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Supporting Information

Carbon–Halogen Bond Activation by Selenium-Based Chalcogen Bonding

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Table of Contents

1. Experimental Section

1.1. General Remarks

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 atmospheric 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 achieved by fluorescence detection under UV light (wavelength λ = 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 and ^{13}C NMR spectra were recorded with a *Bruker DPX-250 NMR*, a *Bruker DPX-400 NMR* or a *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, dddd = doublet of doublet of doublet of doublet, t = triplet, td = triplet of doublet, 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*.

1.4.5. XRD Measurements

XRD Measurements were performed on a single crystal-X-ray-diffractometer *Kappa Apex II* from Bruker.

1.5. Synthesis Procedures of known compounds

1.5.1. Synthesis of Oct-OTf

Oct-OTf

Chemical Formula: $C_9H_{15}F_3O_4S$
Exact Mass: 276.06431 g/mol
Elemental Analysis: C, 39.13; H, 5.47; F, 20.63; O, 23.16; S, 11.60

Octyltrifluoromethansulfoante was synthesised according to an already published procedure.[1] The purity of Oct-OTf was determined by ^{1}H NMR and ^{19}F NMR spectroscopy.

1.5.2. Synthesis of iPr-OTf

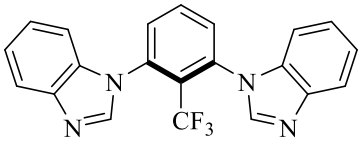
*i*Pr-OTf

Chemical Formula: $C_4H_7F_3O_3S$
Exact Mass: 192.00680 g/mol
Elemental Analysis: C, 25.00; H, 3.67; F, 29.66; O, 24.98; S, 16.68

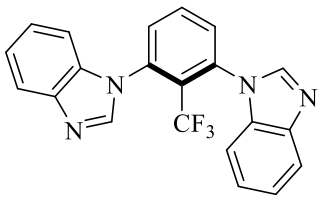
iso-Propyltrifluoromethansulfoante was synthesised according to an already published procedure.[1] The purity of *i*Pr-OTf was determined by ^{1}H NMR and ^{19}F NMR spectroscopy.

1.5.3. Synthesis of syn/anti-3

Syn



Anti

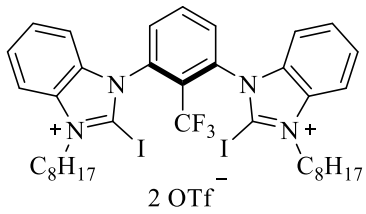


Chemical Formula: $C_{21}H_{13}F_3N_4$
Exact Mass: 378.10923 g/mol
Elemental Analysis: C, 66.66; H, 3.46; F, 15.06; N, 14.81

syn/*anti*-**3** was synthesised according to an already published procedure.[1] The *syn* and *anti*-isomer cannot be separated by column chromatography. The *anti*-isomer represents the major product (ratio *anti* : *syn* = 60:40).

1.5.4. Synthesis of syn-10^{I}

Syn

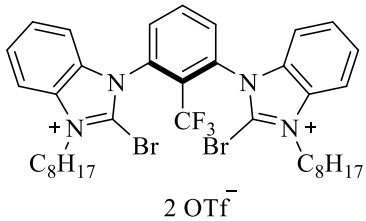


Chemical Formula: $C_{39}H_{45}F_9I_2N_4O_6S_2$
Exact Mass: 1154,07152 g/mol
Elemental Analysis: C, 40.57; H, 3.93; F, 14.81; I, 21.98; N, 4.85; O, 8.31; S, 5.55

Syn-**10^{I}** was synthesised according to an already published procedure.[1]

1.5.5. Synthesis of Syn-10^{Br}

Syn

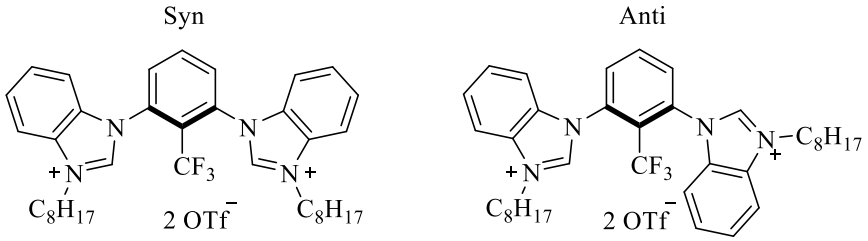


Chemical Formula: $C_{39}H_{45}Br_2F_9N_4O_6S_2$
Exact Mass: 1058,09926 g/mol
Elemental Analysis: C, 44.16; H, 4.28; Br, 15.07; F, 16.12; N, 5.28; O, 9.05; S, 6.04

Syn-**10^{Br}** was synthesised according to an already published procedure.[1]

1.6. Synthesis Procedures of new compounds

1.6.1. Synthesis of syn/anti-4$^{N\text{-}Oct}$



Chemical Formula: $C_{39}H_{47}F_9N_4O_6S_2$
Exact Mass: 902.27823 g/mol
Elemental Analysis: C, 51.88; H, 5.25; F, 18.94; N, 6.21; O, 10.63; S, 7.10

Under an argon atmosphere 3.00 g of compound syn/*anti*-**3** (7.93 mmol, 1 eq.) were dissolved in 50 ml dry DCM (0.16 M) and 8.76 g of octyltrifluoromethanesulfonate (7.30 ml, 31.72 mmol, 4 eq.) were added over a period of 1h under ice bath cooling. After heat development stopped the mixture was stirred for further 4 days while *syn/anti*-**4**$^{N\text{-}Oct}$ precipitated as solid compound. After the solvent was removed crude *syn/anti*-**4**$^{N\text{-}Oct}$ was washed with DEE and pentane yielding 6.00 g (6.65 mmol, 84%) of *syn/anti*-**4**$^{N\text{-}Oct}$ as white solid. A separation of the *syn*- and the *anti*-isomer is not possible. The *anti*-isomer represents the major product (ratio *anti* : *syn* = 60:40).

^{1}H NMR (250 MHz, Acetonitrile-*d*$_3$):
δ [ppm] = 9.56 (s, 2H), 8.29 (m, 1H), 8.14 (m, 2H), 8.06 (m, 2H), 7.75 (m, 6H), 4.60 (ttd, J = 6.8, 4.3, 2.0 Hz, 4H), 2.07 (t, J = 7.3 Hz, 4H), 1.31 (m, 20H), 0.86 (h, J = 3.2 Hz, 6H). Overlap of signals of the *syn*- and the *anti*-isomer.

