioned general procedure (GP 7) to afford the title compound 3k as a colorless oil (391.0 mg, 1.27 mmol, 25%).

R_f = 0.24 (n-pentane:EtOAc = 20:1).

^{1}H-NMR (300 MHz, CDCl_3): δ = 2.04 (s, 3H), 2.99 – 3.37 (m, 4H), 5.22 (s, 2H), 6.89 – 6.99 (m, 2H), 7.15 – 7.35 (m, 4H), 7.38 – 7.51 (m, 2H).

^{13}C-NMR (75 MHz, CDCl_3): δ = 4.4, 31.7, 33.6, 68.4, 77.1, 91.2, 111.9, 112.4, 120.8, 122.5, 126.1, 127.1, 127.7, 127.9, 128.7, 130.9, 132.2, 138.2, 156.7.

IR (ATR) ν (cm⁻¹) = 3067, 3032, 2920, 2852, 2153, 1595, 1491, 1449, 1236, 1012.

C_{19}H_{17}NO_{3} calcd.: 307.1031, found: 307.1016 (GC-HRMS).

Compound 3k was synthesized to obtain a ten-membered ring. Unfortunately, the synthesis of such a product was not possible.
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
((5-Thiocyanatopent-1-yn-1-yl)thio)benzene (5e)

![Chemical Structure]

((5-Hydroxypent-1-yn-1-yl)thio)benzene\(^{41}\) (193 mg, 1.00 mmol) was converted via the aforementioned general procedure (GP 7) to afford the title compound 5e as a colorless oil (94 mg, 0.40 mmol, 40%).

\[ R_f = 0.26 \ (n\text{-pentane}:\text{EtOAc} = 20:1). \]

\(^1\)H-NMR (300 MHz, CDCl\(_3\)): \(\delta = 2.08 \ (p, J = 6.8 \text{ Hz}, 2\text{H}), 2.65 \ (t, J = 6.7 \text{ Hz}, 2\text{H}), 3.07 \ (t, J = 7.0 \text{ Hz}, 2\text{H}), 7.17 - 7.25 \ (m, 1\text{H}), 7.29 - 7.41 \ (m, 3\text{H}).\)

\(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): \(\delta = 18.5, 28.3, 32.6, 67.3, 96.5, 111.7, 125.9, 126.4, 129.1, 132.7.\)

IR (ATR) \(\tilde{\nu} \ (\text{cm}^{-1}) = 3061, 2937, 2841, 2152, 1581, 1476, 1436, 1281, 1080, 1022.\)

\( \text{C}_{12}\text{H}_{11}\text{NS}_2 \) calcd.: 233.0333, found: 233.0350 (GC-HRMS).

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$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
((5-Thiocyanatopent-1-yn-1-yl)selanyl)benzene (5f)

\[
\text{SCN} \quad \text{\&}
\]

((5-Hydroxypent-1-yn-1-yl)selanyl)benzene (prepared similar to 3-hydroxy-1-propynyl phenyl sulfide,\textsuperscript{42} 239 mg, 1.00 mmol) was converted via the aforementioned general procedure (GP 7) to afford the title compound 5f as a colorless oil (95 mg, 0.34 mmol, 34%).

\[
R_f = 0.28 \text{ (} n\text{-pentane:EtOAc = 20:1).}
\]

\[
^1H-NMR \text{ (300 MHz, CDCl}_3\text{):} \delta = 2.02 - 2.12 \text{ (m, 2H), 2.65 (t, } J = 6.6 \text{ Hz, 2H), 3.04 - 3.09 \text{ (m, 2H), 7.21 - 7.35 (m, 3H), 7.45 - 7.52 \text{ (m, 2H).}}
\]

\[
^{13}C-NMR \text{ (75 MHz, CDCl}_3\text{):} \delta = 18.7, 28.4, 32.6, 60.3, 101.1, 111.7, 127.0, 128.5, 128.8, 129.4.
\]

IR (ATR) \( \tilde{\nu} \text{ (cm}^{-1}\text{)} = 3056, 2933, 2844, 2152, 1576, 1475, 1436, 1279, 1020.

\[
C_{12}H_{11}NSe \quad \text{calcd.: 280.9777, found: 280.9791 (GC-HRMS).}
\]

\textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}).

\textsuperscript{13}C-NMR (75 MHz, CDCl\textsubscript{3}).
3-(5-Thiocyanatopent-1-yn-1-yl)oxazolidin-2-one (5g)

Tosylate 15g (130 mg, 0.40 mmol, 1.00 equiv.) was dissolved in anhydrous DMF (5 ml) in a sealable tube. After addition of KSCN (300 mg, 3.1 mmol, 7.75 equiv.), the tube was capped and the mixture heated at 100 °C for 5 h. The reaction mixture was cooled to RT and water was added (50 ml). The aqueous phase was extracted with DCM (2 x 50 ml) and the combined organic layers were dried over Na₂SO₄. The solvent was removed in vacuo. After flash column chromatography (n-pentane:EtOAc = 1:1) the title compound was afforded as an orange solid (70 mg, 0.33 mmol, 83%).

\[ R_f = 0.11 \] (n-pentane:EtOAc = 2:1).

\[ \text{H-NMR} \ (300 \text{ MHz, CDCl}_3): \delta = 2.06 \ (p, J = 6.8 \text{ Hz}, 2H), \ 2.55 \ (t, J = 6.7 \text{ Hz}, 2H), \ 3.11 \ (t, J = 7.0 \text{ Hz}, 2H), \ 3.80 - 3.97 \ (m, 2H), \ 4.35 - 4.50 \ (m, 2H). \]

\[ \text{C-NMR} \ (75 \text{ MHz, CDCl}_3): \delta = 16.6, 28.4, 32.5, 46.6, 62.9, 68.3, 71.7, 111.9, 156.4. \]

\[ \text{IR} \ (\text{ATR}) \ \tilde{\nu} \ (\text{cm}^{-1}) = 3519, 2987, 2951, 2929, 2270, 2150, 1759, 1486, 1415, 1303, 1198, 1113, 1030, 965. \]

\[ C_9H_{10}N_2O_2S_2 \] caled.: 210.0463, found: 210.0480 (GC-HRMS).
$^{1}H$-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
11-Thiocyanatoundeca-2,7-diyne (9c)

Undeca-4,9-diyn-1-ol (130 mg, 0.80 mmol) was converted via the aforementioned general procedure (GP 7) to afford the title compound 9c as a colorless oil (36 mg, 0.18 mmol, 22%).

\[ \text{RF} = 0.22 \text{ (n-pentane:EtOAc = 50:1).} \]

\(^1\text{H-NMR}\) (300 MHz, CDCl\(_3\)): \(\delta = 1.58 - 1.70\) (m, 2H), 1.78 (t, \(J = 2.6\) Hz, 3H), 1.99 (pd, \(J = 6.7, 0.5\) Hz, 2H), 2.18 – 2.29 (m, 4H), 2.34 – 2.41 (m, 2H), 3.04 – 3.12 (m, 2H).

\(^{13}\text{C-NMR}\) (75 MHz, CDCl\(_3\)): \(\delta = 3.4, 17.0, 17.8, 17.8, 28.3, 28.7, 32.8, 76.1, 77.7, 78.1, 81.4, 112.0.\)

\(\text{IR (ATR) } \tilde{\nu} \text{ (cm}^{-1}\) = 2936, 2919, 2858, 2843, 2154, 1433, 1347, 1283, 1259.\)

\(\text{C}_{12}\text{H}_{15}\text{NS}\) calcd.: 205.0925, found: 205.0910 (GC-HRMS).
\( ^1H\text{-NMR (600 MHz, CDCl}_3). \)

\( ^13C\text{-NMR (151 MHz, CDCl}_3). \)
(Z)-2-{Benzo[b][1,4]oxathiin-3(2H)-ylidene}propanenitrile (2a)

\[
\text{\includegraphics[width=0.5\textwidth]{image.png}}
\]

Compound 1a (20.3 mg, 100 µmol, 1.00 equiv.) was transformed according to GP CAT1 to obtain product 2a after flash column chromatography (n-pentane:EtOAc = 50:1 → 20:1) as a colorless solid (18.9 mg, 93 µmol, 93%). The reaction time was 4 h.

\textbf{m.p.:} 95 °C.

\textbf{Rf} = 0.14 (n-pentane:EtOAc = 20:1).

\textbf{\textsuperscript{1}H-NMR} (600 MHz, CDCl\textsubscript{3}): \(\delta = 2.03\) (s, 3H), 4.71 (s, 2H), 6.99 – 7.05 (m, 2H), 7.14 (tdd, \(J = 8.0, 1.6, 0.8\) Hz, 1H), 7.17 – 7.19 (m, 1H).

\textbf{\textsuperscript{13}C-NMR} (151 MHz, CDCl\textsubscript{3}): \(\delta = 15.9, 64.5, 99.8, 117.5, 118.2, 118.6, 123.6, 126.3, 127.3, 147.0, 152.2\).

\textbf{IR (ATR)} \(\tilde{\nu}\) (cm\textsuperscript{-1}) = 3078, 3013, 2922, 2855, 2202, 1597, 1572, 1472, 1442, 1260, 1215, 1117, 1033, 1006.

\textbf{C\textsubscript{11}H\textsubscript{9}NOS} calcd.: 203.0405, found: 203.0415 (GC-HRMS).
$^1$H-NMR (600 MHz, CDCl$_3$).

$^{13}$C-NMR (151 MHz, CDCl$_3$).
(2)-2-(Benzo[b][1,4]oxathiin-3(2H)-ylidene)-3,3-dimethylbutanenitrile (2b)

Compound 1b (25.0 mg, 102 µmol, 1.00 equiv.) was transformed according to GP CAT1 to obtain product 2b after flash column chromatography (n-pentane:EtOAc = 40:1) as a colorless solid (23.4 mg, 96 µmol, 94%).

m.p.: 97 °C.

Rf = 0.33 (n-pentane:EtOAc = 20:1).

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta =$ 1.36 (s, 9H), 4.92 (s, 2H), 6.98 – 7.06 (m, 2H), 7.10 – 7.16 (m, 1H), 7.18 (dd, $J =$ 7.7, 1.7 Hz, 1H).

$^{13}$C-NMR (101 MHz, CDCl$_3$): $\delta =$ 31.3, 34.9, 65.3, 115.6, 116.5, 118.2, 119.1, 123.6, 126.2, 127.2, 148.6, 152.3.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3057, 2973, 2938, 2872, 2199, 1579, 1555, 1473, 1443, 1364, 1262, 1225, 1071.

C$_{14}$H$_{15}$NO$\text{s}$ calcd.: 245.0874, found: 245.0884 (GC-HRMS).
$^1$H-NMR (400 MHz, CDCl$_3$).

$^{13}$C-NMR (101 MHz, CDCl$_3$).
Compound 1c (24.0 mg, 105 µmol, 1.00 equiv.) was transformed according to GP CAT1 to obtain product 2c after flash column chromatography (n-pentane:EtOAc = 100:1) as an off-colorless solid (17.0 mg, 74 µmol, 71%).

m.p.: 68 °C.

Rf = 0.22 (n-pentane:EtOAc = 20:1).

$^{1}H$-NMR (500 MHz, CDCl$_3$): $\delta$ = 0.78 – 0.83 (m, 2H), 0.94 – 0.99 (m, 2H), 1.62 (tt, $J$ = 8.2, 5.0 Hz, 1H), 4.89 (s, 2H), 7.00 – 7.04 (m, 2H), 7.14 (td, $J$ = 7.7, 1.6 Hz, 1H), 7.17 (m, 1H).

$^{13}$C-NMR (126 MHz, CDCl$_3$): $\delta$ = 7.3, 10.2, 64.9, 108.0, 115.3, 118.2, 118.6, 123.5, 126.3, 127.3, 147.1, 152.4.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3080, 3004, 2921, 2865, 2203, 1594, 1571, 1468, 1443, 1253, 1216, 122, 1034, 1000.

C$_{13}$H$_{11}$NOS  calcd.: 229.0561, found: 229.0564 (GC-HRMS).
$^1$H-NMR (500 MHz, CDCl$_3$).

$^{13}$C-NMR (126 MHz, CDCl$_3$).

S210
(2)-2-{Benzo[b][1,4]oxathiin-3(2H)-ylidene)-5,5-dimethylhex-3-ynenitrile (2d)

Compound 1d (39.0 mg, 145 μmol, 1.00 equiv.) was transformed according to GP CAT2 to obtain product 2d after flash column chromatography (n-pentane:EtOAc = 100:1) as a brownish solid (18.0 mg, 67 μmol, 46%).

m.p.: 79 °C.

Rf = 0.65 (n-pentane:EtOAc = 20:1).

1H-NMR (500 MHz, CDCl₃): δ = 1.29 (s, 9H), 4.87 (s, 2H), 7.03 – 7.08 (m, 2H), 7.16 – 7.23 (m, 2H).

13C-NMR (126 MHz, CDCl₃): δ = 28.4, 30.5, 66.3, 69.8, 88.2, 107.4, 114.2, 117.1, 118.8, 123.7, 126.5, 128.0, 152.4, 156.7.

IR (ATR) v (cm⁻¹) = 3063, 2969, 2927, 2866, 2242, 1726, 1579, 1542, 1468, 1448, 1214, 1122, 1040.

C₁₆H₁₅NOS  calcd.: 269.0874, found: 269.0897 (GC-HRMS).
$^1$H-NMR (500 MHz, CDCl$_3$).

$^{13}$C-NMR (126 MHz, CDCl$_3$).
(Z)-2-{Benzo[b][1,4]oxathiin-3(2H)-ylidene}-2-phenylacetonitrile (syn-2e)

Compound 1e (27.0 mg, 102 µmol, 1.00 equiv.) was transformed according to GP CAT1 to obtain the compounds syn-2e and anti-2e after flash column chromatography (n-pentane:EtOAc = 100:1) as a mixture (24.5 mg, 92 µmol, 90%). The isomers were separated by HPLC and the ratio of syn/anti (1.0/2.0) was determined by 1H-NMR.

Compound syn-2e was isolated as a colorless solid.

m.p.: 116 °C.

Rf = 0.27 (n-pentane:EtOAc = 20:1).

1H-NMR (300 MHz, CDCl3): δ = 4.79 (s, 2H), 7.01 (dd, J = 8.0, 1.4 Hz, 1H), 7.03 – 7.10 (m, 1H), 7.16 (ddd, J = 8.0, 7.4, 1.7 Hz, 1H), 7.25 – 7.30 (m, 3H), 7.40 – 7.49 (m, 3H).

13C-NMR (151 MHz, CDCl3): δ = 65.0, 106.6, 116.5, 117.9, 118.6, 123.7, 126.4, 127.5, 129.1, 129.1, 129.3, 131.8, 149.4, 152.7.

IR (ATR) ν (cm⁻¹) = 3061, 2956, 2920, 2852, 2199, 1580, 1557, 1470, 1440, 1258, 1221, 1143, 1047, 998.

C₁₆H₁₁NOS calcd.: 265.0561, found: 265.0574 (GC-HRMS).
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (151 MHz, CDCl$_3$).
(E)-2-{Benzo[b][1,4]oxathiin-3(2H)-ylidene}-2-phenylacetonitrile (anti-2e)

Compound anti-2e was isolated as an off-white solid.

m.p.: 115 °C.

Rf = 0.35 (n-pentane:EtOAc = 20:1).

\[^{1}\text{H-NMR}\] (600 MHz, CDCl\textsubscript{3}): \( \delta = 5.06\ (s, 2H), 6.99 - 7.03\ (m, 1H), 7.06\ (dd, J = 8.2, 1.4 Hz, 1H), 7.11\ (dd, J = 8.0, 1.7 Hz, 1H), 7.15 - 7.19\ (m, 1H), 7.40 - 7.44\ (m, 1H), 7.46 - 7.50\ (m, 2H), 7.54 - 7.58\ (m, 2H).

\[^{13}\text{C-NMR}\] (151 MHz, CDCl\textsubscript{3}): \( \delta = 68.4, 105.6, 116.7, 117.5, 118.8, 123.5, 126.2, 127.8, 128.5, 129.1, 129.5, 132.0, 149.3, 153.2.\)

\[^{\text{IR}}\] (ATR) \( \vec{\nu}\ (\text{cm}^{-1}) = 3057, 2923, 2901, 2850, 2198, 1586, 1469, 1441, 1259, 1214, 1157, 1034.\)

\( \text{C}_{16}\text{H}_{11}\text{NOS} \) calcd.: 265.0561, found: 265.0574 (GC-HRMS).
$\text{H-NMR (600 MHz, CDCl}_3\text{).}$

$\text{C-NMR (151 MHz, CDCl}_3\text{).}$
(Z)-2-{Benzo[b][1,4]oxathiin-3(2H)-ylidene}-2-(naphthalen-2-yl)acetonitrile (syn-2f)

Compound 1f (32.0 mg, 101 µmol, 1.00 equiv.) was transformed according to GP CAT1 to obtain the compounds syn-2f and anti-2f after flash column chromatography (n-pentane:EtOAc = 100:1) as a mixture (24.0 mg, 76 µmol, 75%). The isomers were separated by HPLC and the ratio of syn/anti (1.0/2.0) was determined by 1H-NMR. Compound syn-2f was isolated as a colorless solid.

m.p.: 160 °C.

Rf = 0.33 (n-pentane:EtOAc = 20:1).

1H-NMR (600 MHz, CDCl₃): δ = 4.87 (s, 2H), 7.01 (dd, J = 8.0, 1.3 Hz, 1H), 7.08 (ddd, J = 7.9, 7.4, 1.3 Hz, 1H), 7.17 (ddd, J = 8.0, 7.4, 1.6 Hz, 1H), 7.29 (dd, J = 7.9, 1.6 Hz, 1H), 7.41 (dd, J = 8.5, 1.9 Hz, 1H), 7.54 – 7.59 (m, 2H), 7.69 – 7.71 (m, 1H), 7.84 – 7.90 (m, 2H), 7.90 – 7.93 (m, 1H).

13C-NMR (151 MHz, CDCl₃): δ = 65.1, 106.6, 116.6, 117.9, 118.6, 123.7, 125.9, 126.4, 127.1, 127.3, 127.6, 127.8, 128.1, 128.9, 129.0, 129.1, 132.9, 133.1, 149.6, 152.8.

IR (ATR) ν (cm⁻¹) = 3054, 2921, 2852, 2208, 1579, 1552, 1469, 1441, 1263, 1214, 1119, 1048, 1000.

C₂₀H₁₃NOS calcd.: 315.0718, found: 315.0745 (GC-HRMS).
$^1$H-NMR (600 MHz, CDCl$_3$).

$^{13}$C-NMR (151 MHz, CDCl$_3$).
(E)-2-{Benzo[b][1,4]oxathiin-3(2H)-ylidene}-2-(naphthalen-2-yl)acetonitrile (anti-2f)

Compound anti-2f was isolated as an off-white solid.

m.p.: 106 °C.

\[ R_f = 0.42 \ (n\text{-pentane}:\text{EtOAc} = 20:1). \]

\[ ^1H\text{-NMR} \ (600 \text{ MHz, CDCl}_3): \delta = 5.11 \ (s, 2\text{H}), 7.01 \ (\text{td}, \ J = 7.5, 1.3 \text{ Hz}, 1\text{H}), 7.08 \ (\text{dd}, \ J = 8.1, 1.3 \text{ Hz}, 1\text{H}), 7.11 \ (\text{dd}, \ J = 7.8, 1.6 \text{ Hz}, 1\text{H}), 7.17 \ (\text{ddd}, \ J = 8.6, 7.2, 1.5 \text{ Hz}, 1\text{H}), 7.54 – 7.59 \ (\text{m}, 2\text{H}), 7.65 \ (\text{dd}, \ J = 8.5, 1.9 \text{ Hz}, 1\text{H}), 7.86 – 7.91 \ (\text{m}, 2\text{H}), 7.94 \ (\text{d}, \ J = 8.6 \text{ Hz}, 1\text{H}), 8.05 \ (\text{d}, \ J = 1.8 \text{ Hz}, 1\text{H}). \]

\[ ^{13}C\text{-NMR} \ (151 \text{ MHz, CDCl}_3): \delta = 68.5, 105.6, 116.7, 117.5, 118.8, 123.5, 125.3, 126.2, 126.9, 127.4, 127.8, 127.8, 128.3, 128.5, 129.0, 129.3, 133.0, 133.3, 149.5, 153.3. \]

\[ \text{IR (ATR) } \tilde{\nu} \ (\text{cm}^{-1}) = 3051, 3019, 2923, 2900, 2851, 2203, 1579, 1551, 1469, 1439, 1266, 1210, 1145, 1015. \]

\[ \text{C}_{20}\text{H}_{13}\text{NOS} \quad \text{calcd.:} \ 315.0718, \ \text{found:} \ 315.0740 \ (\text{GC-HRMS}). \]
$^1$H-NMR (600 MHz, CDCl$_3$).

