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Supporting Information

# Catalytic Carbon–Chlorine Bond Activation by Selenium-Based Chalcogen Bond Donors

Patrick Wonner, Lukas Vogel, Florian Kniep, and Stefan M. Huber*[a]

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# Catalytic carbon-chlorine bond activation by selenium-based chalcogen bond donors

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# 1. Experimental Section

## 1.1. General Comments

All experiments were carried out in flame dried *Schlenk* flasks under argon atmosphere and with dry solvents. Solvents used for chromatography were previously distilled. All used chemicals are commercially available and were used without further purification. Thin-layer chromatography was performed by using *Merck TLC aluminium sheets* (silica gel 60, F254). Column chromatography was performed with silica gel (grain size 0.04-0.063 cm, *Merck Si60*) at atmosphere pressure (1-1.5 atm using in some cases a hand pump). The corresponding solvents that were used as eluents as well as the $R_f$ values are listed at the corresponding experiment. Detection of the substances was obtained by fluorescence detection under UV light (wavelength $\lambda = 254$ nm).

## 1.2. Solvents

Dry DCM, ether and THF were received from a *MBRAUN MB SPS-800*. At first solvents were distilled, dried over 4 Å molecular sieve and finally dried on an Alox column. Further dry solvents were dried over flame dried 4Å molecular sieve. The moisture content was determined with a Karl Fischer *Titroline®7500KF trace*.

## 1.3. Chemicals

Chemicals were obtained from *ABCR, Alfa Aesar, Carbolution, Merck, ChemPur, Sigma Aldrich* or *VWR*. Commercially available reagents and starting materials were used without further purification (unless mentioned otherwise).

## 1.4. Analysis Methods

### 1.4.1. NMR Spectroscopy

$^1$H NMR spectra were recorded with a *Bruker DPX-250 NMR* or an *Aviii 300* spectrometer at 298.5 K. $^{13}$C NMR spectra were recorded wiht an *Aviii 300* spectrometer at 298.5 K. $^{19}$F NMR spectra were recorded with a *Bruker DPX-250 NMR* spectrometer at 298.5 K. Peaks were referenced to residual $^1$H signals and $^{13}$C signals from the deuterated solvents and are reported in parts per million (ppm). For $^1$H NMR spectroscopically data, $^{13}$C NMR spectroscopically data and $^{19}$F NMR spectroscopically data, multiplicity (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet), the relative integral and the coupling constant ($J$ in Hz) are indicated if possible.

### 1.4.2. ATR-IR Measurements

IR spectra were recorded with a *Shimadzu IR Affinity - 1S* spectrometer and are reported in $\nu$ = cm$^{-1}$ and are indicted with w (weak), m (middle), s (strong) or vs (very strong).

### 1.4.3. EI and ESI Measurements

Mass spectra were recorded with either a Bruker Daltonics Esquire 6000 instrument (ESI) or a VG Instruments Autospec / EBEE-Geometrie (EI).

### 1.4.4. Elemental Aanalysis

CHNS Elemental Analysis was performed with a *vario Micro cube* from *Elementar Analysentechnik*.

## 1.5. Synthesis of starting materials and known compounds

1-methoxyisochroman[1], 1-chloroisochroman[1] (**1**), tert-butyl((1-methoxyvinyl)oxy)dimethylsilane[2] (**2**) (TBS), *m*-HH-Im$^{\text{Oct}}$/OTf, (**4**$^{\mathbf{N\text{-}OCt}}$)[3], *m*-HH-Im$^{\text{Me}}$/OTf (**4**$^{\mathbf{N\text{-}Me}}$)[3], octyl trifluoromethanesulfonate (Oct–OTf)[4], 1,3-bis(imidazole-1-yl)benzene (**4**)[5], **syn-8**$^{\mathbf{Br}}$[6], **syn-8**$^{\mathbf{I}}$[6], **syn-7**$^{\mathbf{N\text{-}R/Se\text{-}R'}}$[7], **anti-7**$^{\mathbf{N\text{-}R/Se\text{-}R'}}$[7], **syn/anti-9**$^{\mathbf{N\text{-}R/H}}$[7], **syn-10**$^{\mathbf{Se}}$[7] and **syn-11**$^{\mathbf{Se}}$[7] were synthesized according to literature procedures.

Commercially available methy ltrifluoromethanesulfonate was used as received and was stored under argon at 7 °C.

# *1.6. Synthesis Procedures of new compounds*

## *1.6.1. General Selenation Procedure*

Under an argon atmosphere the respective bisimidazolium (1 eq.) compound was added to a schlenk flask and dissolved in dry methanol (0.17 M; dried for 24h over molecular sieve). To the solution elemental selenium powder (2.5 eq.) and caesium carbonate (2.5 eq) were added. The mixture was refluxed for 24 h and finally filtered (hot solution) over a plug of silica and rinsed with DCM. After the solvent was removed the crude solid was purified by column chromatography (solvents are mentioned for specific compounds). Finally, the solvent was removed under reduced pressure and the respective selenated compound was obtained.

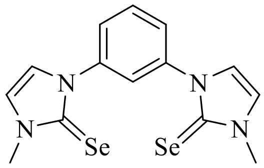
## *1.6.2. General Octylation Procedure for Selenated Compounds*

Under an argon atmosphere the respective bisselenated compound (1 eq.) was dissolved in dry DCM and cooled to 0 °C. Then octyl trifluoromethanesulfonate (4 eq.) was slowly added and the reaction mixture was stirred for (24 h) at room temperature. After the solvent was removed under reduced pressure the crude residual was washed several times with DEE, dissolved in DCM and was stirred for 2 h in the presence of charcoal. Finally, the mixture was filtered over a plug Celite® and removal of the solvent yielded the octylated selenium compound.

## *1.6.3. General Methylation Procedure for Selenated Compounds*

Under an argon atmosphere the respective bisselenated compound (1 eq.) was dissolved in dry DCM and cooled to 0 °C. Then methyl trifluoromethanesulfonate (4 eq.) was slowly added and the reaction mixture was stirred for (24 h) at room temperature. After the solvent was removed under reduced pressure the crude residual was washed several times with DEE, dissolved in DCM and was stirred for 2 h in the presence of charcoal. Finally, the mixture was filtered over a plug Celite® and removal of the solvent yielded the methylated selenium compound.

## *1.6.4. Synthesis of $5^{N\text{-}Me}$*



Chemical Formula: $C_{14}H_{14}N_4Se_2$
Exact Mass: 397.9549 g/mol
Elemental Analysis: C, 42.44; H, 3.56; N, 14.14; Se, 39.86

**$5^{N\text{-}Me}$** was synthesised in accord to general selenation procedure. For the reaction 7.48 g of **$4^{N\text{-}Me}$** (13.9 mmol, 1 eq.), 2.74 g selenium powder (34.7 mmol, 2.5 eq.) and 11.3 g caesium carbonate (34.7 mmol, 2.5 eq.) were used. Purification by column chromatography with ethyl acetate yielded 1.21 g **$5^{N\text{-}Me}$** (3.05 mmol, 22%) as slightly yellowish solid.