^{13}C NMR (75 MHz, Acetonitrile-*d*$_3$):
δ [ppm] = 143.18 (d, *J* = 10.7 Hz), 137.15, 135.37, 134.62 (d, *J* = 15.6 Hz), 133.10 (m), 131.87 (d, *J* = 6.7 Hz), 129.54 (d, *J* = 2.6 Hz), 128.90, 121.57 (q, *J* = 320 Hz), 114.82 (dd, *J* = 34.6, 2.4 Hz), 49.23, 32.37 (d, *J* = 1.6 Hz), 29.63 (d, J = 12.28 Hz), 29.38 (d, *J* = 5.50 Hz) 26.86, 23.30, 14.34. Overlap of signals of the *syn*- and the *anti*-isomer.

^{19}F NMR (235 MHz, Acetonitrile-*d*$_3$):
δ [ppm] = −55.54 (s, 3F), −55.94 (s, 3F), −79.34 (s, 6F).

ATR-IR:

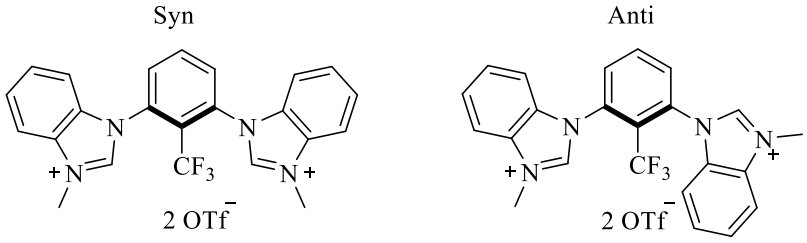
$\tilde{\nu}$ [cm^{-1}] = 3007 (w), 2929 (m), 2858 (m), 1737 (w), 1606 (w), 1595 (w), 1558 (s), 1489 (m), 1463 (m), 1415 (w), 1253 (s), 1222 (m), 1139 (vs), 1045 (w), 1028 (vs), 914 (w), 831 (w), 775 (w), 752 (m), 634 (vs), 572 (m), 514 (vs).

ESI-MS:

m/*z* (+) = calc. 302.18 $[M]^{2+}$ and 604.37 $[M]^{+}$; found 319.07 $[M + NH_4]^{2+}$, 603.00 $[M]^{+}$.

m/*z* (−) = calc. 148.95 $[M]^{-}$; found 148.57 $[M]^{-}$.

1.6.2. Synthesis of syn/anti-*4*$^{N\text{-}Me}$



Chemical Formula: $C_{25}H_{19}F_9N_4O_6S_2$
Exact Mass: 706.05913 g/mol
Elemental Analysis: C, 42.50; H, 2.71; F, 24.20; N, 7.93; O, 13.59; S, 9.08

Under an argon atmosphere 3.00 g of compound syn/*anti*-**3** (7.93 mmol, 1 eq.) were dissolved in 50 ml dry DCM (0.16 M) and 5.21 g of metyhltrifluoromethnasulfoante (3.47 ml, 31.72 mmol, 4 eq.) were added over a period of 1h under ice bath cooling. After heat development stopped the mixture was stirred for further 4 days while *syn/anti*-**4**$^{N\text{-}Me}$ precipitated as solid compound. After the solvent was removed crude *syn/anti*-**4**$^{N\text{-}Me}$ was washed with DEE and pentane yielding 5.40 g (7.64 mmol, 96%) of *syn/anti*-**4**$^{N\text{-}Me}$ as dark solid. A separation of the *syn*- and the *anti*-isomer is not possible. The *anti*-isomer represents the major product (ratio *anti* : *syn* = 60:40).

^{1}H NMR (250 MHz, Acetonitrile-*d*$_3$):

δ [ppm] = 9.51 (d, *J* = 23.0 Hz, 2H), 8.26 (m, 1H), 8.08 (s, 4H), 7.78 (m, 6H), 4.23 (s, 6H). Overlap of signals of the *syn*- and the *anti*-isomer.

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

δ [ppm] = 143.89, 137.20 (d, *J* = 9.4 Hz), 135.44 (d, *J* = 9.26 Hz), 134.37 (d, *J* = 10.16 Hz), 132.79, 29.24 (dd, *J* = 2.93 Hz, 43.24 Hz), 120.75 (q, *J* = 320.02 Hz), 114.89, 114.38 (d, *J* =7.66 Hz), 14, 36.02, 35.13 (d, *J* = 2.83 Hz). Overlap of signals of the *syn*- and the *anti*-isomer.

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

δ [ppm] = −55.52 (s, 3F), −55.74 (s, 3F), −79.58 (s, 6F).

ATR-IR:

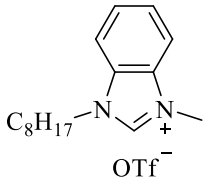
$\tilde{\nu}$ [cm^{-1}] = 3142 (w), 3084 (w), 1616 (w), 1593 (w), 1566 (s),1463 (m), 1425 (w), 1402 (w), 1327 (w), 1244 (s), 1224 (m), 1182 (w), 1165 (w), 1145 (w), 1132 (w), 1111 (w), 1028 (vs), 893 (w), 833 (m), 796 (w), 775 (w), 758 (s), 696 (w), 678 (w), 572 (m), 563 (w), 516 (vs), 445 (w).

ESI-MS:

m/*z* (+) = calc. 204.07 $[M]^{2+}$ and 408.15 $[M]^{+}$; found 204.21 $[M0]^{2+}$, 406.86 $[M]^{+}$.

m/*z* (−) = calc. 148.95 $[M]^{-}$; found 148.57 $[M]^{-}$.

1.6.3. Synthesis of 7^{H}



Chemical Formula: $C_{17}H_{25}F_3N_2O_3S$
Exact Mass: 394.15380 g/mol
m/z: 394.1538 (100.0%), 395.1572 (18.4%), 396.1496 (4.5%), 396.1605 (1.6%)

Under an argon atmosphere 3.07 g of 1-methylbenzimidazole (23.2 mmol, 1 eq.) was dissolved in 60 ml dry DCM (0.38M) and was cooled to 0 °C. After stirring for 15 min. at 0 °C 7.30 g of octyltrifluoromethnasulfoante (6.08 ml, 27.8 mmol, 1.2 eq.) was slowly added over 1h. After stirring for 24 h at r.t. the solvent was removed under reduced pressure. The colourless liquid was washed with 50 ml DEE and pentane (3×50 ml) under precipitation of **7^{H}**. After filtration and removal of solvent residuals 8.24 g of **7^{H}** (20.8 mmol, 90%) were obtained as white solid.

^{1}H NMR (300 MHz, Chloroform-*d*):

δ [ppm] = 9.79 (s, 1H), 7.72 (m, 4H), 4.48 (m, 2H), 4.18 (s, 3H), 2.02 (m, 2H), 1.28 (m, 12H), 0.82 (m, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*):

δ [ppm] = 142.60, 131.80 (d, *J* = 70.0 Hz), 127.44, 120.75 (q, *J* = 320.1 Hz), 113.01 (d, *J* = 16.0 Hz), 47.82, 33.67, 31.75, 29.22 (d, *J* = 27.6 Hz), 26.67, 22.65, 14.12.