$^{13}$C-NMR (151 MHz, CDCl$_3$).

S220
(Z)-2-{Benzo[b][1,4]oxathiin-3(2H)-ylidene}-2-{(4-fluorophenyl)acetonitrile (syn-2g)

Compound 1g (29.0 mg, 102 µmol, 1.00 equiv.) was transformed according to GP CAT1 to obtain the compounds syn-2g and anti-2g after flash column chromatography (n-pentane:EtOAc = 100:1) as a mixture (22.3 mg, 79 µmol, 77%). The isomers were separated by HPLC and the ratio of syn/anti (1.0/1.5) was determined by ¹H-NMR.

Compound syn-2g was isolated as an off-white solid.

M.p.: 108 °C.

Rº = 0.29 (n-pentane:EtOAc = 20:1).

¹H-NMR (500 MHz, CDCl₃): δ = 4.74 (s, 2H), 7.01 (dd, J = 8.0, 1.4 Hz, 1H), 7.04 – 7.10 (m, 1H), 7.11 – 7.20 (m, 3H), 7.23 – 7.30 (m, 3H).

¹³C-NMR (126 MHz, CDCl₃): δ = 64.88, 105.33, 116.29 (d, J = 22.0 Hz), 117.75, 118.63, 123.74, 126.43, 127.63, 127.79, 127.82, 131.04 (d, J = 8.5 Hz), 149.75, 152.64, 163.00 (d, J = 250.8 Hz).

¹⁹F NMR (377 MHz, CDCl₃) δ = -111.15.

IR (ATR) ν (cm⁻¹) = 3063, 2956, 2920, 2853, 2197, 1589, 1555, 1502, 1474, 1444, 1222, 1141, 1042, 1002.

C₁₆H₁₀FNOS   calcd.: 283.0467, found: 283.0486 (GC-HRMS).
$\text{H-NMR (500 MHz, CDCl}_3\text{).}$

$\text{13C-NMR (126 MHz, CDCl}_3\text{).}$
$^{19}$F-NMR (377 MHz, CDCl$_3$).
(E)-2-(Benzo[b][1,4]oxathiin-3(2H)-ylidene)-2-(4-fluorophenyl)acetonitrile (anti-2g)

Compound anti-2g was isolated as an off-white solid.

m.p.: 110 °C.

\( R_f = 0.39 \) (n-pentane:EtOAc = 20:1).

\(^1\)H-NMR (500 MHz, CDCl\(_3\)): \( \delta = 5.04 \) (s, 2H), 7.00 – 7.03 (m, 1H), 7.07 (dd, \( J = 8.1, 1.1 \) Hz, 1H), 7.12 (dd, \( J = 7.9, 1.5 \) Hz, 1H), 7.15 – 7.20 (m, 3H), 7.52 – 7.57 (m, 2H).

\(^{13}\)C-NMR (126 MHz, CDCl\(_3\)): \( \delta = 68.33, 104.49, 116.26 \) (d, \( J = 22.1 \) Hz), 116.50, 117.24, 118.83, 123.55, 126.19, 127.89, 127.93 (d, \( J = 3.4 \) Hz), 130.62 (d, \( J = 8.6 \) Hz), 149.67, 153.14, 162.88 (d, \( J = 250.8 \) Hz).

\(^{19}\)F NMR (471 MHz, CDCl\(_3\)) \( \delta = -110.66 \).

IR (ATR) \( \tilde{\nu} \) (cm\(^{-1}\)) = 3078, 2915, 2852, 2205, 1583, 1553, 1502, 1470, 1441, 1216, 1147, 1039, 1019.

\( \text{C}_{16}\text{H}_{10}\text{FNOS} \) calcd.: 283.0467, found: 283.0488 (GC-HRMS).
$^1$H-NMR (500 MHz, CDCl$_3$).

$^{13}$C-NMR (126 MHz, CDCl$_3$).
$^{19}\text{F-NMR (471 MHz, CDCl}_3\text{).}$
(Z)-2-{Benzo[b][1,4]oxathiin-3(2H)-ylidene}-2-{(4-chlorophenyl)acetonitrile (syn-2h)

Compound 1h (31.0 mg, 103 µmol, 1.00 equiv.) was transformed according to GP CAT1. Purification by flash column chromatography (1\textsuperscript{st}: n-pentane:EtOAc = 60:1, 2\textsuperscript{nd}: n-pentane:DCM 3:1, 1\textsuperscript{st} and 2\textsuperscript{nd} fcc with reversed elution of isomers) lead to compounds syn-2h and anti-2h with a ratio of 1.0/2.0 (Σ = 28.1 mg, 94 µmol, 91%). Compound syn-2h was isolated as a colorless solid.

\textbf{m.p.:} 122 °C.

\textbf{R} = 0.32 (n-pentane:EtOAc = 20:1).

\textbf{\textsuperscript{1}H-NMR} (500 MHz, CDCl\textsubscript{3}): δ = 4.75 (s, 2H), 7.01 – 7.03 (m, 1H), 7.06 – 7.10 (m, 1H), 7.15 – 7.19 (m, 1H), 7.20 – 7.23 (m, 2H), 7.25 – 7.28 (m, 1H), 7.41 – 7.45 (m, 2H).

\textbf{\textsuperscript{13}C-NMR} (126 MHz, CDCl\textsubscript{3}): δ = 64.9, 105.2, 116.2, 117.7, 118.6, 123.8, 126.4, 127.7, 129.4, 130.2, 130.4, 135.5, 150.3, 152.6.

\textbf{IR} (ATR) \bar{\nu} (cm\textsuperscript{-1}) = 3060, 2921, 2851, 2202, 1580, 1551, 1470, 1262, 1218, 1092, 1045, 1008.

\textbf{C}_{16}H_{10}ClNO\textsubscript{S} calcd.: 299.0172, found: 299.0180 (GC-HRMS).
$^{1}$H-NMR (500 MHz, CDCl$_3$).

$^{13}$C-NMR (126 MHz, CDCl$_3$).
(E)-2-{Benzo[b][1,4]oxathiin-3(2H)-ylidene}-2-{4-chlorophenyl}acetonitrile (anti-2h)

![Chemical Structure](image)

Compound **anti-2h** was isolated as an off-white solid.

**m.p.:** 125 °C.

**Rf** = 0.36 (n-pentane:EtOAc = 20:1).

**1H-NMR** (400 MHz, CDCl₃): δ = 5.04 (s, 2H), 6.99 – 7.05 (m, 1H), 7.07 (dd, J = 8.2, 1.3 Hz, 1H), 7.12 (dd, J = 7.8, 1.6 Hz, 1H), 7.15 – 7.21 (m, 1H), 7.43 – 7.54 (m, 4H).

**13C-NMR** (101 MHz, CDCl₃): δ = 68.4, 104.4, 116.3, 117.2, 118.8, 123.6, 126.2, 128.0, 129.4, 129.9, 130.4, 135.4, 150.1, 153.2.

**IR** (ATR) ν (cm⁻¹) = 3078, 2956, 2920, 2852, 2204, 1583, 1549, 1470, 1439, 1260, 1214, 1149, 1093, 1015.

**C₁₆H₁₀ClNOS** calcd.: 299.0172, found: 299.0185 (GC-HRMS).
$^1$H-NMR (400 MHz, CDCl$_3$).

$^{13}$C-NMR (101 MHz, CDCl$_3$).
(Z)-2-{Benzo[b][1,4]oxathiin-3(2H)-ylidene}-2-{o-tolyl}acetonitrile (syn-2i)

Compound 1i (22.0 mg, 79 µmol, 1.00 equiv.) was transformed according to GP CAT1 to obtain the compounds syn-2i and anti-2i after flash column chromatography (n-pentane:EtOAc = 100:1) as a mixture (19.0 mg, 68 µmol, 86%). The isomers were separated by HPLC and the ratio of syn/anti (2.0/1.0) was determined by ¹H-NMR.

Compound syn-2i was isolated as a colorless oil.

Rf = 0.38 (n-pentane:EtOAc = 20:1).

¹H-NMR (400 MHz, CDCl₃): δ = 2.37 (s, 3H), 4.51 (s, 2H), 6.98 (dd, J = 8.0, 1.3 Hz, 1H), 7.06 (td, J = 7.6, 1.4 Hz, 1H), 7.10 (dd, J = 7.5, 1.4 Hz, 1H), 7.12 – 7.17 (m, 1H), 7.22 – 7.36 (m, 4H).

¹³C-NMR (101 MHz, CDCl₃): δ = 19.7, 65.2, 105.5, 115.7, 117.7, 118.7, 123.6, 126.5, 126.5, 127.5, 129.8, 130.2, 130.6, 131.0, 137.3, 150.1, 152.6.

IR (ATR) ν (cm⁻¹) = 3063, 3018, 2917, 2856, 2202, 1583, 1471, 1444, 1261, 1215, 1148, 1045, 1001.

C₁₇H₁₃NOS calcd.: 279.0718, found: 279.0741 (GC-HRMS).
$^1$H-NMR (400 MHz, CDCl$_3$).

$^{13}$C-NMR (101 MHz, CDCl$_3$).
(E)-2-{Benzo[b][1,4]oxathiin-3(2H)-ylidene}-2-(o-tolyl)acetonitrile (anti-2i)

Compound anti-2i was isolated as a colorless oil.

$R_f = 0.40 \text{ (n-pentane:EtOAc = 20:1).}$

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 2.37$ (s, 3H), 5.05 (s, 2H), 6.96 – 7.01 (m, 1H), 7.02 – 7.09 (m, 2H), 7.15 (ddd, $J = 8.2$, 7.1, 1.8 Hz, 1H), 7.27 – 7.40 (m, 4H).

$^{13}$C-NMR (101 MHz, CDCl$_3$): $\delta = 19.3, 67.6, 104.5, 115.8, 117.9, 118.8, 123.5, 126.2, 126.7, 127.7, 129.5, 130.0, 130.7, 131.1, 137.0, 152.0, 152.9.$

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3063, 3020, 2916, 2855, 2201, 1587, 1474, 1444, 1266, 1217, 1154, 1034.

C$_{17}$H$_{13}$NOS calcd.: 279.0718, found: 279.0739 (GC-HRMS).
$^1$H-NMR (400 MHz, CDCl$_3$).

$^{13}$C-NMR (101 MHz, CDCl$_3$).
(Z)-2-{Benzo[b][1,4]oxathiin-3(2H)-ylidene}-2-(m-tolyl)acetonitrile (syn-2j)

![Chemical structure of the compound](image)

Compound 1j (28.0 mg, 100 µmol, 1.00 equiv.) was transformed according to GP CAT1. Purification by flash column chromatography (n-pentane:EtOAc = 60:1) lead to compounds syn-2j and anti-2j with a ratio of 1.0/1.0 (Σ = 23.6 mg, 84 µmol, 84%). Compound syn-2j was isolated as a colorless solid.

**m.p.:** 108 °C.

**Rf** = 0.36 (n-pentane:EtOAc = 20:1).

**1H-NMR** (500 MHz, CDCl3): δ = 2.39 (s, 3H), 4.78 (s, 2H), 7.00 (dd, J = 8.1, 1.3 Hz, 1H), 7.03 – 7.08 (m, 2H), 7.09 – 7.12 (m, 1H), 7.13 – 7.18 (m, 1H), 7.21 – 7.23 (m, 1H), 7.26 (dd, J = 7.8, 1.6 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H).

**13C-NMR** (126 MHz, CDCl3): δ = 21.4, 65.0, 106.7, 116.6, 118.0, 118.6, 123.6, 126.3, 126.4, 127.5, 128.9, 129.6, 130.0, 131.7, 139.0, 149.1, 152.7.

**IR (ATR) v (cm⁻¹):** 3061, 2953, 2919, 2856, 2199, 1582, 1556, 1471, 1443, 1261, 1219, 1138, 1059, 998.

**C₁₇H₁₃NOS** calcd.: 279.0718, found: 279.0734 (GC-HRMS).
**$^{1}$H-NMR (500 MHz, CDCl$_3$).**

**$^{13}$C-NMR (126 MHz, CDCl$_3$).**
(E)-2-{Benzo[b][1,4]oxathiin-3(2H)-yli dine}-2-(m-tolyl)acetonitrile (anti-2)

Compound anti-2j was isolated as a colorless oil.

R_f = 0.45 (n-pentane:EtOAc = 20:1).

^1H-NMR (500 MHz, CDCl_3): δ = 2.42 (s, 3H), 5.05 (s, 2H), 6.98 – 7.03 (m, 1H), 7.06 (dd, J = 8.1, 1.3 Hz, 1H), 7.11 (dd, J = 7.9, 1.6 Hz, 1H), 7.14 – 7.18 (m, 1H), 7.21 – 7.25 (m, 1H), 7.34 – 7.38 (m, 3H).

^13C-NMR (126 MHz, CDCl_3): δ = 21.4, 68.4, 105.8, 116.7, 117.6, 118.8, 123.4, 125.6, 126.2, 127.7, 128.9, 129.1, 130.3, 131.9, 139.0, 149.0, 153.2.

IR (ATR) v (cm^-1) = 3059, 2918, 2857, 2205, 1584, 1473, 1444, 1262, 1219, 1143, 1038.

C_{17}H_{13}NOS calcd.: 279.0718, found: 279.0722 (GC-HRMS).
$^1$H-NMR (500 MHz, CDCl$_3$).

$^{13}$C-NMR (126 MHz, CDCl$_3$).
(Z)-2-{Benzo[b][1,4]oxathiin-3(2H)-ylidene}-2-({p-toly})acetonitrile (syn-2k)

Compound 1k (9.0 mg, 32 µmol, 1.00 equiv.) was transformed according to GP CAT1 to obtain the compounds syn-2k and anti-2k after flash column chromatography (n-pentane:EtOAc = 100:1) as a mixture (6.5 mg, 23 µmol, 72%). The isomers were separated by HPLC and the ratio of syn/anti (1.0/1.7) was determined by $^1$H-NMR.

Compound syn-2k was isolated as a colorless solid.

m.p.: 150 °C.

$R_f$ = 0.34 (n-pentane:EtOAc = 20:1).

$^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ = 2.40 (s, 3H), 4.78 (s, 2H), 7.00 (dd, $J$ = 8.1, 1.3 Hz, 1H), 7.06 (td, $J$ = 7.6, 1.4 Hz, 1H), 7.13 – 7.17 (m, 3H), 7.23 – 7.27 (m, 3H).

$^{13}$C-NMR (126 MHz, CDCl$_3$): $\delta$ = 21.3, 65.0, 106.6, 116.7, 118.0, 118.6, 123.6, 126.4, 127.4, 128.9, 129.0, 129.7, 139.4, 148.5, 152.7.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 2952, 2920, 2851, 2208, 1580, 1555, 1469, 1443, 1262, 1215, 1141, 1118, 1052, 1003.

C$_{17}$H$_{13}$NOS calcd.: 279.0718, found: 279.07280 (GC-HRMS).
\( ^1 \text{H-NMR (500 MHz, CDCl}_3) \). 

\( ^{13} \text{C-NMR (126 MHz, CDCl}_3) \).
(E)-2-{Benzo[b][1,4]oxathiin-3(2H)-ylidene}-2-{(p-toly)acetonitrile (anti-2k)

Compound *anti-2k* was isolated as a colorless solid.

**m.p.:** 88 °C.

\[ R_f = 0.42 \ (n\text{-pentane}:\text{EtOAc} = 20:1). \]

\[ ^1H-NMR \ (500 \text{ MHz, CDCl}_3): \delta = 2.41 \ (s, 3H), 5.05 \ (s, 2H), 6.98 - 7.03 \ (m, 1H), 7.04 - 7.07 \ (m, 1H), 7.11 \ (dd, J = 7.9, 1.5 \text{ Hz, 1H}), 7.14 - 7.18 \ (m, 1H), 7.26 - 7.30 \ (m, 2H), 7.43 - 7.47 \ (m, 2H). \]

\[ ^13C-NMR \ (126 \text{ MHz, CDCl}_3): \delta = 21.4, 68.4, 105.7, 116.7, 117.6, 118.8, 123.4, 126.2, 127.7, 128.4, 129.1, 129.7, 139.7, 148.4, 153.2. \]

\[ \text{IR (ATR) } \tilde{\nu} \ (\text{cm}^{-1}) = 3061, 3022, 2916, 2857, 2203, 1579, 1505, 1469, 1438, 1263, 1209, 1142, 1027. \]

\[ C_{17}H_{13}NO \] calcd.: 279.0718, found: 279.0742 (GC-HRMS).
$\text{H-NMR (500 MHz, CDCl}_3\text{).}$

$\text{C-NMR (126 MHz, CDCl}_3\text{).}$
2-(3-Methyl-2,3-dihydrobenzo[b][1,4]oxathiin-3-yl)acetonitrile (2l)

Compound 1l (20.5 mg, 100 µmol, 1.00 equiv.) was transformed according to GP CAT2 (160 °C, DMF, 6 h) to obtain product 2l after flash column chromatography (n-pentane:EtOAc = 20:1→10:1) as an off-colorless oil (2.1 mg, 10.0 µmol, 10%).

Rf = 0.05 (n-pentane:EtOAc = 10:1).

1H-NMR (300 MHz, CDCl3): δ = 1.7 (t, J=1.1, 3H), 3.4 (s, 2H), 4.7 – 4.8 (m, 1H), 4.8 – 4.9 (m, 1H), 7.0 – 7.2 (m, 4H).

13C-NMR (126 MHz, CDCl3): δ = 22.3, 29.7, 38.1, 111.9, 112.6, 120.9, 124.3, 128.0, 133.9, 134.2, 155.3.

IR (ATR) v (cm⁻¹) = 3186, 3075, 2924, 2854, 2207, 1651, 1600, 1471, 1442, 1344, 1253, 1205, 1135.

C₁₁H₁₁NOS calcd.: 205.0561, found: 205.0558 (GC-HRMS).
\[ ^1H\text{-NMR (300 MHz, CDCl}_3\text{).} \]

\[ ^{13}C\text{-NMR (126 MHz, CDCl}_3\text{).} \]
2-{2,3-Dihydrobenzo[b][1,4]oxathiin-3-yl}-2-phenylacetonitrile (2m)

Compound 1l (244 mg, 0.91 mmol, 1.00 equiv.) was transformed according to GP CAT2 (160 °C, DMF, 6 h) to obtain product 2m after flash column chromatography (n-pentane:EtOAc = 10:1) as a colorless oil (67.0 mg, 0.25 mmol, 27%).

Rf = 0.23 (n-pentane:EtOAc = 10:1).

$^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ = 5.00 (dt, $J$=17.1, 1.5, 1H), 5.09 (m, 1H), 5.26 (dt, $J$=10.3, 1.4, 1H), 6.28 (ddd, $J$=17.0, 10.2, 6.7, 1H), 7.02 (dd, $J$=7.7, 1.6, 1H), 7.07 (t, $J$=7.6, 1H), 7.12 (dd, $J$=7.7, 1.5, 1H), 7.19 – 7.26 (m, 4H), 7.28 – 7.33 (m, 2H).

$^{13}$C-NMR (126 MHz, CDCl$_3$): $\delta$ = 48.5, 116.6, 117.2, 119.8, 123.8, 124.3, 126.7, 126.8, 128.4, 138.5, 141.2, 148.7.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3061, 3027, 2979, 1643, 1469, 1436, 1252, 1233, 997.

C$_{16}$H$_{13}$NOS calcd.: 267.0718, found: 267.0734 (GC-HRMS).
$^1$H-NMR (500 MHz, CDCl$_3$).