**$R_f$** **=** 0.375 (ethyl acetate)

**$^1$H NMR (250 MHz, Chloroform-*d*):**

δ [ppm] = 7.95 (m, 1H, $H_{Arom.}$), 7.76 (t, 1H, $J = 1.5$ Hz, $H_{Arom.}$), 7.72 (d, 1H, $J = 2.2$ Hz, $H_{Arom.}$), 7.62 (dd, 1H, $J = 7.5$ Hz, 1.5 Hz, $H_{Arom.}$), 7.18 (d, 2H, $J = 2.3$ Hz, $H_{Imidazol}$), 7.01 (d, 2H, $J = 2.3$ Hz, $H_{Imidazol}$), 3.78 (s, 6H, $-N_{(Arom.)}-CH_3$).

**$^{13}$C NMR (75 MHz, DMSO-*d*$_6$):**

δ [ppm] = 155.61 (C=Se), 138.71, 129.00, 125.46, 123.32, 121.84, 120.27, 36.79.

**ATR-IR:**

$\tilde{\nu}$ [cm$^{-1}$] = 3153 (w), 3074 (w), 1597 (s), 1568 (m), 1492 (s), 1463 (s), 1446 (s), 1404 (m), 1352 (s), 1280 (vs), 1261 (vs), 1232 (vs), 1219 (vs), 1193 (m), 1170 (vs), 1078 (m), 1035 (vs), 977 (m), 920 (w), 879 (s), 833 (w), 800 (m), 779 (s), 729 (vs), 690 (vs), 661 (m), 632 (s), 607 (w), 509 (m), 493 (w).

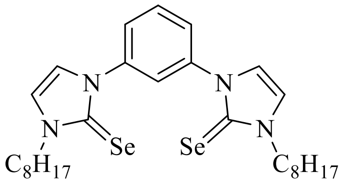
**EI-MS (70 EV):**

*m*/*z* (%) = 397 (60) $[M]^+$, 317 (100) $[M-Se]^+$, 236 (40) $[M-C_4N_2SeH_5]^+$, 159 (15) $[C_4N_2SeH_5]^+$.

**CHNS:**

| | C | H | N | S |
|---|---|---|---|---|
| calc. | 42.44 | 3.56 | 14.14 | / |
| found | 42.66 | 3.54 | 14.41 | / |

## 1.6.5. *Synthesis of* $5^{N\text{-}Oct}$



Chemical Formula: $C_{28}H_{42}N_4Se_2$
Exact Mass: 594.1740 g/mol
Elemental Analysis: C, 56.75; H, 7.14; N, 9.45; Se, 26.65

**$5^{N\text{-}Oct}$** was synthesised in accord to general selenation procedure. For the reaction 6.62 g of **$4^{N\text{-}Oct}$** (8.68 mmol, 1 eq.), 1.71 g selenium powder (21.7 mmol, 2.5 eq.) and 7.07 g caesium carbonate (21.7 mmol, 2.5 eq.) were used. Purification by column chromatography with pentane:ethyl acetate (1:1) yielded 2.52 g **$5^{N\text{-}Oct}$** (4.23 mmol, 49%) as slightly yellowish solid.

**$R_f$** **=** 0.68 (pentane:ethyl acetate, 1:1)

**$^1$H NMR (250 MHz, Chloroform-*d*):**

δ [ppm] = 7.92 (m, 1H, $H_{Arom.}$), 7.70 (dd, 2H, $J$ = 7.5 Hz, 1.6 Hz, $H_{Arom.}$), 7.57 (dd, 1H, $J$ = 8.0 Hz, 1.7 Hz, $H_{Arom.}$), 7.17 (d, 2H, $J$ = 1.9 Hz, $H_{Imidazol}$), 6.98 (d, 2H, $J$ = 2.4 Hz, $H_{Imidazol}$), 4.17 (t, 4H, $J$ = 7.5 Hz, -$N_{(Arom.)}$-C$H_2$-$CH_2$-$(CH_2)_5$-$CH_3$), 1.83 (m, 4H, -$N_{(Arom.)}$-$CH_2$-C$H_2$-$(CH_2)_5$-$CH_3$), 1.33 (m, 20H, -$N_{(Arom.)}$-$CH_2$-$CH_2$-(C$H_2$)$_5$-$CH_3$), 0.85 (t, 6H, $J$ = 6.5 Hz, -$(CH_2)_7$-C$H_3$).

**$^{13}$C NMR (75 MHz, Acetonitrile-*d*$_3$):**

δ [ppm] = 157.39 (C=Se), 140.25, 129.98, 127.21, 125.49, 121.20, 50.49, 32.52, 29,51, 27.12, 23.36, 14.39.

**ATR-IR:**

$\tilde{\nu}$ [cm$^{-1}$] = 3103 (w), 3084 (w), 2954 (m), 2922 (vs), 2852 (s); 1604 (s), 1492 (vs), 1413 (vs), 1390 (vs), 1328 (m), 1307 (m), 1253 (s), 1236 (w), 1220 (w), 1168 (w), 1130 (w), 1095 (m), 945 (m), 908 (w), 869 (m), 839 (w), 794 (s), 773 (m), 719 (s), 707 (w), 686 (vs), 673 (w), 659 (s), 613 (w), 601 (w), 542 (w), 453 (w).

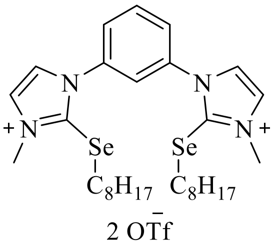
**EI-MS (70 EV):**

*m*/*z* (%) = 594 (10) $[M]^+$, 513 (40) $[M-Se]^+$, 334 (15) $[M-C_{11}N_2H_{19}Se]^+$.

**CHNS:**

| | C | H | N | S |
|---|---|---|---|---|
| calc. | 56.75 | 7.14 | 9.45 | / |
| found | 56.89 | 7.09 | 9.57 | / |

## 1.6.6. *Synthesis of 6$^{N\text{-}Me/Se\text{-}Oct}$*



Chemical Formula: $C_{32}H_{48}F_6N_4O_6S_2Se_2$
Exact Mass: 922.1239 g/mol
Elemental Analysis: C, 41.74; H, 5.25; F, 12.38; N, 6.08; O, 10.43; S, 6.96; Se, 17.15

**6$^{\mathbf{N\text{-}Me/Se\text{-}Oct}}$** was synthesised in accord to general octylation procedure for selenated compounds. For the reaction 0.40 g **5$^{\mathbf{N\text{-}Me}}$** (1.01 mmol, 1 eq.) and 1.12 g octyl trifluoromethanesulfonate (0.93 ml, 4.04 mmol, 4 eq.) were used. After purification 0.54 g **6$^{\mathbf{N\text{-}Me/Se\text{-}Oct}}$** (0.59 mmol, 56%) was obtained as slightly yellowish crystalline foam.

**$^1$H NMR (250 MHz, Chloroform-*d*):**

δ [ppm] = 8.00 (s, 1H, $H_{Arom.}$), 7.85 (m, 7H, $H_{Arom.}$ and $H_{Imidazol}$), 4.07 (s, 6H, -$N_{(Arom.)}$-C$H_3$),
2.85 (t, 4H, $J$ = 7.5 Hz, -$N_{(Arom.)}$-C$H_2$-$CH_2$-$(CH_2)_5$-$CH_3$),
1.50 (m, 4H, -$N_{(Arom.)}$-$CH_2$-C$H_2$-$(CH_2)_5$-$CH_3$),
1.20 (m, 20H, -N $_{Arom.)}$-$CH_2$-$CH_2$-(C$H_2$)$_5$-$CH_3$),
0.85 (t, 6H, $J$ = 6.5 Hz, -$(CH_2)_7$-C$H_3$) ppm.