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

δ [ppm] = −78.54 (s, 3F)

ATR-IR:

$\tilde{\nu}$ [cm^{-1}] = 3157 (w), 2929 (m), 2858 (m), 1739 (w), 1622 (w), 1571 (m), 1433 (m), 1379 (w), 1355 (w), 1251 (vs), 1224 (m), 1161 (vs), 1099 (w), 1028 (vs), 947 (w), 887 (m), 752 (s), 636 (vs), 605 (m), 572 (m), 516 (s), 424 (m).

ESI-MS:

m/*z* (+) = calc. 245.20 $[M]^+$; found 244.99 $[M]^+$.

m/*z* (−) = calc. 148.95 $[M]^-$; found 148.56 $[M]^-$.

1.6.4. General Selenation Procedure A

Under an argon atmosphere the respective benzimidazolium compound (1 eq.), elemantel selenium powder (2 eq.) and DBU (5 eq.) were added to a microwave flask. Finally, dry acetonitrile (0.17 M) was added and the mixture was stirred in the microwave for 1 h at 150 °C and 14 bar (150 Watt). The mixture was filtered over a plug of silica and rinsed through with ethyl acetate. After the solvent was removed under reduced pressure the respective selenated compound was obtained.

1.6.5. General Selenation Prodcedure B

Under an argon atmosphere the respective bisbenzimidazolium compound (1 eq.) 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 short 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.

1.6.6. General Octylation Procedure for Selenated Compounds

Under an argon atmosphere the respective mono- or bisselenated compound (1 eq.) was dissolved in dry chloroform or DCM and was cooled to 0 °C. Then octyltrifluoromethanesulfonate (exact number of equivalents see at specific compound) 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 and pentane. Finally, the respective octylated selenium compound was obtained.

1.6.7. General Methylation Procedure for Selenated Compounds

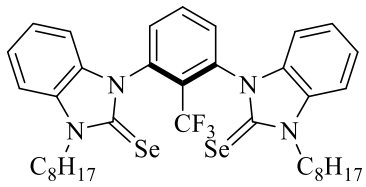
Under an argon atmosphere the respective mono- or bisselenated compound (1 eq.) was dissolved in dry chloroform or DCM and cooled to 0 °C. Then methyltrifluoromethanesulfonate (exact number of equivalents see at specific compound) was slowly added and the reaction mixture was stirred for 24 h at room temperature. After the solvent was removed under reduced pressure the crude residual was washed several times with DEE and pentane. Finally, the respective methylated selenium compound was obtained.

1.6.8. General iso-Propylation Procedure for Selenated Compounds

Under an argon atmosphere the respective mono- or bisselenated compound (1 eq.) was dissolved in dry chloroform or DCM and cooled to 0 °C. Then *iso*-propyltrifluoromethanesulfonate (exact number of equivalents see at specific compound) 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 and pentane. Finally, the respective *iso*-propylated selenium compound was obtained.

1.6.9. Synthesis of syn-5$^{N\text{-}Oct}$

Syn



Chemical Formula: $C_{37}H_{45}F_3N_4Se_2$
Exact Mass: 762.19268 g/mol
Elemental Analysis: C, 58.42; H, 5.96; F, 7.49; N, 7.37; Se, 20.76

Syn-**5**$^{\textbf{N-Oct}}$ was synthesised according to the general selenation procedure B. For the reaction 5.50 g of *syn/anti*-**4**$^{\textbf{N-Oct}}$ (6.09 mmol, 1 eq.), 1.20 g selenium powder (15.2 mmol, 2.5 eq.) and 4.96 g caesium carbonate (15.2 mmol, 2.5 eq.) were used. Purification by column chromatography with pentane:ethyl acetate (2:1) yielded 0.61 g s*yn*-**5**$^{\textbf{N-Oct}}$ (0.80 mmol, 13% applied to used amount of substance of *syn*/ *anti* mixture and 33% applied to the *syn* amount of substance in the mixture) as white solid.

R_f = 0.23 (Pentan:EtOAc 4:1)

^{1}H NMR (300 MHz, Chloroform-*d*):

δ [ppm] = 8.12 (t, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.56 (d, J = 8.0 Hz, 2H), 7.34 (dt, *J* = 20.8, 7.5 Hz, 4H), 7.08 (d, *J* = 7.8 Hz, 2H), 4.46 (m, 4H), 1.94 (m, 4H), 1.39 (m, 20H), 0.90 (t, *J* = 6.7 Hz, 6H).

^{13}C NMR (101 MHz, Acetonitrile-*d*$_3$):

δ [ppm] = 169.76, 137.59, 136.04 (t, J = 13.45 Hz), 134.14, 124.72 (d, *J* = 15.2 Hz), 111.19 (d, *J* = 8.1 Hz), 47.42, 32.46, 29.90 (d, *J* = 5.2 Hz), 28.54, 27.28, 23.33, 14.36.

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

δ [ppm] = −58.16 (s, 3F)

ATR-IR:

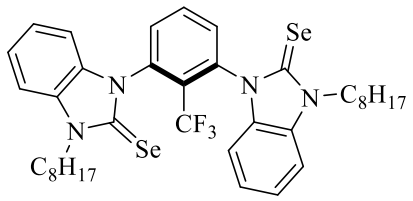
$\tilde{\nu}$ [cm^{-1}] = 3043 (w), 2924 (m), 2848 (m), 1926 (w), 1714 (m), 1598 (w), 1467 (w), 1444 (w), 1404 (w), 1384 (m), 1334 (w), 1303 (m), 1278 (s), 1240 (m), 1180 (m), 1139 (m), 1039 (m), 1010 (w), 935 (w), 916 (w), 804 (w), 781 (w), 754 (w), 736 (s), 675 (w), 623 (w), 607 (w), 557 (w), 503 (w), 447 (w), 428 (m).

EI-MS (70 EV):

m/z (%) = 762.1 (8) $[M]^+$, 691 (5) $[M-Se+Li]^+$, 492 (5) $[C_{29}H_{28}N_4F_3Se]^+$, 379 (2) $[C_{21}H_{11}N_4F_3]^+$.

1.6.10. Synthesis of anti-5$^{N\text{-}Oct}$

Anti



Chemical Formula: $C_{37}H_{45}F_3N_4Se_2$
Exact Mass: 762.19268 g/mol
Elemental Analysis: C, 58.42; H, 5.96; F, 7.49; N, 7.37; Se, 20.76

Anti-**5$^{N\text{-}Oct}$** was synthesised according to the general selenation procedure B. For the reaction 5.50 g of *syn/anti*-**4$^{N\text{-}Oct}$** (6.09 mmol, 1 eq.), 1.20 g selenium powder (15.2 mmol, 2.5 eq.) and 4.96 g caesium carbonate (15.2 mmol, 2.5 eq.) were used. Purification by column chromatography with pentane:ethyl acetate (2:1) yielded 1.76 g *anti*-**5$^{N\text{-}Oct}$** (2.31 mmol, 40% applied to used amount of substance of *syn*/ *anti* mixture and 63% applied to the *anti* amount of substance in the mixture) as beige solid.