$^{13}$C-NMR (126 MHz, CDCl$_3$).
Compound 1n (29.0 mg, 144 µmol, 1.00 equiv.) was transformed according to GP CAT2 (3 h reaction time) to obtain product 2m after flash column chromatography (n-pentane:EtOAc = 100:1) as a yellow solid (25.0 mg, 124 µmol, 86%).

m.p.: 80 °C.

R_f = 0.26 (n-pentane:EtOAc = 20:1).

^1^H-NMR (400 MHz, CDCl_3): δ = 1.98 (t, J = 1.1 Hz, 3H), 2.68 – 2.72 (m, 2H), 2.83 – 2.88 (m, 2H), 7.12 – 7.27 (m, 4H).

^1^3^C-NMR (101 MHz, CDCl_3): δ = 16.5, 28.3, 29.6, 98.2, 118.4, 126.4, 126.5, 127.5, 128.5, 130.6, 135.4, 153.5.

IR (ATR) v (cm^{-1}) = 2960, 2919, 2850, 2196, 1581, 1471, 1438, 1065, 1034, 1004.

C_{12}H_{11}NS \quad \text{calcd.:} \ 201.0612, \ \text{found:} \ 201.0624 \ (\text{GC-HRMS}).
$^1$H-NMR (400 MHz, CDCl$_3$).

$^{13}$C-NMR (101 MHz, CDCl$_3$).
2-(Benzo[b]thien-2-yl)propanenitrile (20)

Compound 1o (19.0 mg, 100 µmol, 1.00 equiv.) was transformed according to GP CAT2 (3 h reaction time) to obtain product 2l after flash column chromatography (n-pentane:EtOAc = 100:1) as a pale yellow solid (14.0 mg, 75 µmol, 75%).

m.p.: 63 °C.
Rf = 0.42 (n-pentane:EtOAc = 20:1).

$^1$H-NMR (600 MHz, CDCl₃): $\delta = 1.79$ (d, $J = 7.3$ Hz, 3H), 4.22 (qd, $J = 7.2$, 1.1 Hz, 1H), 7.31 – 7.39 (m, 3H), 7.74 (dd, $J = 7.5$, 1.5 Hz, 1H), 7.77 – 7.81 (m, 1H).

$^{13}$C-NMR (151 MHz, CDCl₃): $\delta = 21.1$, 27.4, 120.2, 122.3, 122.3, 123.7, 124.8, 124.9, 139.1, 139.4, 139.8.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3055, 2990, 2932, 2241, 1436, 1136, 1058, 967.

C$_{11}$H$_9$NS calcd.: 187.0456, found: 187.0456 (GC-HRMS).
$^1$H-NMR (600 MHz, CDCl$_3$).

$^{13}$C-NMR (151 MHz, CDCl$_3$).
(Z)-2-(2,3-Dihydro-4H-benzo[b][1,4]oxathiepin-4-ylidene)propanenitrile (2p)

Compound 1p (22.0 mg, 100 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (12 h reaction time) to furnish product 2p after flash column chromatography (n-pentane:EtOAc = 20:1) as an off-white solid (12.8 mg, 59 µmol, 59%).

m.p.: 89 °C.

RI = 0.06 (n-pentane:EtOAc = 20:1).

1H-NMR (400 MHz, CDCl3): δ = 2.01 (s, 3H), 2.77 (t, J = 6.1 Hz, 2H), 4.30 (t, J = 6.1 Hz, 2H), 7.11 (dd, J = 7.9, 1.4 Hz, 1H), 7.16 (td, J = 7.5, 1.5 Hz, 1H), 7.33 (td, J = 7.7, 1.7 Hz, 1H), 7.40 (dd, J = 7.7, 1.7 Hz, 1H).

13C-NMR (101 MHz, CDCl3): δ = 16.7, 31.0, 72.9, 99.0, 118.1, 123.2, 125.6, 126.2, 130.3, 131.2, 151.8, 154.9.

IR (ATR) ν (cm⁻¹) = 3055, 2925, 2876, 2203, 1588, 1473, 1440, 1254, 1222, 1032.

C₁₂H₁₁NOS calcd.: 201.0612, found: 201.0624 (GC-HRMS).
$^{1}H$-NMR (400 MHz, CDCl$_3$).

$^{13}$C-NMR (101 MHz, CDCl$_3$).
(2)-2-(Dibenzo[b,f][1,4]oxathiocin-11(6H)-ylidene)propanenitrile (2q)

Compound 1q (28.0 mg, 100 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT2 (alternative B, 6 h reaction time) to furnish product 2q after flash column chromatography (n-pentane:EtOAc = 20:1) as a colorless solid (27.0 mg, 96 µmol, 96%).

m.p.: 141 °C.
Rf = 0.19 (n-pentane:EtOAc = 10:1).

\(^1\)H-NMR (500 MHz, CDCl\(_3\)): \(\delta = 1.75 \) (s, 3H), 5.00 (d, \(J=13.0\), 1H), 5.51 (d, \(J=13.0\), 1H), 6.88 (td, \(J=7.6, 1.4\), 1H), 6.99 – 7.08 (m, 3H), 7.12 – 7.21 (m, 3H), 7.22 – 7.28 (m, 1H).

\(^{13}\)C-NMR (126 MHz, CDCl\(_3\)): \(\delta = 18.2, 75.3, 104.4, 118.3, 122.3, 124.5, 126.9, 127.9, 128.3, 129.0 \) (2 C), 129.8, 131.4, 134.6, 135.1, 154.5, 156.2.

IR (ATR) \(\nu \) (cm\(^{-1}\)) = 3060, 3005, 2923, 2862, 2202, 1579, 1467, 1441, 1208, 1005.

\(\text{C}_{17}\text{H}_{13}\text{NOS} \quad \text{calcd.: } 279.0718, \text{found: } 279.0727 \) (GC-HRMS).
S254
(Z)-2-(6,7-Dihydro-12H-dibenz[b,f][1,4]oxathionin-12-ylidene)propanenitrile (2r)

Compound 1r (28.0 mg, 100 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT2 (alternative B, 6 h reaction time) to furnish product 2r after flash column chromatography (n-pentane:EtOAc = 20:1 → 10:1) as a colorless solid (27.0 mg, 92 µmol, 92%).

m.p.: 207 °C.

R_f = 0.15 (n-pentane:EtOAc = 10:1).

^{1}H-NMR (400 MHz, CDCl_3): δ = 1.75 (s, 3H), 2.59 (dt, J=13.8, 2.0, 1H), 3.17 (ddd, J=13.7, 12.2, 4.3, 1H), 4.12 (ddd, J=12.0, 11.2, 1.9, 1H), 4.73 (ddd, J=11.2, 4.3, 2.1, 1H), 6.68 – 6.75 (m, 2H), 6.90 (dt, J=7.0, 1.3, 1H), 6.99 – 7.10 (m, 4H), 7.19 (dd, J=7.7, 1.7, 1H).

^{13}C-NMR (101 MHz, CDCl_3): δ = 18.3, 35.0, 75.8, 101.4, 118.2, 118.4, 122.1, 122.7, 127.1, 128.3, 129.1, 129.4, 130.6, 134.1, 134.9, 137.0, 157.3, 160.5.

IR (ATR) ν (cm^{-1}) = 3065, 3018, 2963, 2950, 2923, 2854, 2210, 1586, 1466, 1442, 1274, 1220, 1030, 995.

C_{18}H_{15}NOS calcd.: 293.0874, found: 293.0893 (GC-HRMS).
$^{1}H$-NMR (400 MHz, CDCl$_3$).

$^{13}C$-NMR (101 MHz, CDCl$_3$).
3-Methylbenzo[b]thiophene-2-carbonitrile (2s)

Compound 1s (17.3 mg, 100 µmol, 1.00 equiv.) was transformed according to GP CAT1 (31 h reaction time) to obtain product 2s after flash column chromatography (n-pentane:EtOAc = 50:1 → 20:1) as a colorless solid (3.0 mg, 17 µmol, 17%).

m.p.: 84 °C.

Rf = 0.58 (n-pentane:EtOAc = 20:1).

$^1$H-NMR (500 MHz, CDCl$_3$): $\delta = 2.79$ (s, 3H), 7.40 (ddd, $J = 8.4$, 7.2, 1.3 Hz, 1H), 7.48 (ddd, $J = 8.1$, 7.3, 1.1 Hz, 1H), 7.77 – 7.79 (m, 1H), 7.85 (dt, $J = 8.1$, 1.0 Hz, 1H).

$^{13}$C-NMR (126 MHz, CDCl$_3$): $\delta = 15.7$, 105.4, 114.2, 121.9, 122.3, 125.5, 125.8, 137.4, 137.9, 153.9.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 2921, 2853, 2217, 1527, 1431, 1380, 1181, 1019.

C$_{10}$H$_7$NS calcd.: 173.0299, found: 173.0298 (GC-HRMS).
S258

$^{1}H$-NMR (500 MHz, CDCl$_3$).

$^{13}$C-NMR (126 MHz, CDCl$_3$).
(E)-3-Ethylidene-2,3-dihydrobenzo[b][1,4]oxathiine (2t)

Compound 1a (20.3 mg, 100 µmol, 1.00 equiv.) was transformed according to GP CAT1 (ligand: [Me₃PH][BF₄], 1.0 equiv.) to obtain product 2t after flash column chromatography (n-pentane:EtOAc = 100:1) as a colorless oil (8.0 mg, 45 µmol, 45%).

Rf = 0.79 (n-pentane:EtOAc = 20:1).

¹H-NMR (500 MHz, CDCl₃): δ = 1.79 – 1.82 (m, 3H), 4.54 (t, J = 1.0 Hz, 2H), 5.64 – 5.69 (m, 1H), 6.88 – 6.94 (m, 2H), 6.99 – 7.03 (m, 1H), 7.12 (dd, J = 7.6, 1.6 Hz, 1H).

¹³C-NMR (126 MHz, CDCl₃): δ = 14.0, 70.2, 118.6, 119.3, 120.9, 122.4, 125.6, 126.5, 127.2, 153.1.

IR (ATR) ν (cm⁻¹) = 3064, 2970, 2908, 2853, 1727, 1648, 1472, 1439, 1212, 1033, 994.

C₁₀H₁₀OS calcd.: 178.0452, found: 178.0451 (GC-HRMS).
$^1\text{H-NMR (500 MHz, CDCl}_3\text{)}.\,$

$^{13}\text{C-NMR (126 MHz, CDCl}_3\text{)}.\,$
(Z)-2-Phenyl-2-(tetrahydro-2H-thiopyran-2-ylidene)acetonitrile (syn-4a)

![Image of compound syn-4a]

Compound 4a (21.5 mg, 100 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (14 h reaction time) to furnish product syn-4a and anti-4a (Σ = 19.1 mg, 89 µmol, 89%, ratio 8.0/1.0) which were separated by flash column chromatography (n-pentane:EtOAc = 100:1).

Product syn-4a was obtained as a colorless oil.

Rf = 0.28 (n-pentane:EtOAc = 20:1).

\[ ^1H-NMR \text{ (500 MHz, CDCl}_3\text{): } \delta = 1.65 - 1.72 \text{ (m, 1H), 1.95 - 2.03 \text{ (m, 1H), 2.60 - 2.65 \text{ (m, 1H), 2.93 - 2.98 \text{ (m, 1H), 7.27 - 7.30 \text{ (m, 1H), 7.31 - 7.35 \text{ (m, 1H), 7.36 - 7.40 \text{ (m, 1H).}}}}\]

\[ ^13C-NMR \text{ (126 MHz, CDCl}_3\text{): } \delta = 24.1, 24.4, 29.6, 30.1, 108.7, 118.1, 128.3, 128.7, 129.2, 133.4, 156.9. \]

IR (ATR) \[ \tilde{\nu} \text{ (cm}^{-1}\text{)} = 3056, 2933, 2857, 2200, 1551, 1440, 1238, 1101, 963. \]

C\text{_{13}H_{13}NS} \text{ calcd.: 215.0769, found: 215.0797 (GC-HRMS).}
$^1$H-NMR (500 MHz, CDCl$_3$).

$^{13}$C-NMR (126 MHz, CDCl$_3$).
(E)-2-Phenyl-2-(tetrahydro-2H-thiopyran-2-ylidene)acetonitrile (anti-4a)

Product anti-4a was obtained as a colorless oil.

Rf = 0.22 (n-pentane:EtOAc = 20:1).

$^1$H-NMR (500 MHz, CDCl$_3$): $\delta = 1.85 - 1.92$ (m, 2H), 1.97 – 2.02 (m, 2H), 2.74 – 2.80 (m, 2H), 2.97 – 3.04 (m, 2H), 7.31 – 7.36 (m, 1H), 7.37 – 7.42 (m, 2H), 7.43 – 7.45 (m, 2H).

$^{13}$C-NMR (126 MHz, CDCl$_3$): $\delta = 23.0, 23.7, 28.6, 32.7, 106.9, 118.2, 128.5, 128.5, 129.1, 133.4, 157.9$.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3056, 2934, 2859, 2198, 1551, 1442, 1269, 1121, 965.

C$_{13}$H$_{13}$NS calcd.: 215.0769, found: 215.0787 (GC-HRMS).
$^{1} \text{H-NMR}$ (500 MHz, CDCl$_3$).

$^{13} \text{C-NMR}$ (126 MHz, CDCl$_3$).
(Z)-3,3-Dimethyl-2-(tetrahydro-2H-thiopyran-2-ylidene)butanenitrile (4b)

Compound 3b (20.0 mg, 102 µmol, 1.00 equiv.) was transformed according to GP CAT2 (3 h reaction time) to obtain product 4b after flash column chromatography (n-pentane:EtOAc = 50:1) as a slight yellow oil (19.8 mg, 101 µmol, 99%).

Rf = 0.62 (n-pentane:EtOAc = 10:1).

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 1.30$ (s, 9H), 1.74 – 1.80 (m, 2H), 1.91 – 2.02 (m, 2H), 2.75 – 2.81 (m, 2H), 2.84 – 2.92 (m, 2H).

$^{13}$C-NMR (101 MHz, CDCl$_3$): $\delta = 24.2, 24.5, 30.0, 31.0, 31.1, 34.2, 128.4, 129.0, 155.6$.

IR (ATR) $\tilde{\nu} \ (cm^{-1}) = 2967, 2935, 2869, 2197, 1617, 1550, 1450, 1248, 1189, 1093, 964$.

C$_{11}$H$_{17}$NS calcd.: 195.1082, found: 195.1089 (GC-HRMS).
$^{1}H$-NMR (400 MHz, CDCl$_3$).

$^{13}$C-NMR (101 MHz, CDCl$_3$).
(Z)-2-(Tetrahydro-2H-thiopyran-2-ylidene)pentanenitrile (4c)

Compound 3c (30.0 mg, 165 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (14 h reaction time) to furnish product 4c after flash column chromatography (n-pentane:EtOAc = 100:1) as a colorless oil (14.1 mg, 78 µmol, 47%).

$R_f = 0.60$ (n-pentane:EtOAc = 20:1).

$^1$H-NMR (500 MHz, CDCl$_3$): $\delta = 0.94$ (t, $J = 7.4$ Hz, 3H), 1.56 (h, $J = 7.4$ Hz, 2H), 1.69 – 1.77 (m, 2H), 1.92 – 2.01 (m, 2H), 2.21 – 2.28 (m, 2H), 2.53 – 2.57 (m, 2H), 2.81 – 2.87 (m, 2H).

$^{13}$C-NMR (126 MHz, CDCl$_3$): $\delta = 13.3, 21.8, 24.6, 25.1, 29.4, 29.9, 31.8, 109.0, 118.5, 152.8$.

IR (ATR) $\tilde{v}$ (cm$^{-1}$) = 2959, 2932, 2869, 2202, 1577, 1456, 1293, 1257, 1239, 1063, 969.

$C_{10}H_{15}NS$ calcd.: 181.0925, found: 181.0926 (GC-HRMS).
^1^H-NMR (500 MHz, CDCl\textsubscript{3}).

^1^3^C-NMR (126 MHz, CDCl\textsubscript{3}).
(Z)-2-(Isothiochroman-1-ylidene)-2-(naphthalen-1-yl)acetonitrile (4d)

\[ \text{\includegraphics[width=0.5\textwidth]{chemical_structure.png}} \]

Compound 3d (31.3 mg, 100 \( \mu \)mol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (3 h reaction time) to furnish product 4d after flash column chromatography (n-pentane:EtOAc = 10:1) as a yellow solid (20.0 mg, 64 \( \mu \)mol, 64%).

\textbf{m.p.:} 152 °C.

\textbf{R}_f = 0.15 (n-pentane:EtOAc = 10:1).

\textbf{\textsuperscript{1}H-NMR} (300 MHz, CDCl\textsubscript{3}): 6 = 2.98 – 3.20 (m, 4H), 6.54 (dd, 6 = 8.0, 1.3, 1H), 6.63 (td, 6 = 7.6, 1.4, 1H), 7.08 (td, 6 = 7.4, 1.4, 1H), 7.14 – 7.23 (m, 2H), 7.31 (dd, 6 = 8.2, 7.2, 1H), 7.44 – 7.53 (m, 2H), 7.75 – 7.82 (m, 1H), 7.83 – 7.89 (m, 1H), 7.92 – 8.00 (m, 1H).

\textbf{\textsuperscript{13}C-NMR} (101 MHz, CDCl\textsubscript{3}): 6 = 28.3, 32.9, 103.7, 118.5, 124.6, 125.5, 126.3, 126.3, 127.0, 128.2, 128.6, 128.6, 128.9, 129.2, 129.8, 131.3, 131.3, 132.1, 133.8, 138.4, 153.3.

\textbf{IR (ATR) \( \tilde{\nu} \) (cm\textsuperscript{-1})} = 3058, 3025, 2930, 2902, 2841, 2196, 1593, 1542, 1504, 1473, 1430.

\textbf{C\textsubscript{21}H\textsubscript{15}NS} calcd.: 313.0925, found: 313.0915 (GC-HRMS).
$\text{H-NMR (400 MHz, CDCl}_3\text{).}$

$\text{C-NMR (101 MHz, CDCl}_3\text{).}$
(Z)-2-(Isothiochroman-1-ylidene)pentanenitrile (4e)

Compound 3e (30.0 mg, 131 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (14 h reaction time) to furnish product 4e after flash column chromatography (n-pentane:EtOAc = 100:1) as a colorless oil (21.3 mg, 93 µmol, 71%).

R<sub>f</sub> = 0.32 (n-pentane:EtOAc = 20:1).

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ = 0.90 (td, J = 7.3, 1.1 Hz, 3H), 1.62 – 1.72 (m, 2H), 2.41 – 2.46 (m, 2H), 2.97 (s, 4H), 7.23 – 7.27 (m, 2H), 7.31 – 7.39 (m, 2H).

<sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>): δ = 13.4, 22.1, 28.9, 32.5, 33.7, 107.9, 118.6, 126.6, 127.6, 128.2, 129.7, 132.3, 138.8, 148.0.

IR (ATR) ν (~cm<sup>−1</sup>) = 2964, 2932, 2870, 2198, 1561, 1446, 1281, 1236, 1069, 931.

C<sub>14</sub>H<sub>15</sub>NS calcd.: 229.0925, found: 229.0950 (GC-HRMS).
$^1$H-NMR (500 MHz, CDCl$_3$).

$^{13}$C-NMR (126 MHz, CDCl$_3$).
(Z)-2-(Dihydrothiophen-2(3H)-ylidene)-2-phenylacetonitrile (4f)

Compound 3f (30.0 mg, 149 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (14 h reaction time) to furnish product 4f after flash column chromatography (n-pentane:EtOAc = 100:1) as a slightly yellow oil (27.2 mg, 135 µmol, 91%).

\[ \text{Rf} = 0.43 \ (n\text{-pentane:EtOAc} = 20:1). \]

\(^1\text{H-NMR} \ (400 \text{ MHz, CDCl}_3): \delta = 2.19 \ (p, J = 6.6 \text{ Hz, } 2\text{H}), 2.89 \ (t, J = 6.8 \text{ Hz, } 2\text{H}), 3.26 \ (t, J = 6.4 \text{ Hz, } 2\text{H}), 7.26 - 7.41 \ (m, 5\text{H}). \]

\(^13\text{C-NMR} \ (101 \text{ MHz, CDCl}_3): \delta = 30.7, 34.8, 36.8, 100.7, 118.8, 127.7, 127.9, 128.6, 134.5, 167.2. \]

\( \text{IR (ATR) } \tilde{\nu} \ (\text{cm}^{-1}) = 2967, 2937, 2864, 2195, 1557, 1489, 1437, 1156, 1082, 993. \]

\( \text{C}_{12}\text{H}_{11}\text{NS} \quad \text{calcd.: } 201.0612, \text{ found: } 201.0616 \ (\text{GC-HRMS}). \)
$^1$H-NMR (400 MHz, CDCl$_3$).