**$^{13}$C NMR (75 MHz, Acetonitrile-*d*$_3$):**

δ [ppm] = 138.17, 132.40, 130.22, 126.72, 122.14 (d, $J$ = 320.9 Hz), 38.99, 32.48, 31.29, 29.47, 23.34, 14.38.

**$^{19}$F NMR (235 MHz, Chloroform-*d*):**

δ [ppm] = -78.40 (s, 6F, $O_3S$-C$F_3$) ppm.

**ATR-IR:**

$\tilde{\nu}$ [cm$^{-1}$] = 3120 (w), 2922 (m), 2852 (m), 1610 (w), 1573 (w), 1500 (s), 1477 (w), 1456 (w), 1409 (w), 1257 (vs), 1222 (vs), 1134 (vs), 1028 (vs), 985 (w), 896 (w), 785 (s), 750 (s), 723 (w), 690 (s), 632 (vs), 570 (s), 516 (s), 459 (w).

**ESI-MS:**

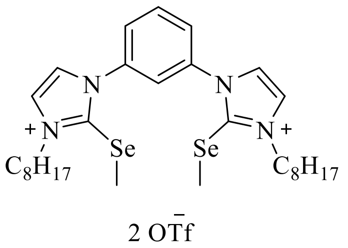
*m*/*z* (+) = found 255.01 [M$^+$−Oct], calculated 312.10.

*m*/*z* (-) = found 148.42 [M$^-$], calculated 148.95.

**CHNS:**

| | C | H | N | S |
|---|---|---|---|---|
| calc. | 41.74 | 5.25 | 6.08 | 6.96 |
| found | 41.82 | 5.19 | 6.05 | 6.90 |

## 1.6.7. *Synthesis of $6^{N\text{-}Oct/Se\text{-}Me}$*



Chemical Formula: $C_{32}H_{48}F_6N_4O_6S_2Se_2$
Exact Mass: 922.1239 g/mol
Elemental Analysis: C, 41.74; H, 5.25; F, 12.38; N, 6.08; O, 10.43; S, 6.96; Se, 17.15

**$6^{N\text{-}Oct/Se\text{-}Me}$** was synthesised in accord to general methylation procedure for selenated compounds. For the reaction 0.85 g **$5^{N\text{-}Oct}$** (1.43 mmol, 1 eq.) and 0.94 g methy ltrifluoromethanesulfonate (0.63 ml, 5.74 mmol, 4 eq.) were used. After purification 0.99 g **$6^{N\text{-}Oct/Se\text{-}Me}$** (1.08 mmol, 75%) was obtained as slightly beige crystalline foam.

**$^1$H NMR (250 MHz, Chloroform-*d*):**

δ [ppm] = 8.11 (s, 1H, $H_{Arom.}$), 7.89 (m, 4H, $H_{Arom.}$), 7.79 (t, 1H, *J* = 7.5 Hz, $H_{Imidazol}$),
7.70 (d, 2H, *J* = 2.0 Hz, $H_{Arom.}$),
4.35 (t, 4H, *3J* = 7.5 Hz, -$N_{(Arom.)}$-C*H*$_2$-$CH_2$-$(CH_2)_5$-$CH_3$),
2.22 (s, 6H, =Se-C*H*$_3$), 1.91 (m, 4H, -$N_{(Arom.)}$-$CH_2$-C*H*$_2$-$(CH_2)_5$-$CH_3$),
1.30 (m, 20H, -$N_{(Arom.)}$-$CH_2$-$CH_2$-(C*H*$_2$)$_5$-$CH_3$),
0.87 (t, 6H, *J* = 6.0 Hz, -$(CH_2)_7$-C*H*$_3$) ppm.

**$^{13}$C NMR (75 MHz, Chloroform-*d*):**

δ [ppm] = 136.8, 131.5, 129.1, 126.2, 125.9, 124.6, 120.6 (q, $J_{C\text{-}F}$ = 318.7 Hz, $O_3S\text{-}CF_3$), 52.0, 31.8, 30.4, 29.1, 29.1, 26.6, 22.7, 14.2, 10.9.

**$^{19}$F NMR (235 MHz, Chloroform-*d*):**

δ [ppm] = -78.35 (s, 6F, O3S-C*F*3) ppm.

**ATR-IR:**

$\tilde{\nu}$ [cm$^{-1}$] = 3115 (w), 2926 (m), 2856 (w), 1606 (w), 1564 (w), 1498 (w), 1485 (w), 1436 (w), 1375 (w), 1251 (vs), 1222 (vs), 1151 (vs), 1028 (vs), 871 (w), 808 (w), 773 (w), 756 (w), 690 (s), 634 (vs), 572 (s), 516 (vs), 462 (w).

**ESI-MS:**

*m*/*z* (+) = found 311.09 [M$^+$], calculated 312.11

*m*/*z* (-) = found 148.43 [M$^-$], calculated 148.95

**CHNS:**

| | C | H | N | S |
|---|---|---|---|---|
| calc. | 41.74 | 5.25 | 6.08 | 6.96 |
| found | 41.18 | 5.11 | 5.98 | 6.98 |

# *2. Catalysis Experiments*

## *2.1. 1-chloroisochroman and silyl enol ether*

tert-Butyl((1-methoxyvinyl)oxy)dimethyl-silane[2] was stored at -32 °C under argon and used purely. 1-Chloroisochroman was stored under argon at -32 °C as 1 M stock solution in dry THF.

## *2.2. General procedure for catalysed additions of silyl enol ether to 1-chloroisochroman*

A flame dried schlenk tube was charged with the chalcogen-, halogen-, hydrogen-bond catalyst, or reference compound, evacuated for 10 minutes, backfilled with argon, and 0.5 mL of THF was added as solvent. The tube was cooled to -78 °C, 1-chloroisochroman (**1**) was added as a 1 M stock solution in dry THF (0.10 mL, 0.10 mmol, 1.00 eq) and the mixture was allowed to stir for 15 minutes before the silyl enol ether **2** (0.15 mmol, 1.50 eq) was added. The reaction mixture was maintained at low temperature for 118 h and quenched by addition of 0.2 mL of a 0.5 M solution of NaOMe in methanol. The reaction was diluted with diethylether, filtered through a pad of silica and rinsed with 200 mL of diethylether. The solvent was evaporated and the crude residue was dissolved in $CDCl_3$. Final $^1H$ NMR analysis yielded the relative amount of formed product **3** compared to methoxyisochroman and the dieether of **1**.

As relative standard, always 1-methoxyisochroman was chosen and the integral was set as 1. Then product **3** and the dieether (if formed) were integrated. Finally, 100% were divided through the sum of all integrals and multiplied by the respective integral, revealing the appropriate NMR yield for each compound (see Figure 5.).