R_f = 0.55 (Pentan:EtOAc 4:1)

^{1}H NMR (300 MHz, Chloroform-*d*):

δ [ppm] = 8.03 (t, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.35 (m, 6H), 7.08 (m, 2H), 4.53 (m, 4H), 1.97 (dq, *J* = 15.2, 7.7, 6.9 Hz, 4H), 1.36 (m, 20H), 0.85 (m, 6H).

^{13}C NMR (101 MHz, Acetonitrile-*d*$_3$):

δ [ppm] = 169.31, 137.71, 136.05, 135.80, 135.50, 134.12, 128.54 (q, *J* = 30.5 Hz) 124.84 (d, *J* = 2.40 Hz),
111.23 (d, *J* = 6.5 Hz), 47.43, 32.44, 29.88 (d, *J* = 4.9 Hz), 28.55, 27.27, 23.32, 14.36.

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

δ [ppm] = −57.51 (s, 3F)

ATR-IR:

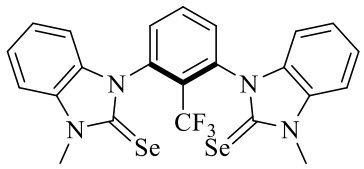
$\tilde{\nu}$ [cm^{-1}] = 3072 (w), 2924 (s), 2852 (m), 1737 (w), 1600 (w), 1583 (w), 1485 (m), 1469 (m), 1392 (s), 1332 (m), 1301 (w), 1282 (m), 1234 (w), 1219 (w), 1180 (w), 1165 (w), 1139 (m), 1041 (m), 921 (m), 798 (m), 736 (vs), 682 (m), 619 (w), 586 (w), 557 (w), 457 (w), 426 (m).

EI-MS (70 EV):

m/*z* (%) = 762.1 (4) [M]$^+$, 240 (18) [$C_{19}H_{12}$]$^+$, 180 (30) [$C_{14}H_{12}$]$^+$.

1.6.11. Synthesis of syn-5$^{N\text{-}Me}$

Syn



Chemical Formula: $C_{23}H_{17}F_3N_4Se_2$
Exact Mass: 565.97357 g/mol
Elemental Analysis: C, 48.95; H, 3.04; F, 10.10; N, 9.93; Se, 27.98

Syn-**5$^{N\text{-}Me}$** was synthesised according to the general selenation procedure B. For the reaction 1.13 g of *syn/anti*-**4$^{N\text{-}Me}$** (1.68 mmol, 1 eq.), 0.32 g selenium powder (3.98 mmol, 2.5 eq.) and 1.30 g caesium carbonate (3.98 mmol, 2.5 eq.) were used. Purification by column chromatography with pentane:ethyl acetate (2:1→1:1→1:2→0:1) yielded 0.32 g *syn*-**5$^{N\text{-}Me}$** (0.54 mmol, 33% applied to used amount of substance of *syn*/ *anti* mixture and 80% applied to *syn* amount of substance in the mixture) as colourless solid.

R_f = 0.41 (Pentane:EtOAc 2:1)

^{1}H NMR (400 MHz, Chloroform-*d*):

δ [ppm] = 8.00 (t, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.27(m, 6H), 6.87 (d, *J* = 7.9 Hz, 2H), 3.99 (d, *J* = 3.5 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*):

δ [ppm] = 169.06, 136.57, 134.63, 134.51, 134.20, 133.84, 128.36 (q, *J* = 30.2 Hz), 123.75 (d, J = 3.4 Hz), 109.65 (d, *J* = 24.6 Hz), 33.41.

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

δ [ppm] = −57.53 (s, 3F)

ATR-IR:

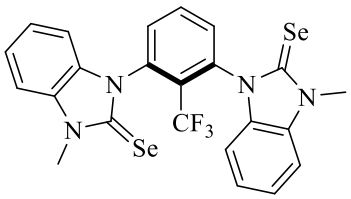
$\tilde{\nu}$ [cm^{-1}] = 3049 (w), 2948 (w), 2179 (w), 1716 (m), 1598 (w), 1577 (w), 1485 (w), 1471 (w), 1435 (m), 1396 (w), 1375 (m), 1344 (w), 1327 (m), 1305 (w), 1286 (s), 1217 (m), 1180 (w), 1151 (m), 1130 (w), 1118 (s), 1039 (m), 1008 (m), 958 (w), 937 (w), 920 (w), 813 (w), 786 (w), 744 (m), 677 (s), 623 (s), 555 (m), 495 (w), 447 (m), 428 (m).

EI-MS (70 EV):

m/*z* (%) = 494 (5) [M−Se+Li]$^+$.

1.6.12. Synthesis of anti-5$^{N\text{-}Me}$

Anti



Chemical Formula: $C_{23}H_{17}F_3N_4Se_2$
Exact Mass: 565.97357 g/mol
Elemental Analysis: C, 48.95; H, 3.04; F, 10.10; N, 9.93; Se, 27.98

Anti-**5$^{N\text{-}Me}$** was synthesised according to the general selenation procedure B. For the reaction 1.13 g of *syn/anti*-**4$^{N\text{-}Me}$** (1.68 mmol, 1 eq.), 0.32 g selenium powder (3.98 mmol, 2.5 eq.) and 1.30 g caesium carbonate (3.98 mmol, 2.5 eq.) were used. Purification by column chromatography with pentane:ethyl acetate (2:1→1:1→1:2→0:1) yielded 0.50 g *anti*-**5$^{N\text{-}Me}$** (0.88 mmol, 52% applied to used amount of substance of *syn*/ *anti* mixture and 87% applied to the *anti* amount of substance in the mixture) as colourless solid.

R_f = 0.82 (Pentane:EtOAc 2:1)

^{1}H NMR (400 MHz, Chloroform-*d*):

δ [ppm] = 8.00 (t, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 7.1 Hz, 2H), 7.33 (m, 6H), 7.16 (m, 2H), 3.99 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*):

δ [ppm] = 168.72, 136.93, 134.78 (d, *J* = 14.7 Hz), 134.36, 133.73, 126.54 (q, *J* = 30.3 Hz), 124.33 (d, *J* = 18.2 Hz), 111.21, 109.53, 33.59.