$^{13}$C-NMR (101 MHz, CDCl$_3$).
(Z)-2-(3,3-Dimethyldihydrothiophen-2(3H)-ylidene)-2-phenylacetonitrile (4f')

![Chemical Structure]

Compound 3f' (23.0 mg, 100 μmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (1 h reaction time, 120 °C) to furnish product 4f' after flash column chromatography (n-pentane:EtOAc = 10:1) as an off-colorless solid (22.0 mg, 96 μmol, 96%).

m.p.: 119 °C.

Rf = 0.16 (n-pentane:EtOAc = 20:1).

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 1.01 (s, 6H), 2.05 (t, $J$=6.5, 2H), 3.12 (t, $J$=6.5, 2H), 7.25 – 7.30 (m, 2H), 7.36 (dd, $J$=5.0, 1.9, 3H).

$^{13}$C-NMR (101 MHz, CDCl$_3$): $\delta$ = 26.5 (2 C), 29.7, 47.9, 48.3, 100.3, 119.3, 128.5 (2 C), 128.6, 130.1 (2 C), 133.8, 173.2.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3055, 2965, 2926, 2864, 2187, 1562, 1446, 1231, 1150, 989.

C$_{14}$H$_{15}$NS  calcd.: 229.0925, found: 229.0900 (GC-HRMS).
$^{1}H$-NMR (400 MHz, CDCl$_{3}$).

$^{13}$C-NMR (101 MHz, CDCl$_{3}$).
(2)-2-(Dihydrothiophen-2(3H)-ylidene)-2-(4-formylphenyl)acetonitrile (4g)

Compound 3g (23.0 mg, 100 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (3 h reaction time) to furnish product 4g after flash column chromatography (n-pentane:EtOAc = 10:1 → 5:1) as an orange solid (13.0 mg, 57 µmol, 57%).

m.p.: 96 °C.

Rf = 0.63 (n-pentane:EtOAc = 1:1).

1H-NMR (500 MHz, CDCl3): δ = 2.27 (p, J = 6.7 Hz, 2H), 3.25 (t, J = 7.0 Hz, 2H), 3.33 (t, J = 6.4 Hz, 2H), 7.78 – 7.81 (m, 2H), 7.90 – 7.94 (m, 2H), 10.01 (s, 1H).

13C-NMR (126 MHz, CDCl3): δ = 28.6, 37.2, 41.0, 100.1, 118.2, 127.8, 130.0, 135.1, 140.2, 168.7, 191.3.

IR (ATR) ν (cm⁻¹) = 2921, 2868, 2774, 2200, 1690, 1599, 1540, 1393, 1304, 1249, 1212, 1167, 1006.

C₁₃H₁₁NOS calcd.: 229.0561, found: 229.0559 (GC-HRMS).
S278
(Z)-2-(Dihydrothiophen-2(3H)-ylidene)-2-(4-methoxyphenyl)acetonitrile (4h)

Compound 3h (23.2 mg, 100 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (3 h reaction time) to furnish product 4h after flash column chromatography (n-pentane:EtOAc = 20:1 → 5:1) as an orange oil (18.0 mg, 76 µmol, 76%).

R_f = 0.67 (n-pentane:EtOAc = 1:1).

^1H-NMR (600 MHz, CDCl_3): δ = 2.18 (p, J = 6.6 Hz, 2H), 2.86 (t, J = 6.9 Hz, 2H), 3.24 (t, J = 6.5 Hz, 2H), 3.82 (s, 3H), 6.87 – 6.92 (m, 2H), 7.24 – 7.29 (m, 2H).

^13C-NMR (151 MHz, CDCl_3): δ = 30.7, 34.7, 36.7, 55.3, 100.3, 114.0, 119.0, 127.1, 129.1, 159.0, 165.4.

IR (ATR) ν (cm⁻¹) = 2935, 2837, 2199, 1571, 1506, 1460, 1246, 1176, 1027, 995.

C_{13}H_{13}NOS calcd.: 231.0718, found: 231.0734 (GC-HRMS).
$^1$H-NMR (600 MHz, CDCl$_3$).

$^{13}$C-NMR (151 MHz, CDCl$_3$).
(Z)-2-(Dihydrothiophen-2(3H)-ylidene)-2-mesitylacetonitrile (4i)

Compound 3i (24.4 mg, 100 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (3 h reaction time) to furnish product 4i after flash column chromatography ($n$-pentane:EtOAc = 10:1) as a colorless solid (16.5 mg, 68 µmol, 68%).

m.p.: 95 °C.

$R_f = 0.23$ ($n$-pentane:EtOAc = 20:1).

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 2.11$ (p, $J = 6.6$ Hz, 2H), 2.21 (s, 6H), 2.27 (s, 3H), 2.34 (t, $J = 6.9$ Hz, 2H), 3.26 (t, $J = 6.4$ Hz, 2H), 6.89 (d, $J = 1.1$ Hz, 2H).

$^{13}$C-NMR (101 MHz, CDCl$_3$): $\delta = 19.8, 21.0, 30.0, 35.5, 36.1, 98.2, 117.9, 128.6, 130.4, 136.9, 138.4, 167.5$.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 2969, 2919, 2857, 2193, 1580, 1440, 1375, 1088, 1000.

C$_{15}$H$_{17}$NS calcld.: 243.1082, found: 243.1096 (GC-HRMS).
\[ ^1\text{H-NMR} \text{ (400 MHz, CDCl}_3\text{).} \]

\[ ^{13}\text{C-NMR (101 MHz, CDCl}_3\text{).} \]
(Z)-2-(Dihydrothiophen-2(3H)-ylidene)-2-(pyridin-3-yl)acetonitrile (4j)

Compound 3j (20.3 mg, 100 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (3 h reaction time) to furnish product 4j after flash column chromatography (n-pentane:EtOAc = 4:1→1:1) as a colorless solid (16.5 mg, 68 µmol, 68%).

m.p.: 26 °C.

Rf = 0.08 (n-pentane:EtOAc = 1:1).

H-NMR (600 MHz, CDCl3): δ = 2.35 (p, J = 6.7 Hz, 2H), 3.05 (t, J = 6.8 Hz, 2H), 3.37 (t, J = 6.5 Hz, 2H), 7.87 (dd, J = 8.2, 5.4 Hz, 1H), 8.32 (ddd, J = 8.3, 2.2, 1.2 Hz, 1H), 8.72 (d, J = 5.4 Hz, 1H), 8.98 (s, 1H).

C-NMR (151 MHz, CDCl3): δ = 31.0, 35.6, 37.6, 94.1, 117.0, 126.5, 134.2, 141.0, 141.6, 141.7, 175.9.

IR (ATR) ν (cm⁻¹) = 3076, 3042, 2948, 2208, 1776, 1670, 1554, 1471, 1121.

$\text{H-NMR (600 MHz, CDCl}_3\text{).}$

$\text{C-NMR (151 MHz, CDCl}_3\text{).}$
2-Phenyl-4,5-dihydrothiophene-3-carbonitrile (4k)

\[
\begin{align*}
\text{S} & \quad \text{Ph} \\
\text{C} & \quad \text{N} \\
\end{align*}
\]

Compound 3j (30.0 mg, 160 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (120 h reaction time) to furnish product 4j after flash column chromatography (n-pentane:EtOAc = 100:1) as a slightly yellow oil (10.0 mg, 53 µmol, 33%).

\[R_f = 0.40 \text{ (n-pentane:EtOAc = 20:1)}.\]

\[\text{H-NMR} \ (500 \text{ MHz, CDCl}_3): \delta = 3.26 \text{ (td, } J = 8.7, 1.0 \text{ Hz, } 2\text{H}), 3.39 – 3.44 \text{ (m, } 2\text{H}), 7.40 – 7.46 \text{ (m, } 3\text{H}), 7.71 – 7.74 \text{ (m, } 2\text{H}).\]

\[\text{C-NMR} \ (126 \text{ MHz, CDCl}_3): \delta = 32.0, 38.7, 97.3, 116.9, 125.8, 127.9, 128.9, 130.8, 131.4, 161.1.\]

\[\text{IR (ATR)} \ \tilde{\nu} \ (\text{cm}^{-1}) = 3057, 2926, 2846, 2199, 1592, 1567, 1489, 1443, 1244, 1172, 1077.\]

\[\text{C}_{11}\text{H}_9\text{NS} \quad \text{calcd.: 187.0456, found: 187.0453 (GC-HRMS)}.\]
$\text{H-NMR (500 MHz, CDCl}_3\text{).}$

$\text{C-NMR (126 MHz, CDCl}_3\text{).}$
(E)-2-{Benzo[b][1,4]oxathiin-3(2H)-ylidene}-2-{ tert-butyldimethylsilyl}acetonitrile (6a)

Compound 5a (35.0 mg, 119 µmol, 1.00 equiv.) was transformed according to GP CAT2 (3 h reaction time) to obtain product 6a after flash column chromatography (n-pentane:DCM = 4:1) as a colorless solid (19.0 mg, 62 µmol, 54%).

m.p.: 57 °C.

R_f = 0.41 (n-pentane:EtOAc = 20:1).

^1H-NMR (300 MHz, CDCl_3): δ = 0.37 (s, 6H), 0.99 (s, 9H), 4.70 (s, 2H), 6.99 – 7.07 (m, 2H), 7.12 – 7.22 (m, 2H).

^13C-NMR (76 MHz, CDCl_3): δ = -3.9, 18.6, 26.3, 68.2, 102.8, 118.2, 118.3, 118.8, 123.6, 126.2, 127.5, 152.5, 162.8.

IR (ATR) ṽ (cm⁻¹) = 2959, 2929, 2883, 2856, 2187, 1533, 1469, 1258, 1216, 1157, 1044, 1003.

C_{16}H_{21}NOSSi calcd.: 303.1113, found: 303.1130 (GC-HRMS).
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (76 MHz, CDCl$_3$).
(E)-2-{4H-Benzo[d][1,3]dithiin-2-ylidene}-2-(phenylthio)acetonitrile (6b)

Compound 5b (32.0 mg, 102 µmol, 1.00 equiv.) was transformed according to GP CAT1 (3 h reaction time) to obtain product 6b after flash column chromatography (n-pentane:EtOAc = 50:1) as a yellow oil (26.0 mg, 83 µmol, 81%).

R_f = 0.12 (n-pentane:EtOAc = 20:1).

^1H-NMR (400 MHz, CDCl_3): δ = 4.00 (s, 2H), 7.23 - 7.40 (m, 8H), 7.49 - 7.54 (m, 1H).

^13C-NMR (101 MHz, CDCl_3): δ = 35.6, 91.8, 116.6, 127.5, 127.8, 128.7, 129.0, 129.3, 129.4, 129.5, 131.7, 133.0, 136.0, 167.1.

IR (ATR) ν (cm⁻¹) = 3058, 2919, 2852, 2193, 1576, 1467, 1446, 1410, 1070, 1022, 941.

C_{16}H_{11}NS_3 calcd.: 313.0054, found: 313.0042 (GC-HRMS).
$^1$H-NMR (400 MHz, CDCl$_3$).

$^{13}$C-NMR (101 MHz, CDCl$_3$).
2-(Benzo[d][1,3]dithiol-2-ylidene)propanenitrile (6c)

![Chemical structure](image)

Compound 5c (21.0 mg, 102 µmol, 1.00 equiv.) was transformed according to GP CAT1 (3 h reaction time) to obtain product 6c after flash column chromatography (n-pentane:EtOAc = 100:1) as an off-white solid (13.0 mg, 63 µmol, 62%).

**m.p.:** 71 °C.

**Rf =** 0.22 (n-pentane:EtOAc = 20:1).

**1H-NMR** (500 MHz, CDCl3): δ = 1.94 (s, 3H), 7.19 – 7.25 (m, 2H), 7.33 – 7.36 (m, 2H).

**13C-NMR** (126 MHz, CDCl3): δ = 18.9, 88.1, 119.0, 122.1, 122.1, 126.2, 126.7, 135.2, 135.6, 154.3.

**IR (ATR) v ~ (~ cm⁻¹) =** 3057, 2921, 2851, 2193, 1571, 1542, 1436, 1232, 1120, 1034, 945.

**C₁₀H₇NS₂** calcd.: 205.0020, found: 205.0025 (GC-HRMS).
$^1$H-NMR (500 MHz, CDCl$_3$).

$^{13}$C-NMR (126 MHz, CDCl$_3$).
(2)-2-{4H-benzo[e][1,3]thiaselenin-2-ylidene}-2-(tert-butyldimethylsilyl)acetonitrile (6d)

Compound 5d (26.0 mg, 70 µmol, 1.00 equiv.) was transformed according to GP CAT1 (5 h reaction time) to obtain product 6d after flash column chromatography (n-pentane:EtOAc = 100:1) as a colorless solid (17.3 mg, 47 µmol, 67%).

m.p.: 134 °C.

Rf = 0.31 (n-pentane:EtOAc = 20:1).

1H-NMR (600 MHz, CDCl3): δ = 0.37 (s, 6H), 0.99 (s, 9H), 3.99 (s, 2H), 7.31 (td, J = 7.5, 1.6 Hz, 1H), 7.36 (td, J = 7.5, 1.4 Hz, 1H), 7.40 (dd, J = 7.5, 1.5 Hz, 1H), 7.53 (dd, J = 7.6, 1.3 Hz, 1H).

13C-NMR (151 MHz, CDCl3): δ = -4.1, 19.6, 26.8, 29.7, 103.1, 119.6, 126.9, 128.3, 128.7, 130.1, 134.4, 137.0, 166.7.

IR (ATR) ν (cm⁻¹) = 2933, 2886, 2854, 2184, 1455, 1245, 1134, 1062.

C16H21NSSeSi calcd.: 367.0329, found: 367.0341 (GC-HRMS).
$^{1}H$-NMR (600 MHz, CDCl$_3$).

$^{13}$C-NMR (151 MHz, CDCl$_3$).
(E)-2-(Dihydrothiophen-2(3H)-ylidene)-2-(phenylthio)acetonitrile (6e)

```
\begin{center}
\includegraphics[width=0.2\textwidth]{molecule.png}
\end{center}
```

Compound 5e (23.4 mg, 100 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (3 h reaction time) to furnish product 6e after flash column chromatography (n-pentane:EtOAc = 20:1 → 10:1) as an orange-brown oil (16.7 mg, 71 µmol, 71%).

\[\text{R}_{\text{f}} = 0.13 \text{ (n-pentane:EtOAc = 20:1).}\]

\[\text{\textsuperscript{1}H-NMR} \text{ (500 MHz, CDCl}_3\text{): } \delta = 2.24 (p, J = 6.8 \text{ Hz}, 2H), 3.02 (t, J = 7.0 \text{ Hz}, 2H), 3.33 (t, J = 6.4 \text{ Hz}, 2H), 7.21 – 7.35 (m, 5H).\]

\[\text{\textsuperscript{13}C-NMR} \text{ (126 MHz, CDCl}_3\text{): } \delta = 29.7, 36.8, 38.0, 88.4, 117.6, 127.0, 128.1, 129.4, 134.5, 178.7.\]

\[\text{IR (ATR) } \tilde{\nu} \text{ (cm}^{-1}\text{) = 3056, 2933, 2859, 2201, 1539, 1475, 1437, 1266, 1131, 1073, 1001.}\]

\[\text{C}_{12}\text{H}_{11}\text{NS}_2 \quad \text{calcd.: 233.0333, found: 233.0347 (GC-HRMS).}\]
$\text{H-NMR (500 MHz, CDCl}_3$). 

$\text{C-NMR (126 MHz, CDCl}_3$).
(E)-2-(Dihydrothiophen-2(3H)-ylidene)-2-(phenylselanyl)acetonitrile (6f)

\[ \text{\begin{tikzpicture} \node[above] at (0,0) {\text{S}}; \node[above right] at (0.5,0.5) {\text{CN}}; \node[above right] at (0.5,-0.5) {\text{Se}}; \node[below right] at (1,0) {\text{H}}; \end{tikzpicture}} \]

Compound 5f (30.0 mg, 107 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (3 h reaction time) to furnish product 6f after flash column chromatography (n-pentane:EtOAc = 50:1 → 20:1) as a yellow oil (13.0 mg, 46 µmol, 43%).

\[ R_f = 0.10 \text{ (n-pentane:EtOAc = 20:1).} \]

\[ ^1H\text{-NMR} \text{ (500 MHz, CDCl}_3\text{):} \delta = 2.23 (p, J = 6.7 \text{ Hz, 2H}), 2.98 (t, J = 7.0 \text{ Hz, 2H}), 3.35 (t, J = 6.5 \text{ Hz, 2H}), 7.27 – 7.34 (m, 3H), 7.43 – 7.47 (m, 2H). \]

\[ ^{13}C\text{-NMR} \text{ (126 MHz, CDCl}_3\text{):} \delta = 29.7, 37.0, 39.7, 81.3, 118.4, 127.8, 129.6, 130.0, 131.4, 176.9. \]

\[ \text{IR (ATR) } \tilde{\nu} \text{ (cm}^{-1}\text{)} = 3056, 2934, 2860, 2195, 1543, 1472, 1432, 1403, 1263, 1226, 1117, 1094, 1009. \]

\[ \text{C}_{12}\text{H}_{11}\text{NSSe} \quad \text{calcd.: 280.9777, found: 280.9789 (GC-HRMS).} \]
$^1$H-NMR (500 MHz, CDCl$_3$).

$^{13}$C-NMR (126 MHz, CDCl$_3$).
Compound 5g (21.0 mg, 100 µmol, 1.00 equiv.) was reacted according to the conditions of GP CAT3 (3 h reaction time) to furnish product 6g after flash column chromatography (n-pentane:EtOAc = 1:1) as a pale red solid (17 mg, 81 µmol, 81%).

**m.p.:** 110 °C.

**Rf** = 0.14 (n-pentane:EtOAc = 1:1).

$^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ = 2.22 (p, $J$ = 6.8 Hz, 2H), 2.85 (t, $J$ = 7.0 Hz, 2H), 3.27 (t, $J$ = 6.4 Hz, 2H), 3.75 – 3.82 (m, 2H), 4.42 – 4.49 (m, 2H).

$^{13}$C-NMR (126 MHz, CDCl$_3$): $\delta$ = 29.7, 35.9, 36.0, 45.3, 62.4, 95.1, 114.5, 155.5, 169.7.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3055, 2984, 2949, 2913, 2201, 1749, 1594, 1405, 1278, 1212, 1148, 1035, 982.

C$_9$H$_{10}$N$_2$O$_2$S  

$^1$H-NMR (500 MHz, CDCl$_3$).

$^{13}$C-NMR (126 MHz, CDCl$_3$).
(Z)-2-Ethyl-3-(phenylthio)pent-2-enenitrile (syn-8a)

Phenyl thiocyanate\textsuperscript{43} (68.0 mg, 500 \mu mol, 1.00 equiv.) and 3-hexyne (82.0 mg, 114 \mu l, 1.0 mmol, 2.0 equiv.) were reacted according to the conditions of GP CAT4 to furnish the products \textit{syn}-8a and \textit{anti}-8a after flash column chromatography (\textit{n}-pentane:EtOAc = 100:1) in a combined yield of 80\%. \textit{syn}-8a was obtained as a yellow oil (46.5 mg, 214 \mu mol).

\textbf{R}f = 0.32 (\textit{n}-pentane:EtOAc = 20:1).

\textbf{\textsuperscript{1}H-NMR} (400 MHz, CDCl\textsubscript{3}): \(\delta = 0.98 (t, J=7.5, 3H), 1.21 (t, J=7.5, 3H), 2.22 (q, J=7.5, 2H), 2.35 (q, J=7.5, 2H), 7.31 – 7.37 (m, 3H), 7.39 – 7.45 (m, 2H).