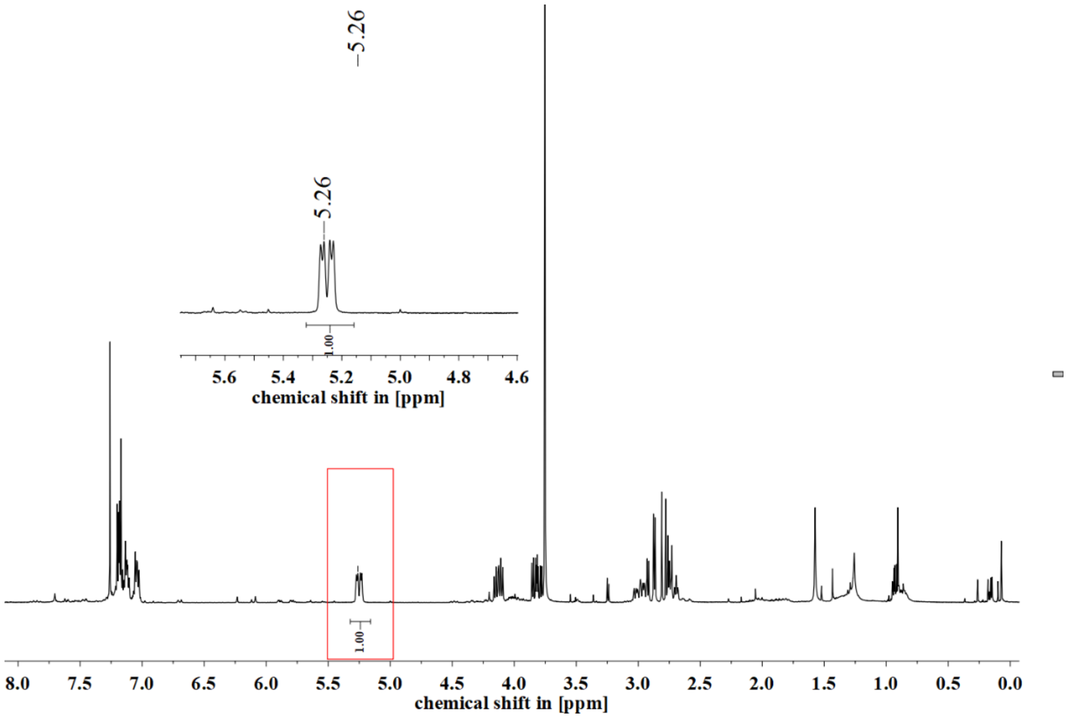


**Figure 1**. $^1$H NMR of **3** in $CDCl_3$. Integration of relevant proton.

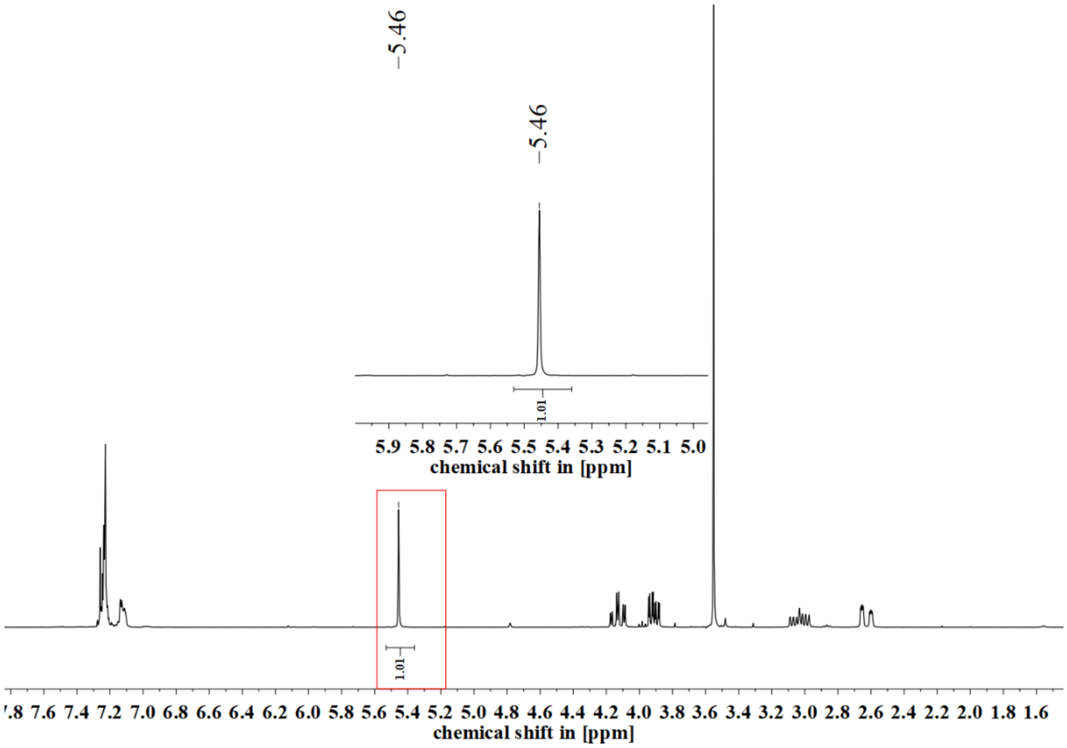


**Figure 2.** $^1$H NMR of 1-methoxyisochroman in $CDCl_3$. Integration of relevant proton.

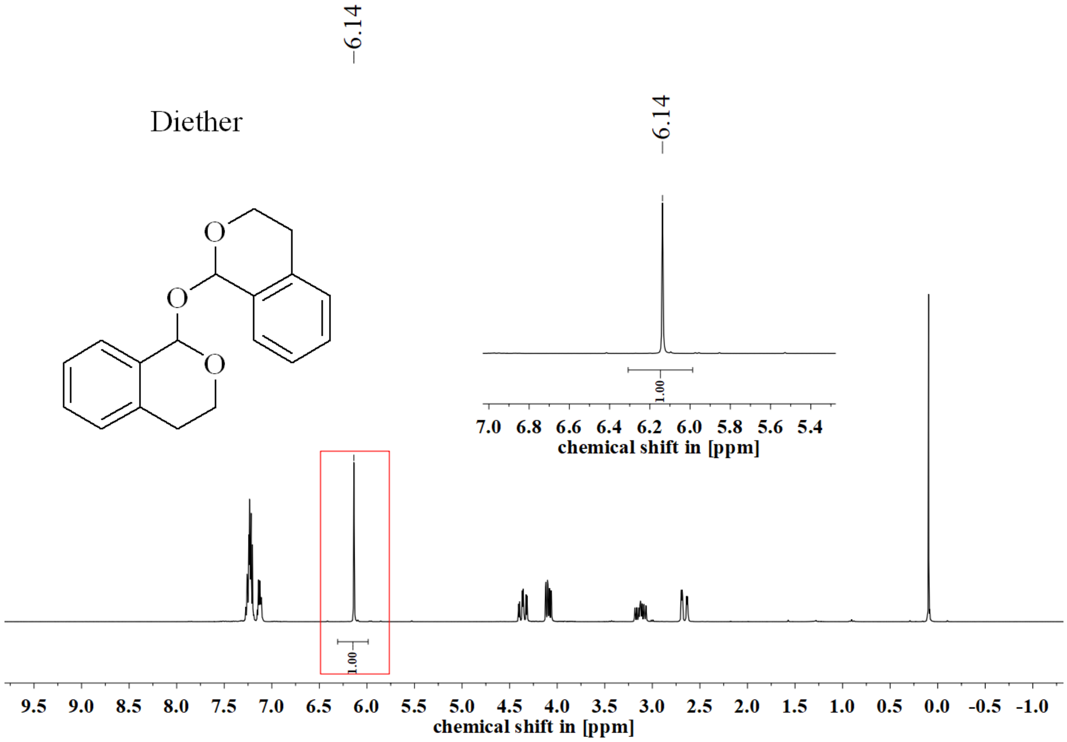


**Figure 3.** $^1$H NMR of diether obtained by hydrolysis of **1** in $CDCl_3$. Integration of relevant proton.

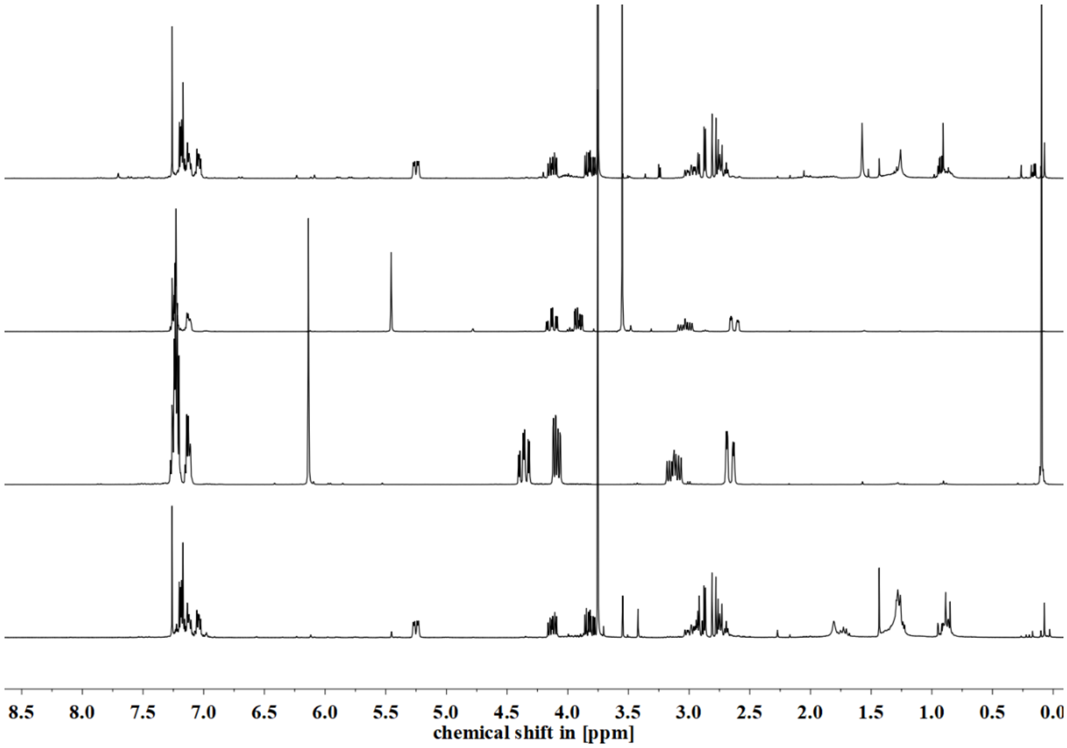


**Figure 4.** $^1$H NMR stack plot of selected reaction (bottom) compared to the dieether (see above) (second), 1-methoxyisochroman (third) and the product **3** (top).

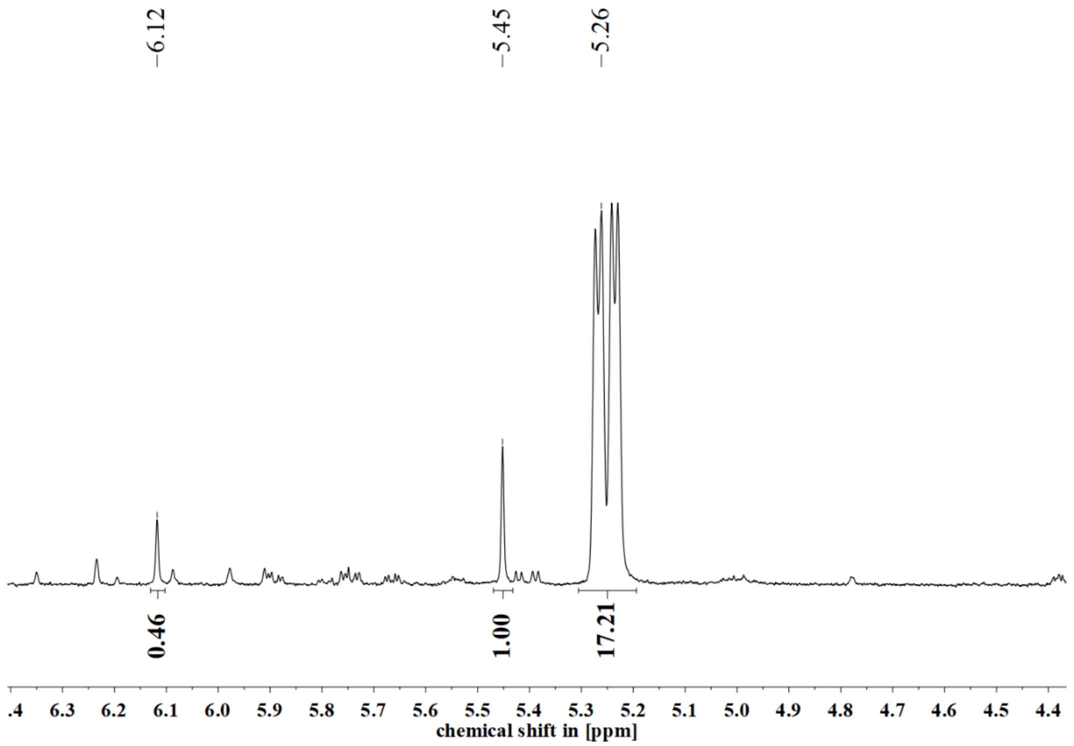


**Figure 5.** Representative $^1$ H NMR spectra as selected example for analysis in $CDCl_3$. Analysis of this spectra shows that the sum of integrals is 18.44. This results in 93.3% of product **3**, 5.4% of 1-methoxyisochroman and 1.3% dieether (see above).

# 3. *Titration Experiments*

For pipetting *Hamilton*®-syringes were used. All experiments were conducted at ambient temperature and in *Norell*® 502 NMR-Tubes. 5.7 mg (5 µmol) of the Host (**XX**) were dissolved in deuterated acetonitrile and diluted in a volumetric flask to give 1 ml of a 5 mM solution. A stock-solution of tetraoctylammonium bromide (ChB-Acceptor/Guest) was prepared in 0.2 M concentration by dissolving 109.4 mg (200 µmol) in deuterated acetonitrile in a 1 ml volumetric flask. For every measured point a NMR-tube was charged with 100 µl of the host solution, 400 µl of $d_3$-MeCN and corresponding amounts of the guest solution were added sequentially. The NMR-spectra were measured with a *Bruker* AVIII-300. $^1$H-Spectra were measured with 16 scans and the host to guest ratio was checked by integration of the signals and corrected if necessary.

For the determination of the binding constants the shift of the C2-proton of the isopropyl group bound to the selenium atoms was observed relative to the signal of the solvent (for **syn-7**$^{\textbf{N-Oct/Se-iPr}}$). In case of **6**$^{\textbf{N-Me/Se-Oct}}$ the Se-C*H*2 proton was observed and for **6**$^{\textbf{N-Oct/Se-Me}}$ the Se-C$H_3$ proton was observed.