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

δ [ppm] = −57.37 (s, 3F)

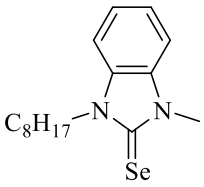
ATR-IR:

$\tilde{\nu}$ [cm^{-1}] = 3037 (w), 2929 (w), 1732 (w), 1598 (w), 1581 (w), 1469 (m), 1433 (m), 1375 (m), 1330(m), 1303 (w), 1278 (m), 1222 (m), 1180 (m), 1165 (w), 1139 (w), 1112 (w), 1041 (m), 1008 (m), 921 (w), 813 (w), 798 (w), 738 (vs), 680 (m), 663 (w), 553 (s),516 (w), 453 (w), 426 (m).

EI-MS (70 EV):

m/*z* (%) = 565.8 (5) $[M]^+$, 494 (3) $[M-Se+Li]^+$, 181 (10) $[C_{14}H_{13}]^+$.

1.6.13. Synthesis of 8



Chemical Formula: $C_{16}H_{24}N_2Se$
Exact Mass: 324.11047 g/mol
Elemental Analysis: C, 59.43; H, 7.48; N, 8.66; Se, 24.42

8 was synthesised according to the general selenation procedure A. For the reaction 2.00 g of **7^{H}** (5.07 mmol, 1 eq.), 0.80 g selenium powder (10.2 mmol, 2.0 eq.) and 3.86 g DBU (3.78 ml, 25.4 mmol, 5.0 eq.) were used. After filtration / purification 1.56 g of **8** (4.81 mmol, 95%) was obtained as white powder.

R_f = 0.90 (DCM)

^{1}H NMR (300 MHz, Chloroform-*d*):

δ [ppm] = 7.13 (m, 4H), 4.27 (t, *J* = 7.62 Hz, 2H), 3.74 (s, 3H), 1.67 (m, 2H), 1.23 (m, 10H), 0.73 (t, *J* = 7.41, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*):

δ [ppm] = 165.71, 132.75 (d, *J* = 51.4 Hz), 122.81 (d, *J* = 3.0 Hz), 109.15 (d, *J* = 4.7 Hz), 46.31, 32.80, 29.13, 28.24 (d, *J* = 78.7 Hz), 22.23, 13.75.

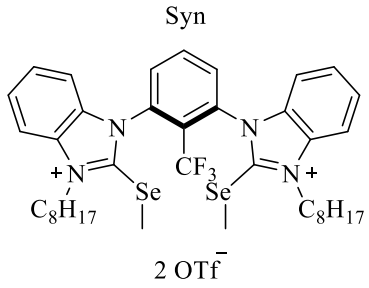
ATR-IR:

$\tilde{\nu}$ [cm^{-1}] = 3024 (m), 2953 (w), 2916 (s), 2870 (w), 2848 (m), 1955 (w), 1911 (w), 1606 (m), 1483 (m), 1465 (m), 1438 (m), 1357 (m), 1336 (m), 1321 (m), 1284 (w), 1274 (w), 1226 (m), 1205 (w), 1188 (m), 1138 (m), 1116 (m), 1095 (w), 1074 (w), 1047 (w), 970 (w), 833 (w), 806 (w), 788 (m), 752 (m), 727 (m), 661 (m), 576 (m), 563 (m), 432 (m).

EI-MS (70 EV):

m/*z* (%) = 324.1 (0.5) $[M]^+$, 322.1 (0.25) $[M]^+$, 243 (5) $[M-Se]^+$, 131 (5) $[M-Se-C_8H_{17}]^+$, 119 (5) $[C_7H_7N_2]^+$.

1.6.14. Synthesis of syn-6$^{N\text{-}Oct/Se\text{-}Me}$



Chemical Formula: $C_{41}H_{51}F_9N_4O_6S_2Se_2$
Exact Mass: 1090.14258 g/mol
Elemental Analysis: C, 45.22; H, 4.72; F, 15.70; N, 5.15; O, 8.82; S, 5.89; Se, 14.50

Syn-**6$^{N\text{-}Oct/Se\text{-}Me}$** was synthesised according to the general methylation procedure for selenated compounds. For the reaction 0.30 g *syn*-**5$^{N\text{-}Oct}$** (0.39 mmol, 1 eq.) and 0.19 g methyltrifluoromethanesulfonate (0.13 ml, 1.18 mmol, 3 eq.) were used. After purification 0.50 g *Syn*-**6$^{N\text{-}Oct/Se\text{-}Me}$** (0.46 mmol, 90%) was obtained as slightly yellowish crystalline foam.

^{1}H NMR (300 MHz, Acetonitrile-*d*$_3$):

δ [ppm] = 8.39 (ddd, *J* = 8.8, 7.4, 0.7 Hz, 1H), 8.23 (dt, *J* = 8.1, 0.8 Hz, 2H), 8.05 (m, 2H), 7.75 (m, 6H), 4.73 (td, *J* = 7.3, 2.7 Hz, 4H), 2.43 (s, 6H), 2.03 (t, *J* = 7.4 Hz, 4H), 1.34 (m, 20H), 0.87 (t, *J* = 7.42 Hz, 6H).

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

δ [ppm] = 147.93, 138.36, 136.35, 135.87, 134.30 (d, *J* = 1.7 Hz), 133.27, 129.30 (d, *J* = 30.1 Hz), 124.94 (q, *J* = 320.0 Hz), 114.66 (d, *J* = 36.8 Hz), 50.42, 32.39, 29.76 (m), 27.14, 23.32, 14.35, 12.07.

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

δ [ppm] = −56.33 (s, 3F), −79.28 (s, 6F).

ATR-IR:

$\tilde{\nu}$ [cm^{-1}] = 3023 (w), 2927 (m), 2856 (m), 1718 (w), 1587 (w), 1473 (m), 1429 (m), 1406 (w), 1361 (w), 1251 (vs), 1222 (m), 1139 (vs), 1028 (s), 931 (m), 844 (w), 802 (m), 754 (vs), 634 (vs), 572 (s), 459 (w), 432 (m), 406 (w).

ESI-MS:

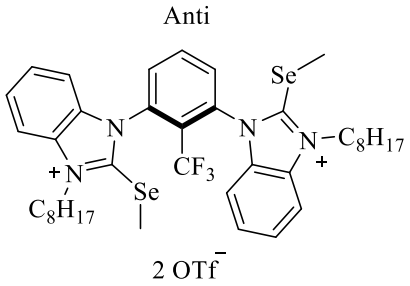
m/*z* (+) = calc. 396.11 $[M]^{2+}$ and 792.23 $[M]^{+}$; found 388.20 $[M-CH_3]^{2+}$, 414.99 $[M+NH_4]^{2+}$ and 600.82 $[M-SeC_8H_{17}]^{+}$.

m/*z* (−) = calc. 148.95 $[M]^{-}$; found 148.59 $[M]^{-}$.