\textbf{\textsuperscript{13}C-NMR} (101 MHz, CDCl\textsubscript{3}): \(\delta = 13.1, 13.2, 24.5, 24.9, 114.7, 118.1, 128.5, 129.2 \text{ (2 C)}, 131.5, 133.2 \text{ (2 C)}, 155.6.

\textbf{IR} (ATR) \(\tilde{\nu} \text{ (cm}^{-1}) = 2974, 2933, 2877, 2206, 1577, 1466, 1450, 1058, 1025.

\textbf{\textsuperscript{13}C\textsubscript{13}H\textsubscript{15}NS} \text{ calcd.: 217.0925, found: 217.0937 (GC-HRMS).}

$^1$H-NMR (400 MHz, CDCl$_3$).

$^{13}$C-NMR (101 MHz, CDCl$_3$).
(E)-2-Ethyl-3-(phenylthio)pent-2-enenitrile (*anti*-8a)

![Chemical Structure](image)

*anti*-8a was obtained as a yellow oil (40.5 mg, 186 µmol).

\[ R_f = 0.50 \text{ (n-pentane:EtOAc = 20:1).} \]

\[ ^{1}H\-\text{NMR} \text{ (400 MHz, CDCl}_3\text{): } \delta = 1.01 \text{ (t, } J=7.4, \text{ 3H), 1.20 (t, } J=7.5, \text{ 3H), 2.41 (q, } J=7.4, \text{ 2H), 2.48 (q, } J=7.5, \text{ 2H), 7.35 – 7.39 (m, 3H), 7.40 – 7.44 (m, 2H).} \]

\[ ^{13}C\-\text{NMR} \text{ (101 MHz, CDCl}_3\text{): } \delta = 12.4, 13.8, 24.7, 28.5, 111.4, 117.9, 128.9, 129.3 \text{ (2 C), 130.4, 134.0 (2 C), 158.3.} \]

\[ \text{IR (ATR) } \tilde{\nu} \text{ (cm}^{-1}\text{) = 2972, 2933, 2875, 2204, 1575, 1450, 1058, 1025.} \]

\[ \text{C}_{13}\text{H}_{15}\text{NS} \text{ calcd.: 217.0925, found: 217.0939 (GC-HRMS).} \]
$^{1}H$-NMR (400 MHz, CDCl$_3$).

$^{13}$C-NMR (101 MHz, CDCl$_3$).
(Z)-3-(Benzylthio)-2-ethylpent-2-enenitrile (8b)

Benzyl thiocyanate (75.0 mg, 500 µmol, 1.00 equiv.) and 3-hexyne (82.0 mg, 114 µl, 1.0 mmol, 2.0 equiv.) were reacted according to the conditions of GP CAT4 to furnish 8b after flash column chromatography (n-pentane:EtOAc = 100:1 → 50:1) as a yellow oil (50.0 mg, 220 µmol, 44%).

\[ \text{Rf} = 0.26 \ (n\text{-pentane}:\text{EtOAc} = 20:1). \]

\[ \begin{align*}
^{1}H\text{-NMR} \ (400 \text{ MHz, CDCl}_3): & \quad \delta = 1.04 (t, J=7.5, 3H), 1.09 (t, J=7.5, 3H), 2.24 (q, J=7.5, 2H), 2.33 (q, J=7.5, 2H), 4.06 (s, 2H), 7.20 - 7.36 (m, 5H). \\
^{13}C\text{-NMR} \ (101 \text{ MHz, CDCl}_3): & \quad \delta = 12.9, 13.0, 24.3, 25.6, 36.9, 114.8, 118.2, 127.4, 128.5 (2 \text{ C}), 128.8 (2 \text{ C}), 136.4, 155.1.
\end{align*} \]

\[ \text{IR} \ (\text{ATR}) \ \tilde{\nu} \ (\text{cm}^{-1}) = 3061, 3029, 2973, 2933, 2877, 2204, 1574, 1454, 1059, 1038. \]

\[ \text{C}_{14}\text{H}_{17}\text{NS} \quad \text{calcd.:} \ 231.1082, \ \text{found:} \ 231.1094 \ (\text{GC-HRMS}). \]
$\text{H-NMR (400 MHz, CDCl}_3\text{).}$

$\text{C-NMR (101 MHz, CDCl}_3\text{).}$
(Z)-3-(Butylthio)-2-ethylpent-2-enenitrile (8c)

\[
\begin{array}{c}
\text{S} \\
\text{CN}
\end{array}
\]

n-Butyl thiocyanate (58.0 mg, 61.0 µl, 500 µmol, 1.00 equiv.) and 3-hexyne (82.0 mg, 114 µl, 1.0 mmol, 2.0 equiv.) were reacted according to the conditions of GP CAT4 to furnish 8c after flash column chromatography (n-pentane:EtOAc = 50:1) as a colorless oil (89.0 mg, 450 µmol, 90%).

Rf = 0.35 (n-pentane:EtOAc = 20:1).

\(^1\text{H-NMR}\) (500 MHz, CDCl\(_3\)): δ = 0.93 (t, J=7.4, 3H), 1.12 (t, J=7.5, 3H), 1.16 (t, J=7.5, 3H), 1.39 – 1.48 (m, 2H), 1.52 – 1.67 (m, 2H), 2.30 (q, J=7.6, 2H), 2.40 (q, J=7.6, 2H), 2.74 – 2.85 (m, 2H).

\(^{13}\text{C-NMR}\) (126 MHz, CDCl\(_3\)): δ = 13.1, 13.2, 13.5, 21.7, 24.2, 24.7, 31.5, 31.6, 112.6, 118.3, 156.1.

\text{IR}\ (\text{ATR}) \ \bar{\nu} (\text{cm}^{-1}) = 2966, 2932, 2872, 2204, 1574, 1459, 1376, 1217, 1054.

\text{C}_{11}\text{H}_{19}\text{NS} \quad \text{calcd.:} \ 197.1238, \ \text{found:} \ 197.1242 \ (\text{GC-HRMS}).
$^1$H-NMR (500 MHz, CDCl$_3$).

$^{13}$C-NMR (126 MHz, CDCl$_3$).

S308
(Z)-2-Methyl-3-phenyl-3-(phenylthio)acrylonitrile (α-Ph-8d)

Phenyl thiocyanate (68.0 mg, 500 µmol, 1.00 equiv.) and 1-phenyl-1-propyne (116.0 mg, 124 µl, 1.0 mmol, 2.0 equiv.) were reacted according to the conditions of GP CAT4 to furnish the products α-Ph-8d and β-Ph-8d after flash column chromatography (n-pentane:EtOAc = 100:1) in a combined yield of 88%. α-Ph-8d was obtained as a colorless oil (82.5 mg, 330 µmol).

Rf = 0.29 (n-pentane:EtOAc = 20:1).

^1H-NMR (400 MHz, CDCl3): δ = 1.94 (s, 3H), 6.98 – 7.24 (m, 10H).

^13C-NMR (101 MHz, CDCl3): δ = 19.0, 107.4, 118.9, 128.1 (3 C), 128.6 (2 C), 128.9, 129.2 (2 C), 131.2, 133.1 (2 C), 134.9, 154.0.

IR (ATR) v (cm\(^{-1}\)) = 3058, 2954, 2921, 2857, 2206, 1575, 1479, 1439, 1074, 911.

C\(_{16}\)H\(_{13}\)NS calcd.: 251.0769, found: 251.0789 (GC-HRMS).
$^{1}H$-NMR (400 MHz, CDCl$_{3}$).

$^{13}C$-NMR (101 MHz, CDCl$_{3}$).
(Z)-2-Phenyl-3-(phenylthio)but-2-enenitrile (β-Ph-8d)

β-Ph-8d was obtained as a colorless oil (27.5 mg, 110 µmol).

\[ R_f = 0.30 \text{ (n-pentane:EtOAc} = 20:1). \]

\( ^1H-NMR \) (400 MHz, CDCl\(_3\)): \( \delta = 1.91 \text{ (s, 3H), 7.31 \text{ – 7.45 (m, 8H), 7.53 \text{ – 7.59 (m, 2H).}} \)

\( ^13C-NMR \) (101 MHz, CDCl\(_3\)): \( \delta = 20.4, 109.8, 117.8, 128.5, 128.7 \text{ (2 C), 129.1 (2 C), 129.4 (2 C), 129.5, 130.1, 134.0, 134.9 (2 C), 155.1.} \)

\( \text{IR (ATR) } \tilde{\nu} \text{ (cm}^{-1} \text{) = 3059, 2921, 2851, 2204, 1560, 1478, 1436, 1137.} \)

\( C_{16}H_{13}NS \) calcd.: 251.0769, found: 251.0781 (GC-HRMS).
$\text{H-NMR (400 MHz, CDCl}_3\text{).}$

$\text{C-NMR (101 MHz, CDCl}_3\text{).}$
(E)-3-Phenyl-3-(phenylthio)-2-(trimethylsilyl)acrylonitrile (8e)

Phenyl thiocyanate (68.0 mg, 500 µmol, 1.00 equiv.) and 1-(trimethylsilyl)-1-propyne (174.0 mg, 195 µl, 1.0 mmol, 2.0 equiv.) were reacted according to the conditions of GP CAT4 to furnish the products 8e and 8e' after flash column chromatography (n-pentane:EtOAc = 100:1). 8e was obtained as a yellow solid (28.0 mg, 90 µmol).

m.p.: 82 °C.

R_f = 0.34 (n-pentane:EtOAc = 20:1).

^1H-NMR (300 MHz, CDCl_3): δ = 0.00 (s, 9H), 7.01 – 7.26 (m, 10H).

^13C-NMR (75 MHz, CDCl_3): δ = -0.4 (3 C), 108.6, 119.0, 127.6 (2 C), 128.6 (2 C), 128.7, 129.0, 129.1 (2 C), 130.5, 135.0 (2 C), 136.8, 170.8.

IR (ATR) ν (cm⁻¹) = 3061, 2973, 2956, 2898, 2192, 1523, 1476, 1442, 1251, 1225, 1070.

C_{18}H_{19}NSSF_i calcd.: 309.1008, found: 309.1027 (GC-HRMS).
$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
(Z)-3-Phenyl-3-(phenylthio)acrylonitrile (8e')

8e' was obtained as a yellow oil (95.5 mg, 400 µmol).

R<sub>f</sub> = 0.20 (n-pentane:EtOAc = 20:1).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = 5.64 (s, 1H), 7.08 – 7.20 (m, 3H), 7.20 – 7.33 (m, 5H), 7.39 – 7.49 (m, 2H).

<sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 97.2, 116.3, 128.2, 128.3 (2 C), 128.5 (2 C), 129.0 (2 C), 130.4, 131.2, 132.4 (2 C), 136.1, 161.3.

IR (ATR) ν (cm<sup>-1</sup>) = 3053, 2923, 2853, 2209, 1557, 1478, 1440, 1180.

C<sub>15</sub>H<sub>11</sub>NS calcd.: 237.0612, found: 237.0620 (GC-HRMS).
$^1$H-NMR (400 MHz, CDCl$_3$).

$^{13}$C-NMR (101 MHz, CDCl$_3$).
(Z)-2-Phenyl-2-(2-(Z)-thiochroman-2-ylidene)cyclopentylidene)acetonitrile (10a)

Compound 9a (20.0 mg, 61 µmol, 1.00 equiv.) was transformed according to GP CAT2 (110 °C, DMF, 3 h) to obtain product 10a after flash column chromatography (n-pentane:Et₂O = 10:1) as a yellow solid (19.0 mg, 43 µmol, 70%).

m.p.: 60-70 °C.

Rᵣ = 0.20 (n-pentane:EtOAc = 20:1).

¹H-NMR (500 MHz, CDCl₃): δ = 1.82 (p, J = 7.5 Hz, 2H), 2.55 (ddt, J = 8.2, 7.0, 1.5 Hz, 2H), 2.64 (t, J = 7.5 Hz, 2H), 2.75 – 2.78 (m, 2H), 2.92 – 2.96 (m, 2H), 7.09 – 7.19 (m, 3H), 7.21 – 7.24 (m, 1H), 7.32 – 7.37 (m, 1H), 7.38 – 7.44 (m, 2H), 7.49 – 7.52 (m, 2H).

¹H-NMR (400 MHz, CD₂Cl₂): δ = 1.81 (p, J = 7.5 Hz, 2H), 2.55 (ddt, J = 8.1, 6.8, 1.4 Hz, 2H), 2.62 (t, J = 7.5 Hz, 2H), 2.75 – 2.79 (m, 2H), 2.91 – 2.95 (m, 2H), 7.09 – 7.17 (m, 2H), 7.18 – 7.23 (m, 2H), 7.33 – 7.39 (m, 1H), 7.39 – 7.45 (m, 2H), 7.47 – 7.52 (m, 2H).

¹³C-NMR (101 MHz, CD₂Cl₂): δ = 22.7, 30.5, 30.6, 32.1, 34.9, 108.9, 119.2, 126.2, 127.0, 127.4, 128.7, 128.7, 128.8, 129.3, 133.8, 133.9, 135.4, 135.6, 137.4, 159.0.

IR (ATR) ~v (cm⁻¹) = 3057, 2953, 2905, 2843, 2200, 1549, 1473, 1437, 1264, 1123, 1064, 1008, 956.

C₂₂H₁₉NS calcd.: 329.1238, found: 329.1224 (GC-HRMS).
$\text{H-NMR (500 MHz, CDCl}_3\text{).}$

$\text{H-NMR (400 MHz, CD}_2\text{Cl}_2\text{).}$
$^{13}$C-NMR (101 MHz, CD$_2$Cl$_2$).
(Z)-2-{(Z)-Thiochroman-2-ylidene)cyclopentylidene}propanenitrile (10b)

Compound 9b (14.0 mg, 52 µmol, 1.00 equiv.) was transformed according to GP CAT2 (160 °C, PhMe, 3 h) to obtain product 10b after flash column chromatography (n-pentane:EtOAc = 50:1→20:1) as a pale yellow solid (9.3 mg, 34.5 µmol, 66%).

m.p.: 103 °C.
Rf = 0.21 (n-pentane:EtOAc = 20:1).

$^1$H-NMR (500 MHz, CDCl3): δ = 1.80 (p, J = 7.6 Hz, 2H), 2.06 (s, 3H), 2.44 – 2.52 (m, 4H), 2.71 – 2.75 (m, 2H), 2.88 – 2.91 (m, 2H), 7.07 – 7.11 (m, 1H), 7.12 – 7.16 (m, 2H), 7.23 – 7.25 (m, 1H).

$^{13}$C-NMR (126 MHz, CDCl3): δ = 18.8, 21.6, 30.3, 31.5, 31.6, 31.8, 101.6, 120.3, 125.7, 126.8, 126.9, 128.2, 132.6, 132.8, 133.5, 136.8, 157.3.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3067, 2968, 2913, 2886, 2850, 2195, 1572, 1466, 1433, 1059, 1022.

C$_{17}$H$_{17}$NS calcd.: 267.1082, found: 267.1092 (GC-HRMS).
$^1$H-NMR (500 MHz, CDCl$_3$).

$^{13}$C-NMR (126 MHz, CDCl$_3$).
(Z)-2-((Z)-2-(Dihydrothiophen-2(3H)-ylidene)cyclopentylidene)propanenitrile (10c)

Compound 9c (26.0 mg, 126 µmol, 1.00 equiv.) was transformed according to GP CAT2 (160 °C, PhMe, 3 h) to obtain product 10c after flash column chromatography (n-pentane:EtOAc = 50:1 → 20:1) as a colorless oil (3.9 mg, 19.0 µmol, 15%).

Rf = 0.37 (n-pentane:EtOAc = 20:1).

$^1$H-NMR (500 MHz, CDCl$_3$): δ = 1.76 – 1.84 (m, 2H), 1.96 (s, 3H), 2.11 (p, J = 6.6 Hz, 2H), 2.39 (tt, J = 7.6, 2.1 Hz, 2H), 2.44 (ddq, J = 8.2, 7.3, 1.2 Hz, 2H), 2.70 (tt, J = 6.8, 2.1 Hz, 2H), 3.09 (t, J = 6.4 Hz, 2H).

$^{13}$C-NMR (126 MHz, CD$_2$Cl$_2$): δ = 18.5, 21.7, 30.9, 32.3, 33.6, 34.1, 38.8, 96.7, 121.6, 127.0, 145.9, 158.8.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 2947, 2861, 2198, 1587, 1434, 1197, 1018, 988.

C$_{12}$H$_{15}$NS calcd.: 205.0925, found: 205.0930 (GC-HRMS).
$^1$H-NMR (500 MHz, CDCl$_3$).

$^{13}$C-NMR (126 MHz, CDCl$_3$).
\((Z)-2-([Z]-2'-(Z)-thiochroman-2-ylidene)-[1,1'-bi(cyclopentylidene)]-2-ylidene)propanenitrile (Z,Z,Z-10d) and 
\((Z)-2-([E]-2'-(Z)-thiochroman-2-ylidene)-[1,1'-bi(cyclopentylidene)]-2-ylidene)propanenitrile (Z,E,Z-10d)

Compound 9d (36.0 mg, 108 µmol, 1.00 equiv.) was transformed according to GP CAT2 (110 °C, DMF, 5 h)
to obtain products \(Z,Z,Z-10d\) and \(Z,E,Z-10d\) as isomeric mixture after flash column chromatography
\((n\text{-pentane}:\text{EtOAc} = 100:1\rightarrow 50:1)\) as a sticky mass (18.3 mg, 55.0 µmol, 51%).
Compound \(Z,E,Z-10d\) was crystallized as yellow solid.

\[\text{m.p.: 119-126 °C.}\]
\[\text{R}_f = 0.41/0.52 \ (n\text{-pentane}:\text{EtOAc} = 20:1).\]
\[^1H\text{-NMR} \ (600 \text{ MHz, CDCl}_3): \delta = 1.73 \ (s, 2H), 1.78 – 1.91 \ (m, 2H), 1.99 \ (t, J = 1.5 \text{ Hz, 3H}), 2.38 – 2.52 \ (m, 6H), 2.54 – 2.66 \ (m, 2H), 2.68 \ (t, J = 6.2 \text{ Hz, 2H}), 2.83 – 2.86 \ (m, 2H), 7.03 – 7.07 \ (m, 1H), 7.10 – 7.13 \ (m, 2H), 7.15 – 7.17 \ (m, 1H).\]
\[^{13}C\text{-NMR (Isomer 1, 151 MHz, CDCl}_3): \delta = 18.4, 21.9, 22.2, 30.2, 30.9, 31.8, 31.9, 33.2, 34.1, 98.3, 119.9, 125.2, 125.4, 126.5, 126.6, 128.3, 133.5, 134.2, 135.2, 137.1, 139.2, 158.6.\]
\[^{13}C\text{-NMR (Isomer 2, 151 MHz, CDCl}_3): \delta = 18.4, 23.3, 23.4, 29.9, 30.3, 30.6, 31.2, 36.0, 36.6, 100.4, 120.8, 125.0, 126.3, 126.8, 128.4, 129.1, 133.7, 133.8, 134.3, 136.2, 142.1, 160.1.\]
\[^\text{IR (ATR) } \tilde{\nu} \ (\text{cm}^{-1}) = 3060, 2924, 2850, 2199, 1559, 1469, 1432, 1204, 1119, 1065, 965.\]
\(\text{C}_{22}\text{H}_{23}\text{NS} \quad \text{calcd.: 333.1551, found: 333.1576 (GC-HRMS).}\)
$^{1}H$-NMR (600 MHz, CDCl$_3$).

$^{13}C$-NMR (126 MHz, CDCl$_3$).

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$^{13}$C-NMR (126 MHz, CDCl$_3$).
(E)-2-{4-[Benzo[b][1,4]oxathiin-3(2H)-ylidene]-3-methyltetrahydrofuran-3-yl}acetonitrile (11)

Compound 9e (32.0 mg, 117 µmol, 1.00 equiv.) was transformed according to GP CAT2 (6.5 h reaction time, DMF, 110 °C) to obtain product 11 after flash column chromatography (n-pentane:EtOAc = 20:1→10:1) as a yellow oil (7.2 mg, 26.7 µmol, 23%).

R_f = 0.75 (n-pentane:EtOAc = 1:1).