The measured shifts (Δppm) were plotted against the guest-equivalents and the resulting curve was fitted.[8] For the calculations of the binding constants (K) a 1:1 stoichiometry was assumed. No decomposition of the host / ChB was observed in $^{1}H$ NMR (and $^{19}F$ NMR spectra for selected compound).

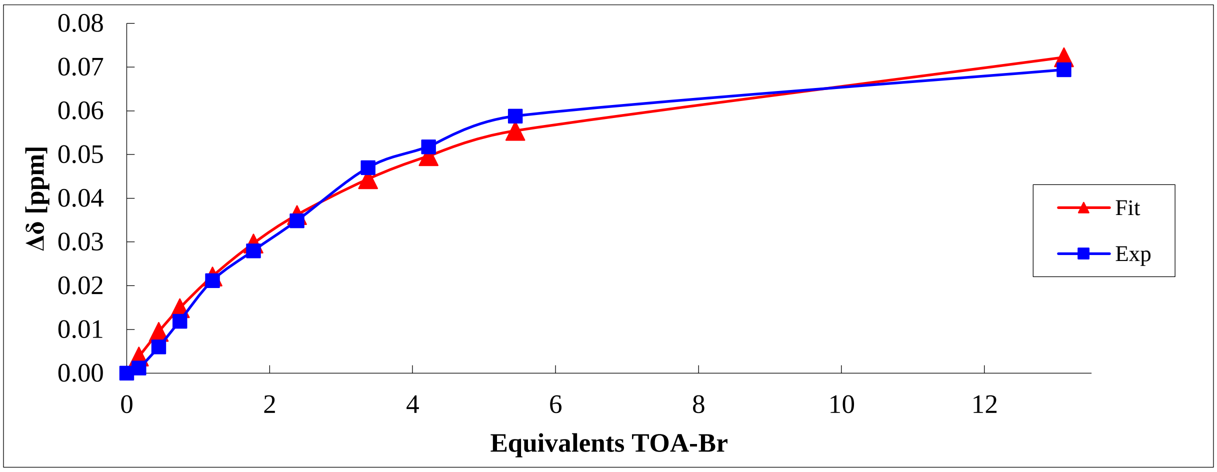


**Figure 6.** Titration Plot of **syn-7**$^{\mathbf{N\text{-}Oct/Se\text{-}iPr}}$ (host) in MeCN-$d_3$ and N(Oct)$_4$Br as guest molecule. The determined value for binding constant is 341 M$^{-1}$.

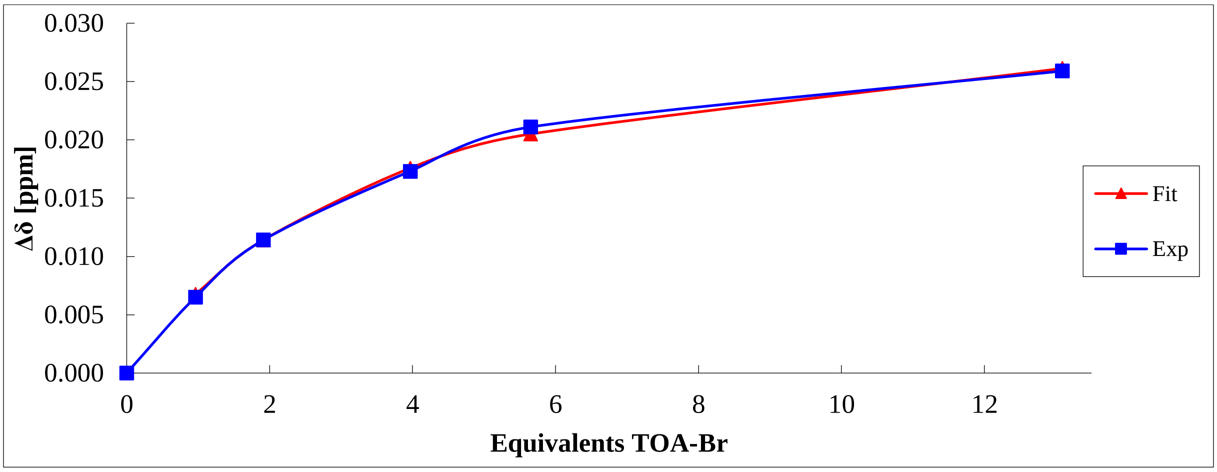


**Figure 7.** Titration Plot of **6**$^{\mathbf{N\text{-}Me/Se\text{-}Oct}}$ (host) in MeCN-$d_3$ and N(Oct)$_4$Br as guest molecule. The determined value for binding constant is 351 M$^{-1}$.

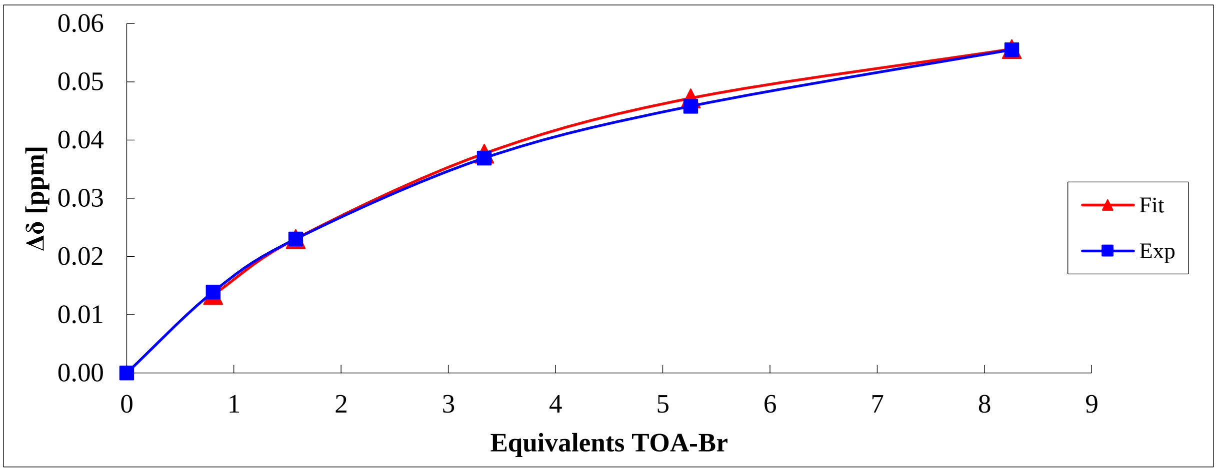


**Figure 8.** Titration Plot of **6**$^{\text{N-Oct/Se-Me}}$ (host) in MeCN-*d3* and $N(Oct)_4Br$ as guest molecule. The determined value for binding constant is 317 $M^{-1}$.