CHNS:

	C	H	N	S
calc.	45.22	4.72	5.15	5.89
found	45.39	4.63	5.10	6.50

1.6.15. Synthesis of anti-6$^{N\text{-}Oct/Se\text{-}Me}$



Chemical Formula: $C_{41}H_{51}F_9N_4O_6S_2Se_2$
Exact Mass: 1090.14258 g/mol
Elemental Analysis: C, 45.22; H, 4.72; F, 15.70; N, 5.15; O, 8.82; S, 5.89; Se, 14.50

Anti-**6**$^{\textbf{N-Oct/Se-Me}}$ was synthesised according to the general methylation procedure for selenated compounds. For the reaction 0.79 g *anti*-**5**$^{\textbf{N-Oct}}$ (1.03 mmol, 1 eq.) and 0.68 g methyltrifluoromethanesulfonate (0.45 ml, 4.13 mmol, 4 eq.) were used. After purification 1.02 g a*nti*-**6**$^{\textbf{N-Oct/Se-Me}}$ (0.94 mmol, 91%) was obtained as white solid.

^{1}H NMR (300 MHz, Acetonitrile-*d*$_3$):

δ [ppm] = 8.42 (ddd, *J* = 8.9, 7.3, 0.7 Hz, 1H), 8.28 (dt, *J* = 8.1, 0.8 Hz, 2H), 8.06 (m, 2H), 7.78 (m, 4H), 7.48 (m, 2H), 4.75 (td, *J* = 7.2, 2.4 Hz, 4H), 2.50 (s, 6H), 2.04 (p, *J* = 7.2 Hz, 4H), 1.32 (m, 20H), 0.86 (m, 6H).

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

δ [ppm] = 147.59, 138.49, 136.52, 135.91, 134.14, 133.30, 129.72, 128.51 (q, *J* = 30.6 Hz), 124.16 (q, *J* = 320 Hz), 115.75, 114.11, 50.46, 32.37, 30.06, 29.70 (d, J = 6.4 Hz), 27.14, 23.30, 14.35, 12.23.

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

δ [ppm] = −56.43 (s, 3F), −79.22 (s, 6F).

ATR-IR:

$\tilde{\nu}$ [cm^{-1}] = 3037 (w), 2927 (m), 2856 (m), 1737 (s), 1597 (w), 1475 (m), 1429 (m), 1373 (w), 1249 (s), 1222 (w), 1141 (s), 1028 (s), 927 (m), 850 (w), 806 (w), 754 (s), 634 (s), 572 (m), 516 (m), 432 (w).

ESI-MS:

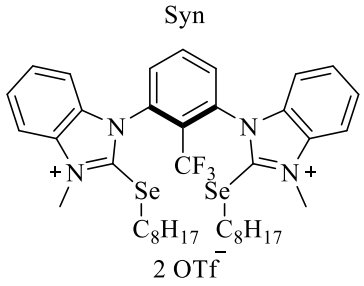
m/*z* (+) = calc. 396.11 $[M]^{2+}$ and 792.23 $[M]^{+}$; found 388.18 $[M-CH_3]^{2+}$ and 415.02 $[M + NH_4]^{2+}$.

m/*z* (−) = calc. 148.95 $[M]^{-}$; found 148.57 $[M]^{-}$.

CHNS:

	C	H	N	S
calc.	45.22	4.72	5.15	5.89
found	45.26	4.60	5.16	6.12

1.6.16. Synthesis of syn-$6^{N\text{-}Me/Se\text{-}Oct}$



Chemical Formula: $C_{41}H_{51}F_9N_4O_6S_2Se_2$
Exact Mass: 1090.14258 g/mol
Elemental Analysis: C, 45.22; H, 4.72; F, 15.70; N, 5.15; O, 8.82; S, 5.89; Se, 14.50

Syn-$\mathbf{6}^{\mathbf{N\text{-}Me/Se\text{-}Oct}}$ was synthesised according to the general octylation procedure for selenated compounds. For the reaction 0.09 g *syn*-$\mathbf{5}^{\mathbf{N\text{-}Me}}$ (0.15 mmol, 1 eq.) and 0.13 g octyltrifluoromethanesulfonate (0.11 ml, 0.46 mmol, 3 eq.) were used. After purification 0.13 g s*yn*-$\mathbf{6}^{\mathbf{N\text{-}Me/Se\text{-}Oct}}$ (0.12 mmol, 80%) was obtained as slightly greyish solid.

^{1}H NMR (300 MHz, Acetonitrile-d_3):

δ [ppm] = 8.34 (t, *J* = 8.1 Hz, 1H), 8.12 (dd, *J* = 8.3, 4.4 Hz, 2H), 8.01 (m, 2H), 7.74 (m, 6H), 4.28 (s, 6H), 3.15 (t, *J* = 7.1 Hz, 4H), 1.68 (dd, *J* = 14.2, 7.0 Hz, 4H), 1.27 (m, 20H), 0.88 (td, *J* = 6.3, 3.2 Hz, 6H).

^{13}C NMR (101 MHz, Acetonitrile-*d*$_3$):

δ [ppm] = 148.27, 138.15, 136.44, 135.66, 134.43 (d, *J* = 17.5 Hz), 129.64, 129.06, 127.49 (d, *J* = 30.6 Hz), 123.80 (q, *J* = 320.41 Hz), 114.83, 114.34, 36.55, 33.62, 32.55, 31.42, 30.40 – 29.05 (t, *J* = 24.09 Hz), 23.38, 14.40.

^{19}F NMR (235 MHz, Acetonitrile-*d*$_3$):

δ [ppm] = −56.02 (s, 3F), −79.37 (s, 6F).

ATR-IR:

$\tilde{\nu}$ [cm^{-1}] = 3058 (w), 2927 (m), 2856 (m), 1737 (m), 1587 (w), 1506 (w), 1477 (m), 1456 (w), 1404 (m), 1382 (w), 1354 (w), 1251 (vs), 1222 (m), 1141 (vs), 1028 (s), 852 (m), 812 (m), 754 (s), 684 (w), 634 (vs), 572 (m), 555 (w), 516 (s), 457 (w), 432 (m).

ESI-MS:

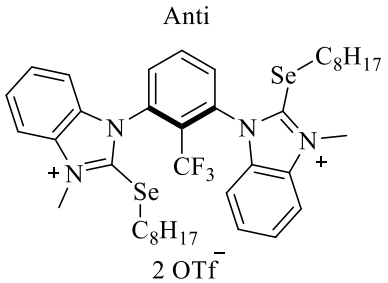
m/*z* (+) = calc. 396.11 $[M]^{2+}$ and 792.23 $[M]^{+}$; found 339.08 $[M-C_8H_{17}]^{2+}$, 437.03 [M+Potassium]$^{2+}$ and 678.75 $[M-C_8H_{17}]^{+}$.

m/*z* (−) = calc. 148.95 $[M]^{-}$; found 148.61 $[M]^{-}$.