^1H-NMR (400 MHz, CDCl_3): δ = 1.55 (s, 3H), 2.76 (d, J = 16.9 Hz, 1H), 3.00 (dd, J = 16.8, 1.3 Hz, 1H), 3.67 (dd, J = 9.2, 1.1 Hz, 1H), 4.03 (d, J = 9.2 Hz, 1H), 4.38 – 4.43 (m, 1H), 4.48 (d, J = 9.4 Hz, 1H), 4.51 (d, J = 8.8 Hz, 1H), 4.63 (d, J = 13.3 Hz, 1H), 6.92 (dd, J = 8.0, 1.4 Hz, 1H), 6.97 (td, J = 7.5, 1.4 Hz, 1H), 7.05 – 7.09 (m, 1H), 7.11 (dd, J = 7.7, 1.7 Hz, 1H).

^13C-NMR (101 MHz, CDCl_3): δ = 20.2, 23.8, 45.1, 66.2, 71.6, 79.6, 117.5, 117.9, 118.7, 119.0, 122.9, 126.3, 126.5, 137.5, 152.5.

IR (ATR) ν (cm⁻¹) = 3065, 2966, 2927, 2855, 2249, 1725, 1472, 1447, 1261, 1217, 1071, 990, 941.

C_{15}H_{15}NO_{2}S calcd.: 273.0824, found: 273.0845 (GC-HRMS).
$^1$H-NMR (400 MHz, CDCl$_3$).

$^{13}$C-NMR (101 MHz, CDCl$_3$).
Following a reported procedure, compound 2a (20.0mg, 100μmol, 1.00 equiv.) was dissolved in DCM (2 ml). After addition of m-CPBA (17.3mg, 100μmol, 1.00 equiv.) the mixture was stirred overnight. The solution was then diluted with DCM (8 ml), washed with NaOH solution (2.0 M, 2 × 10 ml) and brine. The organic phase was dried over Na₂SO₄ and the solvent was evaporated. Flash column chromatography (n-pentane:EtOAc = 10:1→5:1) afforded the desired product as a colorless solid (13.5 mg, 61.5 μmol, 62%).

**m.p.**: 163 °C.

**Rₜ** = 0.07 (n-pentane:EtOAc = 4:1).

**¹H-NMR** (400 MHz, CDCl₃): δ 2.28 (d, J = 1.3 Hz, 3H), 5.01 (d, J = 13.1 Hz, 1H), 5.26 (dd, J = 13.1, 1.3 Hz, 1H), 7.03 (dd, J = 8.5, 1.1 Hz, 1H), 7.12 – 7.17 (m, 1H), 7.51 (dd, J = 8.7, 7.2, 1.7 Hz, 1H), 7.65 (dd, J = 7.8, 1.7 Hz, 1H).

**¹³C-NMR** (101 MHz, CDCl₃): δ 17.6, 56.0, 114.9, 117.8, 119.1, 122.4, 124.8, 132.6, 135.0, 149.6, 152.3.

**IR (ATR)** ν (cm⁻¹) = 3076, 3012, 2922, 2854, 2217, 1591, 1565, 1468, 1437, 1377, 1267, 1214, 1030, 993.

**C₁₁H₈NO₂S** calcd.: 219.0354, found: 219.0367 (GC-HRMS).
$^{1}H$-NMR (400 MHz, CDCl$_3$).

$^{13}C$-NMR (101 MHz, CDCl$_3$).

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Following a reported procedure, compound 2a (20.0 mg, 100 μmol, 1.00 equiv.) was dissolved in DCM (2 ml). After addition of m-CPBA (51.9 mg, 300 μmol, 3.00 equiv.) the mixture was stirred overnight. The solution was then diluted with DCM (8 ml), washed with NaOH solution (2.0 M, 2 × 10 ml) and brine. The organic phase was dried over Na₂SO₄ and the solvent was evaporated. Flash column chromatography (n-pentane:EtOAc = 10:1) afforded the desired product as an off-white solid (22.0 mg, 93.5 μmol, 94%).

**m.p.:** 183 °C.

**Rᵣ:** 0.12 (n-pentane:EtOAc = 4:1).

**¹H-NMR** (400 MHz, CD₂Cl₂) δ 2.22 (s, 3H), 5.16 (d, J = 0.9 Hz, 2H), 6.96 (dd, J = 8.4, 1.1 Hz, 1H), 7.14 (ddd, J = 8.3, 7.3, 1.1 Hz, 1H), 7.46 (ddd, J = 8.8, 7.3, 1.7 Hz, 1H), 7.74 (dd, J = 8.0, 1.7 Hz, 1H).

**¹³C-NMR** (101 MHz, CD₂Cl₂) δ 19.5, 66.1, 114.8, 117.9, 119.2, 123.5, 124.6, 127.4, 135.4, 145.1, 154.1.

**IR** (ATR) ν (cm⁻¹) = 3045, 2926, 2856, 2221, 1595, 1568, 1472, 1442, 1304, 1268, 1217, 1141, 1039, 1003.

**C₁₁H₉NO₃S**

Calcd.: 235.0303, found: 235.0324 (GC-HRMS).
$^1$H-NMR (400 MHz, CD$_2$Cl$_2$).

$^{13}$C-NMR (101 MHz, CD$_2$Cl$_2$).
2-(3-(Ethylthio)-2,3-dihydrobenzo[b][1,4]oxathiin-3-yl)propanenitrile, Diastereomer 1 (12c)

Following a reported procedure,\textsuperscript{45} compound 2a (20.0 mg, 100 μmol, 1.00 equiv.) was dissolved in DMSO (0.6 ml). Ethanethiol (74.0 μl, 62.0 mg, 1.0 mmol, 10.00 equiv.) and subsequently piperidine (40.0 μl, 34.4 mg, 0.4 mmol, 4.00 equiv.) were added. The solution was stirred for 1 h at RT and then diluted with water. After extraction with Et\(_2\)O (3 x 10 ml), washing with brine and drying over Na\(_2\)SO\(_4\) the crude mixture was subjected to flash column chromatography (n-pentane:EtOAc = 50:1) to obtain 12c and 12c’ in an overall yield of 83% (22.0 mg, 83.0 μmol, d.r. 50:50).

Compound 12c was obtained as a colorless oil.

\(R_f = 0.42\) (n-pentane:EtOAc = 20:1).

\(^1H\)-NMR (500 MHz, CDCl\(_3\)): \(\delta = 1.29\) (t, \(J = 7.5\) Hz, 3H), 1.60 (d, \(J = 7.2\) Hz, 3H), 2.81 (q, \(J = 7.5\) Hz, 2H), 3.34 (q, \(J = 7.3\) Hz, 1H), 4.13 (d, \(J = 11.8\) Hz, 1H), 4.78 (d, \(J = 11.8\) Hz, 1H), 6.91 – 6.97 (m, 2H), 7.01 (dd, \(J = 7.8\), \(1.7\) Hz, 1H), 7.06 (ddd, \(J = 8.3\), 7.0, 1.6 Hz, 1H).

\(^{13}C\)-NMR (126 MHz, CDCl\(_3\)): \(\delta = 13.6, 14.6, 23.3, 33.5, 56.0, 71.5, 118.2, 118.7, 119.1, 122.7, 126.2, 126.5, 149.9\).

IR (ATR) \(\tilde{\nu}\) (cm\(^{-1}\)) = 3065, 2977, 2933, 2874, 2241, 1573, 1472, 1445, 1301, 1264, 1211, 1123, 1042.

\(\text{C}_{13}\text{H}_{15}\text{NOS}_2\) calcd.: 265.0595, found: 265.0599 (GC-HRMS).

$^{1}H$-NMR (500 MHz, CDCl$_3$).

$^{13}C$-NMR (126 MHz, CDCl$_3$).
2-(3-(Ethylthio)-2,3-dihydrobenzo[b][1,4]oxathiin-3-yl)propanenitrile, Diastereomer 2 (12c’)

Compound 12c’ was obtained as a colorless oil.

Rr = 0.27 (n-pentane:EtOAc = 20:1).

$^1$H-NMR (500 MHz, CDCl$_3$): δ = 1.29 (t, $J = 7.5$ Hz, 3H), 1.52 (d, $J = 7.1$ Hz, 3H), 2.80 (dq, $J = 11.6, 7.3$ Hz, 1H), 2.91 (dq, $J = 11.6, 7.6$ Hz, 1H), 3.41 (q, $J = 7.1$ Hz, 1H), 4.07 (d, $J = 12.1$ Hz, 1H), 4.50 (d, $J = 11.9$ Hz, 1H), 6.89 – 6.92 (m, 1H), 6.93 – 6.97 (m, 1H), 7.03 – 7.08 (m, 2H).

$^{13}$C-NMR (126 MHz, CDCl$_3$): δ = 13.9, 14.6, 23.4, 36.4, 54.9, 69.5, 118.1, 118.5, 119.9, 122.8, 126.1, 126.9, 149.7.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3065, 2976, 2930, 2243, 1573, 1471, 1445, 1301, 1263, 1211, 1130, 1065, 1040, 1011.

C$_{13}$H$_{15}$NOS$_2$ calcd.: 265.0595, found: 265.0609 (GC-HRMS).
$^{1}H$-NMR (500 MHz, CDCl$_3$).

$^{13}C$-NMR (126 MHz, CDCl$_3$).
According to a reported procedure,\textsuperscript{46} compound 2a (51.0 mg, 250 μmol, 1.00 equiv.) was weighed into a sealable tube EtOH (2 mL) and KOH (2 mL, 34% aq. solution) were added via syringe. The resulting reaction mixture was heated at 80 °C overnight. The reaction mixture was then quenched and acidified with HCl (2 M), diluted with EtOAc (5 mL). The aqueous phase was extracted with EtOAc (3 x 10 mL), the combined organic layers were washed with brine and dried over Na\textsubscript{2}SO\textsubscript{4}. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (n-pentane:Et\textsubscript{2}O:AcOH = 20:1:0.1) to provide \textit{exo-12d} and \textit{endo-12d} as a 1:3 mixture in an overall yield of 61% (34.0 mg, 153.0 μmol).

Compound \textit{exo-12d} was obtained as a colorless solid.

\textbf{m.p.:} 168 °C.

\textit{R}_t = 0.20 (n-pentane:Et\textsubscript{2}O:AcOH = 10:1:0.1).

\textbf{\textit{^1H-NMR}} (500 MHz, CDCl\textsubscript{3}): $\delta = 2.09$ (t, $J = 1.2$ Hz, 3H), 5.24 (q, $J = 1.3$ Hz, 2H), 7.00 – 7.04 (m, 2H), 7.13 – 7.17 (m, 1H), 7.21 – 7.24 (m, 1H).

\textbf{\textit{^{13C-NMR}}} (126 MHz, CDCl\textsubscript{3}): $\delta = 16.1, 66.5, 117.9, 118.4, 119.5, 123.2, 126.4, 127.4, 149.6, 153.5, 170.2$.

\textbf{\textit{IR}} (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3085, 2914, 2853, 2690, 2638, 2536, 1649, 1586, 1558, 1433, 1285, 1255, 1188, 1069.

\textbf{\textit{C\textsubscript{11}H\textsubscript{10}O\textsubscript{3}S}} calcd.: 245.0243, found: 245.02 [M+Na]$^+$ (ESI-HRMS).

$^1$H-NMR (500 MHz, CDCl$_3$).

$^{13}$C-NMR (126 MHz, CDCl$_3$).
**2-(Benzo[b][1,4]oxathiin-3-yl)propanoic acid (endo-12d)**

![Chemical Structure](attachment:image)

**endo-12d** was obtained as a yellow sticky compound.

\( R_f = 0.20 \) (n-pentane:Et\(_2\)O:AcOH = 10:1:0.1).

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \( \delta = 1.40 \) (d, \( J = 7.2 \) Hz, 3H), 3.29 (q, \( J = 7.1 \) Hz, 1H), 6.51 (s, 1H), 6.74 – 6.79 (m, 1H), 6.92 – 6.96 (m, 2H), 7.01 – 7.07 (m, 1H).

\(^{13}\)C-NMR (101 MHz, CDCl\(_3\)): \( \delta = 15.8, 41.8, 112.5, 117.0, 118.8, 124.7, 126.9, 127.8, 137.8, 151.2, 178.0 \).

IR (ATR) \( \tilde{\nu} \) (cm\(^{-1}\)) = 3258, 3066, 2980, 2933, 1724, 1637, 1578, 1468, 1277, 1200, 973.

**C\(_{11}\)H\(_{10}\)O\(_3\)S**

- calcd.: 245.0243, found: 245.0245 [M+Na]\(^+\) (ESI-HRMS).
$^1$H-NMR (400 MHz, CDCl$_3$).

$^{13}$C-NMR (101 MHz, CDCl$_3$).
Methyl (Z)-2-(benzo[b][1,4]oxathiin-3(2H)-ylidene)propyl)carbamate (12e)

\[
\text{\begin{center}
\includegraphics[scale=0.5]{structure.png}
\end{center}}\]

Compound 2a was subjected to a reported procedure\(^{47}\) to obtain carbamate 12e after flash column chromatography (n-pentane:EtOAc = 10:1→4:1) as a colorless solid (39.0 mg, 0.15 mmol, 75%).

m.p.: 88 °C.

\[\text{R}_f = 0.31 \text{ (n-pentane:EtOAc = 20:1).} \]

\(^1\text{H-NMR}\) (400 MHz, CDCl\(_3\)): \(\delta = 1.89\) (s, 3H), 3.69 (s, 3H), 4.02 (d, \(J=6.2\), 2H), 4.69 (s, 2H), 4.89 (s, 1H), 6.86 – 6.95 (m, 2H), 6.99 – 7.05 (m, 1H), 7.09 (dd, \(J=7.7, 1.7\), 1H).

\(^{13}\text{C-NMR}\) (101 MHz, CDCl\(_3\)): \(\delta = 16.4, 44.3, 52.3, 65.3, 118.3, 119.4, 122.5, 123.2, 125.8, 126.2, 128.4, 152.8, 157.3.\)

\(\text{IR (ATR) } \tilde{\nu} \text{ (cm}^{-1}) = 3311, 3069, 2988, 2918, 2852, 1692, 1543, 1471, 1438, 1261, 1073, 988.\)

\(\text{C}_{13}\text{H}_{15}\text{NO}_{3}\text{S}\) calcd.: 288.0665 [M+Na\(^{+}\)], found: 288.0668 [M+Na\(^{+}\)] (ESI-HRMS).

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$^1$H-NMR (400 MHz, CDCl$_3$).

$^{13}$C-NMR (101 MHz, CDCl$_3$).
According to a reported procedure, compound 2a (20.0 mg, 100 μmol, 1.00 equiv.) was weighed into a sealable tube. Dry toluene (0.50 mL) was added via and the solution was cooled to -78 °C. DIBAL-H (0.11 ml, 0.11 mmol, 1 M in hexane) was subsequently added and the tube was sealed. The resulting reaction mixture was taken from the cooling bath and stirred under ambient temperature for 30 min while warming. Afterwards, the mixture was directly transferred into a flask, diluted with further toluene. Silica gel was added to adsorb the reaction products. Immediate flash column chromatography (n-pentane:EtOAc 30:1→20:1) provided compound 12f as a yellow solid (9.0 mg, 44 μmol, 44%).

Rf = 0.46 (n-pentane:EtOAc = 10:1).

$^1$H-NMR (300 MHz, CDCl₃): δ = 1.96 (t, J = 1.0 Hz, 3H), 5.19 (q, J = 1.0 Hz, 2H), 7.01 – 7.08 (m, 2H), 7.14 – 7.27 (m, 2H), 9.97 (s, 1H).

$^{13}$C-NMR (75 MHz, CDCl₃): δ = 12.3, 63.2, 118.5, 118.8, 123.5, 126.6, 127.6, 129.0, 151.3, 153.6, 184.8.

IR (ATR) ν (cm⁻¹) = 3069, 2917, 2853, 1646, 1583, 1468, 1437, 1373, 1266, 1001.

C₁₁H₁₀O₂S calcd.: 206.0402, found: 206.0409 (GC-HRMS).
\( ^1H\text{-NMR (300 MHz, CDCl}_3\text{).} \)

\( ^{13}C\text{-NMR (75 MHz, CDCl}_3\text{).} \)
Compound 20a was synthesized via a reported procedure\textsuperscript{48} for methylation from 3-bromo-2-(methylthio)phenol and obtained as a colorless oil (9.5 g, 40.8 mmol, 91%).

The starting material, 3-bromo-2-(methylthio)phenol, was afforded via a 3-step procedure from 3-bromophenol (introduction of carbamate as directing group\textsuperscript{49}, lithiation in ortho-position and substitution with dimethyl disulfide\textsuperscript{50}, removal of the directing group\textsuperscript{51}).

\[ R_f = 0.69 \text{ (n-pentane:EtOAc = 20:1).} \]

\[ {^1}H\text{-NMR} \text{ (300 MHz, CDCl}_3\text{): } \delta = 2.4 \text{ (s, 3H), 3.9 (s, 3H), 6.8 (dd, } J=8.3, 1.3, 1H), 7.0 - 7.1 \text{ (m, 1H), 7.2 (dd, } J=8.0, 1.2, 1H). \]

\[ {^{13}}C\text{-NMR} \text{ (75 MHz, CDCl}_3\text{): } \delta = 17.9, 56.0, 109.8, 124.9, 125.2, 129.6, 130.2, 160.6. \]

\[ \text{IR (ATR) } \nu \text{ (cm}^{-1}\text{) = 2926, 2843, 1693, 1565, 1455, 1422, 1258, 1026.} \]

\[ C_8H_9BrOS \text{ calcd.: 231.9558, found: 231.9557 (GC-HRMS).} \]


\[ ^{1}H\text{-NMR} \ (300 \text{ MHz, CDCl}_3) \].

\[ ^{13}C\text{-NMR} \ (75 \text{ MHz, CDCl}_3) \].
2-(3-Methoxy-2-(methylthio)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (20b)

Compound 20a was subjected to a reported procedure\(^{52}\) to obtain borolane 20b after flash column chromatography (n-pentane:EtOAc = 20:1) as a colorless solid (4.8 g, 17.1 mmol, 47%).

m.p.: 38 °C.
R\(_f\) = 0.79 (n-pentane:EtOAc = 4:1).

\(^1\)H-NMR (300 MHz, CDCl\(_3\)): \(\delta = 1.4\) (s, 12H), 2.4 (s, 3H), 3.9 (s, 3H), 6.9 (dd, \(J=8.2\), 1.3, 1H), 7.0 (dd, \(J=7.4\), 1.3, 1H), 7.2 – 7.3 (m, 1H).

\(^13\)C-NMR (75 MHz, CDCl\(_3\)): \(\delta = 19.1, 24.8\) (4 C), 55.8, 84.1 (2 C), 112.3, 113.7, 125.0, 127.6, 129.2, 159.5.

\(^11\)B NMR (96 MHz, CDCl\(_3\)): \(\delta = 30.7\).

IR (ATR) \(\tilde{\nu}\) (cm\(^{-1}\)) = 2981, 2928, 2838, 1561, 1346, 1312, 1138, 1039.

\(C_{14}H_{21}BO_{3}S\) calcd.: 280.1305, found: 280.1322 (GC-HRMS).

\[^1\text{H-NMR} \,(300 \text{ MHz, CDCl}_3).\]

\[^{13}\text{C-NMR} \,(75 \text{ MHz, CDCl}_3).\]
$^{11}\text{B-NMR (96 MHz, CDCl}_3\text{).}$
Methyl 5-methoxy-3-(((trifluoromethyl)sulfonyl)oxy)-2-naphthoate (21a)

![Chemical Structure]

Compound 21a was synthesized via a reported procedure\textsuperscript{53} from methyl 3-hydroxy-5-methoxy-2-naphthoate\textsuperscript{54} and obtained as a colorless solid (3.9 g, 10.8 mmol, 95%).

\textbf{m.p.:} 105 °C.

\textbf{R}_f = 0.26 (n-pentane:EtOAc = 10:1).

\textbf{\textsuperscript{1}H-NMR} (300 MHz, CDCl\textsubscript{3}): δ = 3.99 (s, 3H), 4.01 (s, 3H), 6.94 (p, J=4.7, 1H), 7.46 – 7.52 (m, 2H), 8.09 – 8.14 (m, 1H), 8.54 (d, J=0.4, 1H).