## 4. *Determinination of $k_{rel}$ values*

$K_{rel}$ was determined by a linear fit from the kinetic plot. Therefore, the gradient between zero hours and 16 h and the corresponding yield of **3** was determined for selected curves. The reaction with selenoureas **syn-11**$^{Se}$ was chosen as standard gradient with a value of $k_{rel}$ = 1. All other $k_{rel}$ values were referred to this value. For the linear fit a straight was (see plot at the end) pasted. The determined values are:

| **Compound** | $k_{rel}$ |
|---|---|
| **syn-11**$^{Se}$ | 1 |
| **syn-9**$^{Br}$ | 3.2 |
| **syn-7**$^{N\text{-}Me/Se\text{-}Oct}$ | 25.3 |

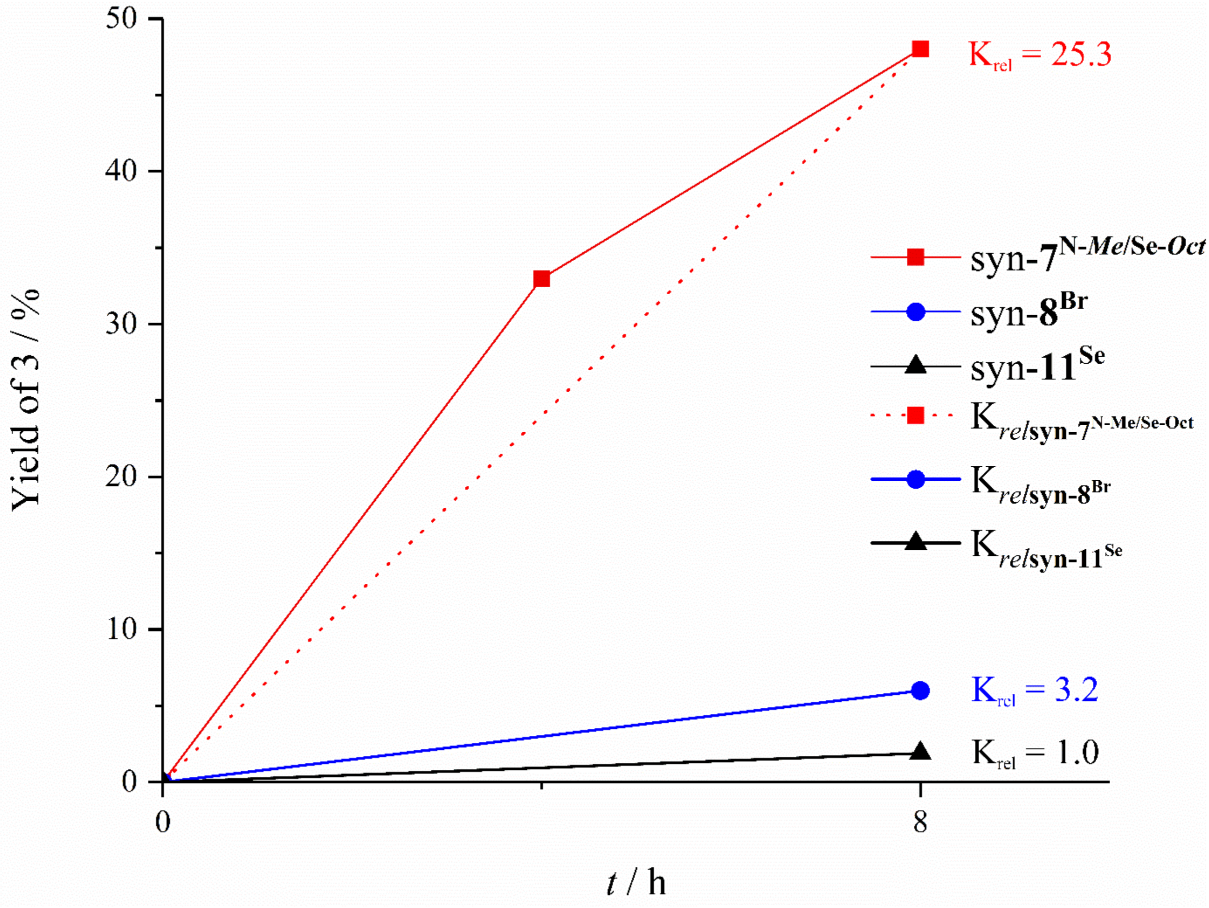


**Figure 9**. Kinetic plot with linear fit for determination of $K_{rel}$.

## 5. Stability Measurements - $^{19}$F NMR

Stability of used chalcogen bond donors before and after the reaction was monitored by $^{19}$F NMR. In the following graph, selected $^{19}$F NMR spectra for the *syn* atropisomers are shown. All compounds proved to be stable under reaction conditions.

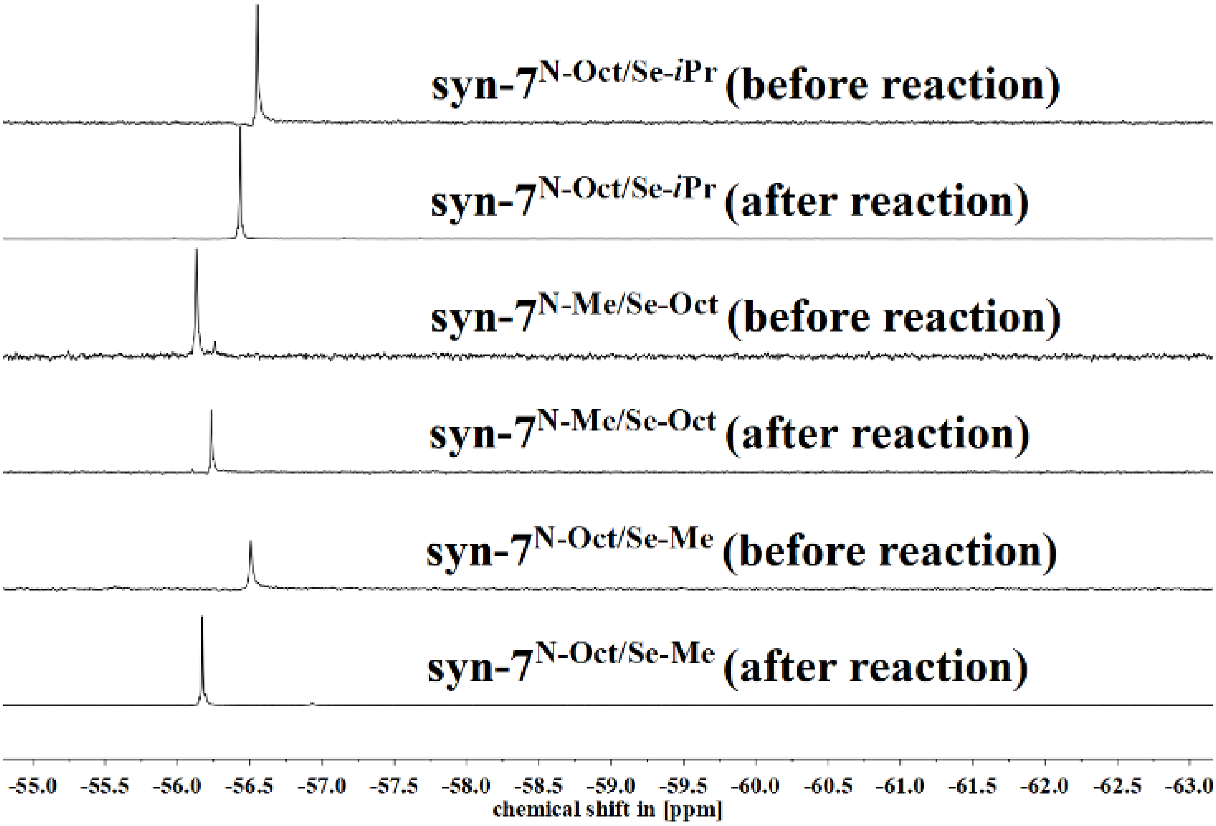
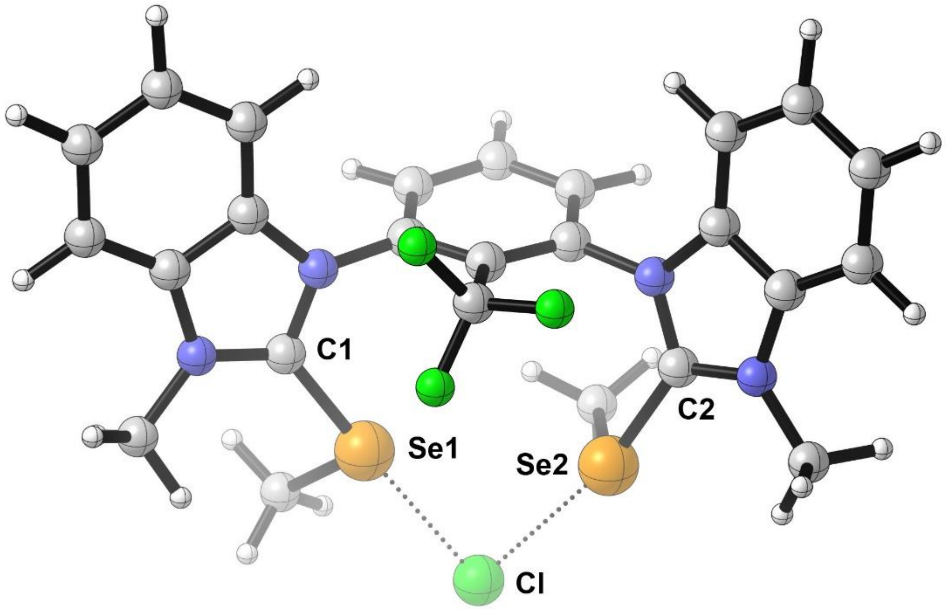