CHNS:

	C	H	N	S
calc.	45.22	4.72	5.15	5.89
found	45.30	4.65	5.21	5.81

1.6.17. Synthesis of anti-6$^{N\text{-}Me/Se\text{-}Oct}$



Chemical Formula: $C_{41}H_{51}F_9N_4O_6S_2Se_2$
Exact Mass: 1090.14258 g/mol
Elemental Analysis: C, 45.22; H, 4.72; F, 15.70; N, 5.15; O, 8.82; S, 5.89; Se, 14.50

Anti-**6$^{N\text{-}Me/Se\text{-}Oct}$** was synthesised according to the general methylation procedure for selenated compounds.

For the reaction 0.14 g *anti*-**5**$^{\mathbf{N\text{-}Me}}$ (0.25 mmol, 1 eq.) and 0.21 g octyltrifluoromethanesulfonate (0.17 ml, 0.75 mmol, 3 eq.) were used. After purification 0.22 g *anti*-**6**$^{\mathbf{N\text{-}Me/Se\text{-}Oct}}$ (0.2 mmol, 80%) was obtained as slightly greyish foam.

^{1}H NMR (300 MHz, Acetonitrile-*d*$_3$):

δ [ppm] = 8.38 (t, *J* = 8.1 Hz, 1H), 8.14 (d, *J* = 8.1 Hz, 2H), 8.03 (d, *J* = 8.1 Hz, 2H), 7.79 (dtd, *J* = 17.1, 7.4, 1.2 Hz, 4H), 7.45 (d, *J* = 8.1 Hz, 2H), 4.29 (s, 6H), 3.21 (t, *J* = 7.4 Hz, 4H), 1.71 (q, *J* = 7.3 Hz, 4H), 1.28 (m, 20H), 0.84 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, Acetonitrile-*d*$_3$):

δ [ppm] = 148.32, 138.35, 136.65, 134.35 (d, *J* = 7.6 Hz), 129.40 (d, *J* = 61.4 Hz), 123.72 (q, *J* = 320.01 Hz), 114.42 (d, *J* = 113.6 Hz), 71.36, 36.57, 33.76, 32.47, 31.29, 30.31 (t, *J* = 28.59 Hz), 23.32, 14.36.

^{19}F NMR (235 MHz, Acetonitrile-*d*$_3$):

δ [ppm] = −56.08 (s, 3F), −79.28 (s, 6F).

ATR-IR:

$\tilde{\nu}$ [cm^{-1}] = 3068 (w), 2927 (m), 2856 (m), 1587 (w), 1506 (w), 1477 (m), 1458 (w), 1404 (m), 1384 (w), 1354 (w), 1253 (vs), 1222 (m), 1143 (vs), 1028 (s), 1012 (w), 852 (m), 812 (m), 754 (vs), 684 (m), 634 (vs), 572 (m), 555 (w), 516 (s), 457 (w), 432 (m).

ESI-MS:

m/*z* (+) = calc. 396.11 $[M]^{2+}$ and 792.23 $[M]^{+}$; found 679.06 $[M-C_8H_{17}]^{+}$.

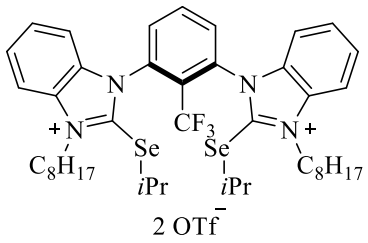
m/*z* (−) = calc. 148.95 $[M]^{-}$; found 148.61 $[M]^{-}$.

CHNS:

	C	H	N	S
calc.	45.22	4.72	5.15	5.89
found	44.87	4.63	5.11	6.43

1.6.18. Synthesis of syn-6$^{N\text{-}Oct/Se\text{-}iPr}$

Syn



Chemical Formula: $C_{45}H_{59}F_9N_4O_6S_2Se_2$
Exact Mass: 1146.20518 g/mol
Elemental Analysis: C, 47.20; H, 5.19; F, 14.93; N, 4.89; O, 8.38; S, 5.60; Se, 13.79

Syn-**6**$^{N\text{-}Oct/Se\text{-}iPr}$ was synthesised according to the general *iso*-propylation procedure for selenated compounds. For the reaction g *syn*-**5**$^{N\text{-}iPr}$ (mmol, 1 eq.) and g *iso*-propyltrifluoromethanesulfonate (ml, mmol, eq.) were used. After purification g *syn*-**6**$^{N\text{-}Oct/Se\text{-}iPr}$ (mmol, 95%) was obtained as slightly beige crystalline foam.

^{1}H NMR (300 MHz, Acetonitrile-*d*$_3$):

δ [ppm] = 8.44 (t *J* = 7.5 Hz, 1H), 8.26 (d, *J* = 7.93 Hz, 2H), 8.12 (dd, *J* = 7.29 Hz, 1.52 Hz, 2H), 7.80 (m, 6H), 4.80 (m, 4H), 3.87 (p, *J* = 6.8 Hz, 2H), 2.05 (m, 4H), 1.58 (d, *J* = 6.8 Hz, 6H), 1.44 (d, *J* = 6.8 Hz, 6H), 1.27 (m, 20H), 0.89 (m, 6H).

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

δ [ppm] = 146.93, 138.36, 136.39, 136.11, 134.39 (d, *J* = 1.8 Hz), 133.28, 129.56 (d, *J* = 49.0 Hz), 124.10 (q, *J* = 320 Hz), 114.95 (d, *J* = 35.8 Hz), 50.59, 45.09, 32.33, 30.05, 29.65 (d, *J* = 7.7 Hz), 26.98, 25.34 (d, *J* = 6.5 Hz), 23.30, 14.35.

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

δ [ppm] = −56.19 (s, 3F), −79.38 (s, 6F).

ATR-IR:

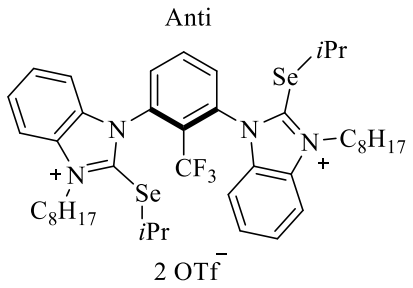
$\tilde{\nu}$ [cm^{-1}] = 3070 (w), 2927 (m), 2856 (m), 1598 (w), 1473 (m), 1427 (m), 1400 (w), 1359 (w), 1255 (vs), 1222 (vs), 1139 (vs), 1028 (vs), 873 (w), 844 (w), 802 (w), 756 (s), 684 (w), 667 (w), 634 (vs), 572 (m), 514 (s), 457 (w), 433 (w), 412 (w).

ESI-MS:

m/*z* (+) = calc. 424.15 $[M]^{2+}$ and 848.30 $[M]^{+}$; found 381.05 $[M-(i\text{Pr})_2]^2$ and 804.85 $[M-i\text{Pr}]^{+}$.

m/*z* (−) = calc. 148.95 $[M]^{-}$; found 148.50 $[M]^{-}$.