\textbf{\textsuperscript{13}C-NMR} (75 MHz, CDCl\textsubscript{3}): δ = 52.6, 55.7, 107.1, 116.1 (d, J=1.5), 118.8 (q, J=320.8), 120.7, 122.3, 127.1, 128.3, 132.3, 134.1, 144.3, 155.0, 164.4.

\textbf{\textsuperscript{19}F NMR} (283 MHz, CDCl\textsubscript{3}): δ = -73.7.

\textbf{IR} (ATR) \textit{v} (cm\textsuperscript{-1}) = 3082, 3010, 2953, 2848, 1723, 1426, 1276, 1197, 1141, 1108, 1046.

\textbf{C\textsubscript{14}H\textsubscript{11}F\textsubscript{3}O\textsubscript{6}S} \quad \text{calcd.:} 364.0228, \text{found:} 364.0232 (GC-HRMS).


$^{1}H$-NMR (300 MHz, CDCl$_3$).

$^{13}C$-NMR (75 MHz, CDCl$_3$).
$^{19}$F-NMR (283 MHz, CDCl$_3$).
3-(Hydroxymethyl)-8-methoxynaphthalen-2-yl trifluoromethanesulfonate (21b)

The reduction of 21a in accordance to a reported procedure\textsuperscript{55} furnished compound 21b as a white solid (7.9 g, 23.4 mmol, 87%)

m.p.: 84 °C.

$R_f = 0.42$ (n-pentane:EtOAc = 4:1).

$^1$H-NMR (300 MHz, CDCl$_3$): δ = 2.2 (s, 1H), 4.0 (s, 3H), 4.9 – 5.0 (m, 2H), 6.9 (dd, $J$=6.8, 1.8, 1H), 7.4 – 7.5 (m, 2H), 7.9 (s, 1H), 8.1 (s, 1H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): δ = 55.6, 60.2, 105.0, 114.5 (d), 119.8, 120.5 (q), 125.0, 127.6, 128.7, 131.9, 133.5, 144.8, 155.2.

$^{19}$F NMR (283 MHz, CDCl$_3$): δ = -73.9.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3381, 3307, 3014, 2945, 2847, 1605, 1416, 1197, 1139, 1060.

C$_{13}$H$_{11}$F$_3$O$_5$S \hspace{1cm} calcd.: 336.0279, found: 336.0272 (GC-HRMS).

S354

$^{1}H$-NMR (300 MHz, CDCl$_3$).

$^{13}C$-NMR (75 MHz, CDCl$_3$).
$^{19}$F-NMR (283 MHz, CDCl$_3$).
3-Formyl-8-methoxynaphthalen-2-yl trifluoromethanesulfonate (21c)

![Chemical structure](attachment:image.png)

Compound 21c was obtained as a pale yellow solid (6.2 g, 18.5 mmol, 79%) by oxidation of 21b with DMP following a reported procedure.\(^{56}\)

**m.p.:** 76 °C.

**R\(_f\):** 0.20 (n-pentane:EtOAc = 10:1).

**\(^1\)H-NMR** (300 MHz, CDCl\(_3\)): \(\delta = 4.0\) (s, 3H), 7.0 (dd, \(J = 6.7, 2.0, 1\)H), 7.5 – 7.7 (m, 2H), 8.2 (s, 1H), 8.4 (s, 1H), 10.3 (s, 1H).

**\(^13\)C-NMR** (75 MHz, CDCl\(_3\)): \(\delta = 55.9, 108.0, 116.1\) (d), 118.8 (q, \(J = 320.8\)), 121.4, 126.9, 127.8, 128.7, 132.5, 134.4, 144.7, 155.2, 187.3.

**\(^19\)F NMR** (283 MHz, CDCl\(_3\)): \(\delta = -73.3\).

**IR (ATR) \(\nu\) (cm\(^{-1}\)):** 3071, 3023, 2978, 2948, 2848, 1696, 1418, 1199, 1129, 1054.

**C\(_{13}\)H\(_8\)F\(_3\)O\(_5\)S**

- calcd.: 334.0123, found: 334.0145 (GC-HRMS).

---

$^{1}H$-NMR (300 MHz, CDCl$_3$).

$^{13}C$-NMR (75 MHz, CDCl$_3$).
$^{19}$F-NMR (283 MHz, CDCl$_3$).
5-Methoxy-3-(3-methoxy-2-(methylthio)phenyl)-2-naphthaldehyde (22a)

Following a reported procedure\(^{57}\), compound 22a was afforded by Suzuki cross-coupling. Under an argon atmosphere, triflate 21c (486 mg, 1.4 mmol, 1.0 equiv.) was added to a suspension of borolane 20b (432 mg, 1.54 mmol, 1.1 equiv.), Pd\(_2\)(dba)\(_3\) (64.1 mg, 5 mol%), SPhos (115.0 mg, 20 mol%) and K\(_2\)CO\(_3\) (387 mg, 2.8 mmol, 2.0 equiv.) in degassed PhMe (7 ml) and degassed H\(_2\)O (7 ml) was added to the sealable vial. The reaction mixture was stirred at 140 °C for 18 h. After cooling, the phases were separated and the aq. phase was extracted with Et\(_2\)O (2 x 50 ml). The combined organic phases were washed with brine, dried over Na\(_2\)SO\(_4\) and the solvent was removed under reduced pressure. After flash column chromatography (n-pentane:EtOAc = 20:1→10:1→5:1) the desired product was yielded as a yellow solid (420 mg, 1.24 mmol, 89%).

m.p.: 104 °C.

\(R_f = 0.19\) (n-pentane:EtOAc = 10:1).

\(^1\)H-NMR (300 MHz, CDCl\(_3\)): \(\delta = 2.13\) (s, 3H), 3.97 (s, 6H), 6.92 (dd, \(J=7.8, 0.9, 1H\)), 6.99 (dd, \(J=8.3, 1.3, 1H\)), 7.03 (dd, \(J=7.6, 1.2, 1H\)), 7.37 (dd, \(J=8.3, 7.6, 1H\)), 7.45 (dd, \(J=8.3, 7.7, 1H\)), 7.57 – 7.62 (m, 1H), 8.14 (t, \(J=0.7, 1H\)), 8.49 (t, \(J=0.6, 1H\)), 9.93 (s, 1H).

\(^13\)C-NMR (75 MHz, CDCl\(_3\)): \(\delta = 17.8, 55.5, 56.0, 106.5, 110.7, 121.7, 123.4, 124.1, 124.2, 127.0, 127.5, 128.4, 128.8, 132.2, 132.9, 138.9, 143.7, 155.2, 159.7, 191.9.

IR (ATR) \(\nu\) (cm\(^{-1}\)) = 3057, 3010, 2930, 2836, 1689, 1566, 1455, 1256, 1067, 1007.

\(C_{20}H_{18}O_3S\) calcd.: 338.0977, found: 338.0976 (GC-HRMS).

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$^1$H-NMR (300 MHz, CDCl$_3$).

$^{13}$C-NMR (75 MHz, CDCl$_3$).
Compound 22a (677 mg, 2.0 mmol) was transformed to an E/Z-mixture of 22b following a reported procedure. After flash column chromatography (n-pentane:DCM = 1:1) a colorless foam (680 mg, 1.86 mmol, 93%) was obtained and used as isomeric mixture in the next step.

m.p.: 81 °C.

$R_f = 0.26$ and $R_f = 0.22$ (n-pentane:EtOAc = 10:1).

$^1$H-NMR (500 MHz, CDCl$_3$, Isomer 1): $\delta = 2.16$ (s, 3H), 3.79 (s, 3H), 3.94 (s, 3H), 3.97 (s, 3H), 4.95 (d, $J=7.2$, 1H), 6.09 (d, $J=7.1$, 1H), 6.74 (d, $J=7.3$, 1H), 6.89 – 6.95 (m, 2H), 7.29 – 7.35 (m, 2H), 7.44 (d, $J=8.3$, 1H), 7.98 (s, 1H), 8.55 (s, 1H).

$^1$H-NMR (500 MHz, CDCl$_3$, Isomer 2): $\delta = 2.18$ (s, 3H), 3.51 (s, 3H), 3.94 (s, 3H), 3.97 (s, 3H), 5.59 (d, $J=12.8$, 1H), 6.73 (d, $J=7.5$, 1H), 6.89 – 6.95 (m, 2H), 6.97 (d, $J=12.8$, 1H), 7.29 – 7.36 (m, 2H), 7.37 – 7.40 (m, 1H), 7.78 (s, 1H), 7.99 (s, 1H).

$^{13}$C-NMR (126 MHz, CDCl$_3$, Isomer 1): $\delta = 18.2$, 55.4, 55.9, 60.8, 103.3, 103.4, 109.8, 120.4, 121.9, 123.2, 123.3, 125.6, 126.7, 128.5, 132.6, 134.2, 138.3, 147.3, 148.5, 155.3, 159.8.

$^{13}$C-NMR (126 MHz, CDCl$_3$, Isomer 1): $\delta = 18.1$, 55.4, 56.0, 56.7, 103.3, 104.2, 110.0, 119.8, 121.6, 122.6, 123.6, 124.0, 124.3, 126.0, 128.5, 133.8, 134.1, 138.2, 146.9, 149.5, 155.5, 159.9.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3051, 3002, 2929, 2832, 1740, 1643, 1565, 1456, 1426, 1091.

C$_{22}$H$_{22}$O$_3$S calcd.: 366.1290, found: 366.1283 (GC-HRMS).

$^1$H-NMR (500 MHz, CDCl$_3$, Isomer 1).

$^{13}$C-NMR (126 MHz, CDCl$_3$, Isomer 1).
$^1$H-NMR (500 MHz, CDCl$_3$, Isomer 2).

$^{13}$C-NMR (126 MHz, CDCl$_3$, Isomer 2).
(2,11-Dimethoxytetraphen-1-yl)(methyl)sulfane (22c)

Following a reported procedure, compound 22c was synthesized from the E/Z-mixture of 22b. Prior to use DCE was degassed and Bi(OTf)$_3$ was dried under vacuum. To a suspension of Bi(OTf)$_3$ (61 mg, 5 mol%) in DCE (3 ml) was added a solution of substrate 22b (680 mg, 1.86 mmol) in DCE (10 ml). The flask was rinsed with additional 2 ml of DCE. The reaction progress was followed by TLC. After 20 min the reaction was stopped and the mixture was added directly to a silica gel column (n-pentane:DCM = 2:1) because a previous experiment showed decomposition of the product when the solvent was evaporated. Finally, the desired product was obtained as a yellow solid (438 mg, 1.31 mmol, 70%).

**m.p.:** 165 °C.

**R**$_f$ = 0.26 (n-pentane:EtOAc = 10:1).

**$^1$H-NMR** (400 MHz, CDCl$_3$): $\delta$ = 2.40 (s, 3H), 4.04 (s, 3H), 4.07 (s, 3H), 6.78 (dd, $J$=7.5, 0.9, 1H), 7.17 (d, $J$=8.6, 1H), 7.39 – 7.46 (m, 2H), 7.54 – 7.61 (m, 2H), 7.66 (d, $J$=8.7, 1H), 8.19 (s, 1H), 10.68 (d, $J$=1.0, 1H).

**$^{13}$C-NMR** (101 MHz, CDCl$_3$): $\delta$ = 19.5, 55.8, 56.6, 102.5, 111.1, 119.4, 122.2, 123.4, 123.8, 125.0, 125.6, 126.4, 127.1, 127.5, 127.9, 129.2, 132.4, 132.8, 133.8, 156.3, 159.4.

**IR (ATR)** $\nu$ (cm$^{-1}$) = 3036, 2997, 2967, 2918, 2832, 1625, 1589, 1558, 1453, 1266, 1236, 1069.

**C$_{21}$H$_{18}$O$_2$S**

calcd.: 334.1028, found: 334.1020 (GC-HRMS).

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$^1$H-NMR (400 MHz, CDCl$_3$).

$^{13}$C-NMR (101 MHz, CDCl$_3$).
1-(Methylthio)tetrathene-2,11-diol (22d)

Compound 22c (488 mg, 1.46 mmol, 1.0 equiv.) was dissolved in DCM (10 ml) and cooled to -83 °C. BBr₃ (3.6 ml of 1M solution in DCM, 3.6 mmol, 2.5 equiv.) was added dropwise to the solution. The reaction mixture was warmed to RT and quenched after 2 h carefully with cooled water. The phases were separated and the aq. phase was extracted with DCM (2 x 50 ml). The combined organic phases were washed with brine, dried over Na₂SO₄ and the solvent was evaporated. Purification by flash column chromatography (n-pentane:EtOAc = 10:1→4:1) afforded the product 22d as a brown, sticky mass (263 mg, 0.54 mmol, 37%).

Rᵣ = 0.16 (n-pentane:EtOAc = 10:1).

¹H-NMR (400 MHz, CDCl₃): δ = 2.36 (s, 3H), 5.63 (s, 1H), 6.85 (dd, J=7.3, 0.9, 1H), 7.31 – 7.43 (m, 2H), 7.49 (d, J=8.9, 1H), 7.61 (dd, J=12.5, 8.6, 2H), 7.73 (d, J=8.5, 1H), 8.26 (d, J=1.5, 2H), 11.42 (d, J=1.0, 1H).

¹³C-NMR (101 MHz, CDCl₃): δ = 18.3, 107.1, 115.2, 115.8, 119.9, 121.1, 123.1, 125.5, 126.1, 126.4, 127.9, 127.9, 128.0, 132.2 (2 C), 132.6, 132.8, 152.3, 157.3.

IR (ATR) ν (cm⁻¹) = 3399, 3285, 3042, 2918, 2850, 1701, 1593, 1491, 1406, 1233, 1188, 1142.

$^1$H-NMR (400 MHz, CDCl$_3$).

$^{13}$C-NMR (101 MHz, CDCl$_3$).
(2,11-Bis(octa-2,6-diyloxy)tetraphen-1-yl)(methyl)sulfane (22e)

Compound 22e was synthesized according GP1.

A solution of 22d (138.0 mg, 0.45 mmol, 1.00 equiv.), PPh$_3$ (472 mg, 1.80 mmol, 4.00 equiv.) and octa-2,6-diyloxy-1-ol$^{60}$ (220 mg, 1.80 mmol, 4.00 equiv.) in dry toluene (14 ml) was cooled to 0 °C. DIAD (364 mg, 354 µl, 1.80 mmol, 4.00 equiv.) in dry toluene (11 ml) was added dropwise to the stirred solution. After completion, the reaction mixture was warmed to RT and stirred overnight. The solvent was removed under reduced pressure and silica gel column chromatography (n-pentane:EtOAc = 20:1→10:1) gave the desired product (134 mg, 0.26 mmol, 58%) as an orange-brown oil.

R$_f$ = 0.40 (n-pentane:EtOAc = 10:1).

$^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ = 1.73 (t, $J=2.4$, 3H), 1.77 (t, $J=2.5$, 3H), 2.31 – 2.46 (m, 8H), 2.49 (s, 3H), 4.98 (d, $J=1.6$, 4H), 6.97 (dd, $J=7.7$, 0.9, 1H), 7.40 (d, $J=8.5$, 1H), 7.45 (dd, $J=8.4$, 7.5, 1H), 7.48 (d, $J=8.9$, 1H), 7.62 (t, $J=8.6$, 2H), 7.72 (d, $J=8.7$, 1H), 8.23 (s, 1H), 10.72 (d, $J=0.9$, 1H).

$^{13}$C-NMR (126 MHz, CDCl$_3$): $\delta$ = 3.7, 3.8, 19.1, 19.1, 19.7, 19.7, 20.0, 57.4, 58.2, 76.1, 76.2, 77.6, 77.7, 86.9, 87.3, 104.7, 113.9, 120.4, 123.8, 123.9, 124.1, 125.3, 126.2, 126.5, 127.4, 128.0, 128.7, 129.3, 132.6, 133.1, 134.2, 154.7, 158.2, 2 C (alkynes) are covered by CDCl$_3$.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3034, 2916, 2852, 1591, 1562, 1490, 1436, 1263, 1236, 1058, 990.

C$_{35}$H$_{30}$O$_2$S  calcd.: 514.1957 [M$^+$], found: 514.1961 [M$^+$] (EI-HRMS).

$^1$H-NMR (500 MHz, CDCl$_3$).

$^{13}$C-NMR (126 MHz, CDCl$_3$).
2,11-Bis(octa-2,6-diyn-1-yloxy)-1-thiocyanatotetraphene (22f)

Compound 22e (134 mg, 0.26 mmol, 1.0 equiv.) was dissolved in CH$_2$CN/THF (1:1, 2 ml) and added to a flask containing X-CN (161 mg, 0.312 mmol, 1.2 equiv.) The mixture was stirred for 30 min and the solvent was evaporated subsequently. Silica gel column chromatography (n-pentane:DCM = 1:3) gave the desired product 22f (17 mg, 32 µmol, 12%) as a yellow solid.

m.p.: 184 °C.

R$_f$ = 0.17 (n-pentane:EtOAc = 10:1).

$^1$H-NMR (500 MHz, CDCl$_3$): δ = 1.74 (t, J=2.5, 3H), 1.77 (t, J=2.5, 3H), 2.31 – 2.55 (m, 8H), 5.01 (t, J=2.0, 2H), 5.07 (t, J=2.1, 2H), 7.02 (d, J=7.5, 1H), 7.48 – 7.52 (m, 2H), 7.54 (d, J=8.6, 1H), 7.64 (d, J=8.4, 1H), 7.69 (d, J=8.6, 1H), 7.90 (d, J=8.7, 1H), 8.29 (s, 1H), 10.13 (s, 1H).

$^{13}$C-NMR (126 MHz, CDCl$_3$): δ = 3.5, 3.5, 18.7, 18.8, 19.4, 19.5, 57.2, 58.3, 75.1, 75.7, 76.8, 77.5, 87.0, 88.0, 104.9, 108.5, 111.3, 113.5, 120.1, 123.3, 123.7, 125.9, 126.2, 126.4, 126.7, 126.9, 128.8, 132.2, 132.3, 133.1, 133.9, 154.3, 157.8, 2 C (alkynes) are covered by CDCl$_3$.

IR (ATR) $\tilde{\nu}$ (cm$^{-1}$) = 3052, 2918, 2851, 2147, 1597, 1562, 1492, 1439, 1416, 1265, 1059.

C$_{35}$H$_{27}$NO$_2$S calcd.: 525.1752 [M$^+$], found: 525.1757 [M$^+$] (EI-HRMS).

Compound 22f was synthesized to obtain a twelve-membered ring formed in a “zipper”-type cascade reaction. Unfortunately, this synthesis was not possible.
$^1$H-NMR (500 MHz, CDCl$_3$).

$^{13}$C-NMR (126 MHz, CDCl$_3$)
Screening of Reaction Conditions

Table S1: Optimization Table.

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<th>Catalyst</th>
<th>Ligand</th>
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<th>Solv.</th>
<th>T [°C]</th>
<th>t</th>
<th>A [%]</th>
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<td>4 h</td>
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<tr>
<td>13</td>
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<td>-</td>
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<td>14</td>
<td>-</td>
<td>XantPhos</td>
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<td>15</td>
<td>PdCl₂(PhCN)₂</td>
<td>-</td>
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<td>DMF</td>
<td>100</td>
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Reaction conditions: 1a (1.00 equiv.), Catalyst (10 mol%), Ligand (20 mol%), Base (5.00 equiv.), Solv. (20 mM); [a] solvent not degassed; [b] 18 mol% of catalyst; [c] from that entry all solvents (DMF, DMA, CH$_3$CN, PhMe) were degassed; [d] 20 mol% of catalyst; [f] NMR yield;

Fu’s salt = [tBu$_3$PH][BF$_4$]; DTBPF = 1,1'-Bis(di-tert-butylphosphino)ferrocene; dppe = 1,2-Bis(diphenylphosphino)ethane; Solv.. = Solvent, A = Yield.
Table S2: Optimization Table.

<table>
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<tr>
<th>Entry</th>
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<th>Solv.</th>
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<th>$t$</th>
<th>A [%]</th>
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<tbody>
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<td>PhMe</td>
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<td>PhMe</td>
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<td>-</td>
<td>PhMe</td>
<td>160</td>
<td>19 h</td>
<td>n.d.$^{[b]}$</td>
</tr>
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</table>
Reaction conditions: 3a (1.00 equiv.), Catalyst (10 mol%), Ligand (20 mol%), Base (5.00 equiv.), Solv. (20 mM); [a] almost no conversion after 4 h at 100 °C, temperature raised to 140 °C for 18 h; [b] significant amount of starting material left; [c] 10 mol%; [d] 5 mol%

Fu-Salt = [tBu₃PH][BF₄]; MeOBiPHEP = 2,2’-Bis(diphenylphosphino)-6,6’-dimethoxy-1,1’-biphenyl; Solv.. = Solvent, A = Yield.
Table S3: Optimization Table.