**Figure 10.** $^{19}$F NMR spectra of cationic selenium based chalcogen bond donors before and after the reaction of Scheme 1. Spectra are normalized to the signal of triflate at -78.3 ppm. Slight variations of the chemical shift are likely due to complex formation during the reaction.

# 6. DFT Calculations

Orientating DFT calculations were performed to demonstrate the feasibility of a bidentate coordination of a bis(benzimidazolium)-based model chalcogen bond donor (with methyl groups on nitrogen and selenium) to chloride. To this end, the M06-2X density functional[9] was employed with the Gaussian09 suite of programs,[10] in combination with a triple-zeta TZVPP basis set.[11] The optimized structure was confirmed as a minimum by the absence of imaginary frequencies. The complex is shown below (plot by CYLview).[12]



Selected bond distances (Å) and angles (°):

Se1-Cl = 2.74

C1-Se1-Cl = 178

Se2-Cl = 2.92

C2-Se2-Cl = 168

Se1-Cl-Se2 = 79

Coordinates:

| | | | |
|---|---|---|---|
| H | -2.09803800 | -1.18491600 | 2.90903700 |
| C | -1.13423800 | -1.13971400 | 2.42029300 |
| C | 1.29574800 | -0.88268900 | 1.12338200 |
| C | -1.08585200 | -1.01305400 | 1.04238900 |

| | | | |
|---|---|---|---|
| C | 0.04216500 | -1.18463500 | 3.15127100 |
| C | 1.25380900 | -1.02046100 | 2.50338800 |
| C | 0.13078000 | -0.95789400 | 0.35951800 |
| H | 0.01090000 | -1.29206500 | 4.22588100 |
| H | 2.18045100 | -0.96767800 | 3.05930700 |
| N | 2.55868400 | -0.60956900 | 0.51898200 |
| N | -2.32225200 | -0.88540600 | 0.33610400 |
| C | -2.84651600 | 0.30025600 | -0.06973100 |
| N | -4.06788800 | 0.05603100 | -0.55399500 |
| C | -3.24855800 | -1.90620900 | 0.12805300 |
| C | -4.36619300 | -1.29977800 | -0.43573600 |
| C | 2.89255400 | 0.56492600 | -0.06988100 |
| N | 4.07619400 | 0.39980500 | -0.66737900 |
| C | 3.56197000 | -1.54887300 | 0.29302200 |
| C | 4.52506300 | -0.90330600 | -0.47398700 |
| C | -4.93154400 | 1.03499100 | -1.19650200 |
| H | -5.67823400 | 1.40628700 | -0.49727900 |
| H | -4.31686500 | 1.85524400 | -1.55609000 |
| H | -5.42429900 | 0.55802500 | -2.04014400 |
| C | 4.82981500 | 1.41226500 | -1.39378000 |
| H | 4.79305200 | 1.20231200 | -2.46082200 |
| H | 4.39339800 | 2.38580500 | -1.19369600 |
| H | 5.86139900 | 1.39284000 | -1.04964600 |
| C | 1.46498500 | 2.21225400 | 1.77565500 |
| H | 0.49973900 | 1.75996700 | 1.98433100 |
| H | 2.27610800 | 1.71801000 | 2.30193200 |
| H | 1.43194100 | 3.27052600 | 2.00693800 |
| C | -3.22793600 | 3.07154000 | 0.70265100 |
| H | -3.67029200 | 3.66828300 | -0.08771700 |
| H | -3.96860600 | 2.45498400 | 1.20297600 |
| H | -2.72300400 | 3.72133700 | 1.40884300 |
| Se | 1.79659800 | 2.15531800 | -0.15499800 |
| Se | -1.80201800 | 1.95231700 | -0.03829500 |
| C | -5.49504700 | -2.03118300 | -0.77721100 |
| C | -3.19544000 | -3.26916700 | 0.37406600 |
| C | 3.68998200 | -2.87722900 | 0.66935600 |
| C | 5.67632600 | -1.55285100 | -0.89719900 |
| H | -6.36805200 | -1.56541900 | -1.21149900 |
| H | -2.31812100 | -3.73406600 | 0.80138100 |
| H | 6.42544000 | -1.05505500 | -1.49612400 |
| H | 2.93255800 | -3.37784200 | 1.25595500 |
| C | -5.44943700 | -3.39166000 | -0.52894500 |
| C | -4.32117300 | -3.99954000 | 0.03647800 |
| C | 4.83673300 | -3.52680100 | 0.24824400 |
| C | 5.81279600 | -2.87607900 | -0.51812700 |
| H | -6.30574600 | -4.00179500 | -0.77810100 |
| H | -4.33036800 | -5.06607800 | 0.20988000 |
| H | 6.69237000 | -3.42422600 | -0.82377900 |
| H | 4.98359300 | -4.56371700 | 0.51463400 |
| C | 0.11735000 | -1.10666800 | -1.15544600 |
| F | -0.59294100 | -2.19703300 | -1.46990500 |

| | | | |
|---|---|---|---|
| F | 1.33412400 | -1.27644900 | -1.66931000 |
| F | -0.44212100 | -0.07856300 | -1.78337000 |
| Cl | -0.26286000 | 4.22184700 | 0.05210000 |

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