<table>
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<tr>
<th>Entry</th>
<th>Catalyst</th>
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<th>Ligand</th>
<th>mol%</th>
<th>Base</th>
<th>Solv.</th>
<th>T [°C]</th>
<th>t</th>
<th>A [%]</th>
</tr>
</thead>
<tbody>
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<td>20</td>
<td>XantPhos</td>
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<td>NEt₃</td>
<td>DMF</td>
<td>100</td>
<td>6 h</td>
<td>(66)²</td>
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<td>PdCl₂(PhCN)₂</td>
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<td>Fu’s salt</td>
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<td>NEt₃</td>
<td>DMF</td>
<td>100</td>
<td>6 h</td>
<td>(17)²</td>
</tr>
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<td>XantPhos</td>
<td>20</td>
<td>NEt₃</td>
<td>DMF</td>
<td>140</td>
<td>12 h</td>
<td>n.d.²</td>
</tr>
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<td>20</td>
<td>NEt₃</td>
<td>PhMe</td>
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<td>12 h</td>
<td>n.d.²</td>
</tr>
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<td>dec.</td>
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</tr>
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<td>12 h</td>
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<td>12 h</td>
<td>[c]</td>
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<td>12 h</td>
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<td>[c]</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td>n.d.²</td>
</tr>
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<td>mol%</td>
<td>Base</td>
<td>Solv.</td>
<td>T [°C]</td>
<td>t</td>
<td>A [%]</td>
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<td>12 h</td>
<td>n.d.$^{[f]}$</td>
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<td>12 h</td>
<td>n.d.$^{[f]}$</td>
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<td>12 h</td>
<td>n.d.$^{[f]}$</td>
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<td>65$^{[e]}$</td>
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<td>12 h</td>
<td>n.d.$^{[f]}$</td>
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<td>19 h</td>
<td>n.d.$^{[f]}$</td>
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<td>110</td>
<td>4 h</td>
<td>60$^{[e]}$</td>
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<td>DavePhos</td>
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<td>3 h</td>
<td>n.d.$^{[f]}$</td>
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<td>19 h</td>
<td>n.d.$^{[f]}$</td>
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<td>12 h</td>
<td>n.d.$^{[f]}$</td>
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<td>2 h</td>
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<td>n.d.$^{[f]}$</td>
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<td>35</td>
<td>Pd(PPh$_3$)$_4$</td>
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<td>SPhos</td>
<td>20</td>
<td>-</td>
<td>DMF</td>
<td>110</td>
<td>3 h</td>
<td>70</td>
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</table>

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Reaction conditions: 3a (1.00 equiv.), Catalyst (10 mol%), Ligand (20 mol%), Base (5.00 equiv.), Solv. (20 mm); [a] single palladation product; [b] DMI = ; [c] protodepalladation product; [d] reaction in microwave; [e] NMR yield; [f] no improvement (TLC) [g] from that entry the catalyst and ligand were prestirred for 30 – 45 min

Fu-Salt = [tBu3PH][BF4]; MeOBiPHEP = 2,2′-Bis(diphenylphosphino)-6,6′-dimethoxy-1,1′-biphenyl; Solv. = Solvent, A = Yield.
**Experiments with Lewis acid as co-catalyst**

As the catalytic system with PdCl$_2$(PhCN)$_2$/XantPhos is not suitable for such experiments due to the use of NEt$_3$ as base, we first investigated the reaction of 1a to 2a with the adjusted conditions of GP CAT2 (100 µmol, PhMe, 80 °C). We followed the reaction progress by GC-MS measurements and took samples after 1, 3, 5, 10, 15 and 30 min from the reaction vial.

![GC-MS chromatogram](image)

The figure shows, that the starting material (retention time 6.552) was consumed after 30 min and seems to be fully converted to the product 2a (retention time 7.153). The other peak shows PPh$_3$ from the catalyst.

Next, we tested the influence of two Lewis acids. The first figure shows the tracking of the reaction in presence of 20 mol% BPh$_3$. 
After an initially fast formation of the product the conversion stopped and stayed at a ratio of 1:2 (1a/2a).

The following figure shows the tracking of the reaction in presence of 20 mol\% AlCl₃.
Until the measurement after 30 min the reaction showed almost no conversion of the starting material 1a to the product 2a. After 30 min there was a sharp increase to a ratio of 1:2 (1a/2a). However, also side products are visible.

In summary, the use of a Lewis acid as co-catalyst for the cyanosulfenylation offers no benefit compared to the established catalytic system.
Configurational experiments (interconversion of $E$ and $Z$ isomers)

We investigated the configurational stability of the separated $E$- and $Z$-isomer of 2e, respectively. Therefore, each of the pure isomers was subjected again to reaction conditions used for the transformation of 1e into 2e.

The crude reaction mixtures (after co-evaporation of the DMF with PhMe) were measured by $^1$H-NMR spectroscopy. In both cases the other isomer arises in the spectrum. For determination, we used the chemical shift of the CH$_2$-signal.

For the syn-isomer it is 4.78 ppm and for the anti-isomer it is 5.05 ppm. In both cases a ratio of approximately 20:1 from one isomer (the one used for the experiment) to the other (the one that is formed in the experiment) results after 7 h.

Scheme: Conversion of the syn-isomer to the anti-isomer.
Scheme: Conversion of the anti-isomer to the syn-isomer.
Investigation of Thorpe-Ingold effect

Under optimized conditions of GP CAT3, we synthesized compound 4f and 4f’ under the same conditions and tracked the reactions by GC-MS. As we assumed that a Thorpe-Ingold effect in substrate 3f’ may facilitate the reaction we decreased the temperature of the reaction to 120 °C.
The first figure shows the reaction of 3f (retention time 6.296) to 4f (retention time 7.593). In general, the substrates for the five-membered form the corresponding product apparently much faster than we observed it for the formation of the six-membered ring during the screening for the cyanosulfenylation of aliphatic thiocyanates (cf. Table S2).

The conversion of 3f was almost complete after 10 minutes (see first figure). After 5 minutes, we determined a ratio of starting material to product of 4:10 (3f/4f).

The second figure shows the reaction of 3f' (retention time 6.859) to 4f' (retention time 7.633). The conversion of 3f' was complete after 10 minutes. After 5 minutes, we determined a ratio of starting material to product of 2.5:10 (3f'/4f').

In conclusion, only a very small Thorpe-Ingold effect can be assumed as the reaction itself is fast for these simple substrates at the chosen reaction conditions.
Photochemical and thermal experiments with compound 10d

As we assumed an isomerization after formation of compound 10d between the \((Z,Z,Z)\)- and \((Z,E,Z)\)-isomer (proved by X-ray) we investigated whether this effect may be caused thermally or photochemically. After the reaction we purified the isomeric mixture via a short silica gel column and subjected it to an HPLC experiment (eluent CH\(_3\)CN/H\(_2\)O 80:20).

The first figure shows the chromatogram of the mixture and the separated fractions (F1 at 23.4 min and F2 at 25.2 min). Both were identified as one product isomer by LC-MS.

Both separated isomers were then either heated to 60 °C for 18 h or irradiated with white light for 14 h. The results are shown in the following figures.

For both isomers F1 and and F2 the thermal experiments showed that the other isomer F2 or F1, resp., was formed again (middle chromatogram in both figures).

Moreover, for both isomers F1 and and F2 the irradiation experiments (lower chromatogram in both figures) showed that a new compound was formed from both isomers F1 and F2 with a retention time of 27.5 minutes. In LC-MS the same mass as for the isomers F1 and F2 was found. A further characterization was not done and should be the considered for further studies.
Thermal (middle) and photochemical (bottom) reaction with isomer F1

Thermal (middle) and photochemical (bottom) reaction with isomer F2
Crystal Structure Determinations

Crystals were mounted in inert oil and transferred to the cold gas stream of the diffractometer; various Rigaku/Oxford instruments using monochromated Mo Kα (6d, 10b, 10d, 2s, 10a'), mirror-focussed Mo Kα (2q, 2r, 8e) or mirror-focussed Cu Kα (2a, 2e) radiation were employed. Absorption corrections were implemented on the basis of multi-scans. The structures were refined anisotropically on $F^2$ using the program SHELXL-97\(^1\) or SHELXL-2017\(^2\). Hydrogen atoms were included using rigid methyl groups or a riding model starting from calculated positions. Special features: For compound 8b, the atom C12 is disordered over two positions with relative occupancy 0.81:0.19. Appropriate restraints were employed, but the dimensions of disordered groups should be interpreted with caution. Compound 8e was a non-merohedral twin (by 180° rotation about the $a$ axis). The structure was refined using the "HKLF 5" method;\(^2\) the relative volume of the smaller twin component refined to 0.4553(6). The dataset comprised non-overlapped reflections from both components as well as overlapped reflections. For such refinements, the number of reflections and the $R$(int) value may not be well-defined.

Crystallographic data are summarized in Table S1. Additionally, complete data have been deposited with the Cambridge Crystallographic Data Centre under the numbers CCDC 1948156-1948162 and 1969696-1969698. Copies of the data can be obtained free of charge from www.ccdc.cam.ac.uk/data_request/cif.

References:


**Table S1a:** Crystallographic data and structure refinement details for compounds 2a, 2e, 6d and 10b.

<table>
<thead>
<tr>
<th>Compound</th>
<th>2a</th>
<th>2e</th>
<th>6d</th>
<th>10b</th>
</tr>
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<tbody>
<tr>
<td>CCDC number</td>
<td>1948156</td>
<td>1948157</td>
<td>1948158</td>
<td>1948159</td>
</tr>
<tr>
<td>Formula</td>
<td>C11H9NOS</td>
<td>C16H11NOS</td>
<td>C16H21NSSeSi</td>
<td>C17H17NS</td>
</tr>
<tr>
<td>$M_r$</td>
<td>203.25</td>
<td>265.32</td>
<td>366.45</td>
<td>267.38</td>
</tr>
<tr>
<td>Cryst. size (mm)</td>
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<td>0.2 x 0.15 x 0.08</td>
<td>0.45 x 0.4 x 0.2</td>
<td>0.4 x 0.35 x 0.10</td>
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<tr>
<td>Crystal system</td>
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<td>orthorhombic</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P2_1/c$</td>
<td>$Pbca$</td>
<td>$P2_1/c$</td>
<td>$P2_1/c$</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>-173</td>
<td>-173</td>
<td>-173</td>
<td>-173</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>10.9143(2)</td>
<td>12.2557(2)</td>
<td>10.6588(4)</td>
<td>11.1885(7)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>7.26579(18)</td>
<td>9.5626(2)</td>
<td>8.0663(3)</td>
<td>11.2630(4)</td>
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<tr>
<td>$c$ (Å)</td>
<td>12.4737(2)</td>
<td>21.5616(4)</td>
<td>20.1272(8)</td>
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<td>$α$ (°)</td>
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<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>$β$ (°)</td>
<td>104.425(2)</td>
<td>90</td>
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<td>116.756(8)</td>
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<tr>
<td>$γ$ (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
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<td>$V$ (Å$^3$)</td>
<td>957.99</td>
<td>2526.94</td>
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<td>1371.50</td>
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<td>$Z$</td>
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<td>8</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>$D_1$ (Mg m$^{-3}$)</td>
<td>1.409</td>
<td>1.395</td>
<td>1.414</td>
<td>1.295</td>
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<tr>
<td>$λ$ (Å)</td>
<td>1.54184</td>
<td>1.54184</td>
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<td>0.71073</td>
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<td>$μ$ (mm$^{-1}$)</td>
<td>2.7</td>
<td>2.2</td>
<td>2.4</td>
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<td>Transmissions</td>
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<td>0.608 – 1.000</td>
<td>0.788 – 1.000</td>
<td>0.970 – 1.000</td>
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<td>$F(000)$</td>
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<td>1104</td>
<td>752</td>
<td>568</td>
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<td>$2θ_{max}$</td>
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<td>152</td>
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<td>58.2</td>
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<tr>
<td>Refl. measured</td>
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<td>49411</td>
<td>88854</td>
<td>31457</td>
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<tr>
<td>Refl. indep.</td>
<td>1990</td>
<td>2638</td>
<td>5310</td>
<td>3577</td>
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<tr>
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<td>0.049</td>
<td>0.049</td>
<td>0.047</td>
</tr>
<tr>
<td>Parameters</td>
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<td>172</td>
<td>186</td>
<td>178</td>
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<td>$wR(F^2, all refl.)$</td>
<td>0.085</td>
<td>0.082</td>
<td>0.072</td>
<td>0.092</td>
</tr>
<tr>
<td>$R(F, &gt;4σ(F))$</td>
<td>0.031</td>
<td>0.030</td>
<td>0.032</td>
<td>0.039</td>
</tr>
<tr>
<td>$S$</td>
<td>1.06</td>
<td>1.06</td>
<td>1.08</td>
<td>1.04</td>
</tr>
<tr>
<td>Max. $Δρ$ (e Å$^{-3}$)</td>
<td>0.28, −0.30</td>
<td>0.23, −0.32</td>
<td>1.4, −0.6</td>
<td>0.49, −0.25</td>
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Table S1b: Crystallographic data and structure refinement details for compounds 10d, 2s and 10a'.

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<tr>
<th>Compound</th>
<th>10d</th>
<th>2s</th>
<th>10a'</th>
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<tr>
<td>CCDC number</td>
<td>1948160</td>
<td>1948161</td>
<td>1948162</td>
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<tr>
<td>Formula</td>
<td>C_{22}H_{23}NS</td>
<td>C_{10}H_{2}NS</td>
<td>C_{21}H_{20}S</td>
</tr>
<tr>
<td>( M_r )</td>
<td>333.47</td>
<td>173.23</td>
<td>304.43</td>
</tr>
<tr>
<td>Cryst. size (mm)</td>
<td>0.4 x 0.25 x 0.2</td>
<td>0.35 x 0.25 x 0.2</td>
<td>0.35 x 0.2 x 0.2</td>
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<td>Crystal system</td>
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<td>triclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>( P_{2_1}/c )</td>
<td>( P(-1) )</td>
<td>( P_{2_1}/n )</td>
</tr>
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<td>Temperature (°C)</td>
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<td>-173</td>
<td>-171</td>
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<td>( a ) (Å)</td>
<td>13.9373(6)</td>
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</tr>
<tr>
<td>( b ) (Å)</td>
<td>7.7203(3)</td>
<td>7.3743(6)</td>
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</tr>
<tr>
<td>( c ) (Å)</td>
<td>17.0136(7)</td>
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<td>8.2645(3)</td>
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<td>( \alpha ) (°)</td>
<td>90</td>
<td>68.861(8)</td>
<td>90</td>
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<tr>
<td>( \beta ) (°)</td>
<td>105.984(5)</td>
<td>73.292(8)</td>
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<tr>
<td>( \gamma ) (°)</td>
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<td>( V ) (Å³)</td>
<td>1759.90</td>
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<td>( Z )</td>
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<td>4</td>
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<td>( D_x ) (Mg m⁻³)</td>
<td>1.259</td>
<td>1.353</td>
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<tr>
<td>( \lambda ) (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
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<tr>
<td>( \mu ) (mm⁻¹)</td>
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<td>0.20</td>
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<td>0.976 – 1.000</td>
<td>0.955 – 1.000</td>
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<td>( F(000) )</td>
<td>712</td>
<td>180</td>
<td>648</td>
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<td>( 2\theta_{\text{max}} )</td>
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<td>62</td>
<td>62</td>
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<tr>
<td>Refl. measured</td>
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<td>22785</td>
<td>82578</td>
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<tr>
<td>Refl. indep.</td>
<td>5123</td>
<td>2532</td>
<td>4812</td>
</tr>
<tr>
<td>( R_{\text{int}} )</td>
<td>0.054</td>
<td>0.037</td>
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<td>Parameters</td>
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<td>110</td>
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<td>( wR(F^2, \text{all refl.}) )</td>
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<td>0.081</td>
<td>0.092</td>
</tr>
<tr>
<td>( R(F, &gt;4\sigma(F)) )</td>
<td>0.042</td>
<td>0.033</td>
<td>0.037</td>
</tr>
<tr>
<td>( S )</td>
<td>1.05</td>
<td>1.05</td>
<td>1.08</td>
</tr>
<tr>
<td>Max. ( \Delta \rho ) (e Å⁻³)</td>
<td>0.43, −0.21</td>
<td>0.43, −0.21</td>
<td>0.46, −0.28</td>
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Table S1c: Crystallographic data and structure refinement details for compounds 8e, 2q and 2r.

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<tr>
<th>Compound</th>
<th>8e (C_{18}H_{19}NSi)</th>
<th>2q (C_{16}H_{13}NOS)</th>
<th>2r (C_{18}H_{15}NOS)</th>
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<td>CCDC number</td>
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<tr>
<td>Formula</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$M_r$</td>
<td>309.49</td>
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</tr>
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<td>Cryst. size (mm)</td>
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<td>Crystal system</td>
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<td>monoclinic</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>P(-1)</td>
<td>C2/c</td>
<td>Pbca</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>-173</td>
<td>-173</td>
<td>-173</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>8.52831(11)</td>
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<td>13.1964(2)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>10.39109(14)</td>
<td>9.4103(3)</td>
<td>13.3812(2)</td>
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<td>$c$ (Å)</td>
<td>11.21545(16)</td>
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<td>16.7048(3)</td>
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<td>$\alpha$ (°)</td>
<td>117.5842(14)</td>
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<td>$\beta$ (°)</td>
<td>92.3119(11)</td>
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<td>90</td>
</tr>
<tr>
<td>$\gamma$ (°)</td>
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<td>90</td>
</tr>
<tr>
<td>$V$(Å$^3$)</td>
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</tr>
<tr>
<td>$Z$</td>
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<td>8</td>
</tr>
<tr>
<td>$D_s$ (Mg m$^{-3}$)</td>
<td>1.177</td>
<td>1.323</td>
<td>1.321</td>
</tr>
<tr>
<td>$\lambda$ (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>$\mu$ (mm$^{-1}$)</td>
<td>0.25</td>
<td>0.23</td>
<td>0.22</td>
</tr>
<tr>
<td>Transmissions</td>
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<td>0.790 – 1.000</td>
<td>0.933 – 1.000</td>
</tr>
<tr>
<td>$F(000)$</td>
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<td>1168</td>
<td>1232</td>
</tr>
<tr>
<td>$2\theta_{max}$</td>
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<td>72</td>
<td>72</td>
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<td>Refl. measured</td>
<td>12628</td>
<td>70418</td>
<td>221112</td>
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<td>Refl. indep.</td>
<td>12628</td>
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<td>6774</td>
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<td>$R_{int}$</td>
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<td>0.041</td>
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<td>Parameters</td>
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<td>182</td>
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<td>0.090</td>
<td>0.088</td>
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<tr>
<td>$R(F, &gt;4\sigma(F))$</td>
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<td>0.031</td>
<td>0.037</td>
</tr>
<tr>
<td>$S$</td>
<td>1.07</td>
<td>1.06</td>
<td>1.06</td>
</tr>
<tr>
<td>Max. $\Delta\rho$ (e Å$^{-3}$)</td>
<td>0.49, −0.23</td>
<td>0.53, −0.26</td>
<td>0.53, −0.31</td>
</tr>
</tbody>
</table>

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Thermal ellipsoid plots (all at the 50% probability level):

Fig. S1. Structure of compound 2a in the crystal.

Fig. S2. Structure of compound 2e in the crystal.
Fig. S3. Structure of compound 6d in the crystal.

Fig. S4. Structure of compound 10b in the crystal.
Fig. S5. Structure of compound 10d in the crystal.

Fig. S6. Structure of compound 2s in the crystal.
Fig. S7. Structure of compound 10a' in the crystal.

Fig. S8. Structure of compound 8e in the crystal.
Fig. S9. Structure of compound 2q in the crystal.

Fig. S10. Structure of compound 2r in the crystal.