1.6.19. Synthesis of anti-6$^{N\text{-}Oct/Se\text{-}iPr}$



Chemical Formula: $C_{45}H_{59}F_9N_4O_6S_2Se_2$
Exact Mass: 1146.20518 g/mol
Elemental Analysis: C, 47.20; H, 5.19; F, 14.93; N, 4.89; O, 8.38; S, 5.60; Se, 13.79

Anti-**6$^{N\text{-}Oct/Se\text{-}Me}$** was synthesised according to the general *iso*-propylation procedure for selenated compounds. For the reaction g *anti*-**5$^{N\text{-}Oct}$** (mmol, 1 eq.) and g *iso*-propyltrifluoromethane-sulfonate (ml, mmol, eq.) were used. After purification g *anti*-**6$^{N\text{-}Oct/Se\text{-}Me}$** (mmol, 90%) was obtained as slightly greenish, sticky oil.

^{1}H NMR (300 MHz, Acetonitrile-*d*$_3$):

δ [ppm] = 8.45 (t, *J* = 8.5 Hz, 1H), 8.27 (d, *J* = 7.95 Hz, 2H), 8.12 (dd, J = 7.45 Hz, 1.99 Hz, 2H), 7.85 (m, 4H), 7.50 (dd, *J* = 7.45 Hz, 1.99 Hz, 2H), 4.83 (td, *J* = 7.8, 4.2 Hz, 4H), 3.93 (p, *J* = 6.8 Hz, 2H), 2.08 (m, 4H), 1.59 (d, *J* = 6.8 Hz, 6H), 1.50 (d, *J* = 6.8 Hz, 6H), 1.22 (m, 20H), 0.88 (td, *J* = 7.2, 5.2 Hz, 6H).

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

δ [ppm] = 146.97, 138.50, 136.70, 136.06, 134.18 (d, *J* = 1.7 Hz), 133.33, 129.63 (d, *J* = 58.0 Hz), 121.75 (d, *J* = 319.8 Hz), 114.77 (d, *J* = 90.7 Hz), 50.63, 45.24, 32.32, 30.02, 29.64 (d, *J* = 6.6 Hz), 27.00, 25.25, 23.28, 14.33.

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

δ [ppm] = −56.43 (s, 3F), −79.22 (s, 6F).

ATR-IR:

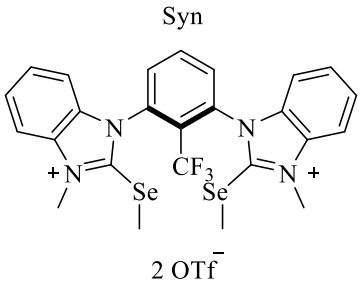
$\tilde{\nu}$ [cm^{-1}] = 3076 (w), 2927 (m), 2856 (m), 1597 (w), 1585 (w), 1473 (m), 1427 (m), 1390 (w), 1373 (w), 1352 (w), 1255 (vs), 1222 (vs), 1139 (vs), 1028 (vs), 873 (w), 850 (w), 806 (w), 75 (s), 686 (w), 634 (vs), 572 (s); 514 (s), 459 (w), 432 (w), 412 (w).

ESI-MS:

m/*z* (+) = calc. 424.15 $[M]^{2+}$ and 848.30 $[M]^{+}$; found 380.05 $[M-(i\text{Pr})_2]^{2+}$ and 804.87 $[M-i\text{Pr}]^{+}$.

m/*z* (−) = calc. 148.95 $[M]^{-}$; found 148.55 $[M]^{-}$.

1.6.20. Synthesis of syn-6$^{N\text{-}Me/Se\text{-}Me}$



Chemical Formula: $C_{27}H_{23}F_9N_4O_6S_2Se_2$
Exact Mass: 893.92348 g/mol
Elemental Analysis: C, 36.33; H, 2.60; F, 19.16; N, 6.28; O, 10.76; S, 7.18; Se, 17.69

Syn-**6**$^{N\text{-}Me/Se\text{-}Me}$ was synthesised according to the general methylation procedure for selenated compounds. For the reaction 0.03 g *syn*-**5**$^{N\text{-}Me}$ (0.05 mmol, 1 eq.) and 0.16 g methyltrifluoromethanesulfonate (0.02 ml, 0.16 mmol, 3 eq.) were used. After purification 0.04 g *syn*-**6**$^{N\text{-}Me/Se\text{-}Me}$ (0.04 mmol, 90%) was obtained as slightly beige solid.

^{1}H NMR (300 MHz, Acetonitrile-*d*$_3$):

δ [ppm] = 8.35 (t, *J* = 8.1 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 2H), 8.02 (m, 2H), 7.78 (dddd, *J* = 13.1, 8.5, 6.1, 1.4 Hz, 4H), 7.67 (d, *J* = 7.6 Hz, 2H), 4.27 (s, 6H), 2.50 (s, 5H).

^{13}C NMR (101 MHz, Acetonitrile-*d*$_3$):

δ [ppm] = 148.94, 138.32, 136.46, 135.52, 134.32 (d, *J* = 14.2 Hz), 129.26 (d, *J* = 54.5 Hz), 123,60 (q, J = 320.40 Hz), 114.45 (d, *J* = 48.9 Hz), 36.31, 11.37.

^{19}F NMR (235 MHz, Acetonitrile-*d*$_3$):

δ [ppm] = −56.22 (s, 3F), −79.32 (s, 6F).

ATR-IR:

$\tilde{\nu}$ [cm^{-1}] = 3062 (w), 1591 (m), 1506 (m), 1475 (s), 1404 (m), 1361 (w), 1255 (vs), 1224 (s), 1190 (w), 1141 (vs), 1043 (w), 1028 (vs), 1014 (m), 939 (m), 842 (m), 810 (m), 752 (vs), 686 (w), 634 (vs), 572 (m), 561 (w), 516 (s), 464 (w), 433 (w), 405 (w).

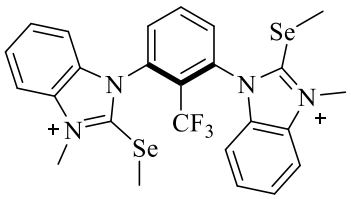
ESI-MS:

m/*z* (+) = calc. 298.00 $[M]^{2+}$ and 596.01 $[M]^{+}$; found 580.67 $[M-CH_3]^{+}$.

m/*z* (−) = calc. 148.95 $[M]^{-}$; found 148.63 $[M]^{-}$.

1.6.21. Synthesis of anti-6$^{N\text{-}Me/Se\text{-}Me}$

Anti



Chemical Formula: $C_{27}H_{23}F_9N_4O_6S_2Se_2$
Exact Mass: 893.92348 g/mol
Elemental Analysis: C, 36.33; H, 2.60; F, 19.16; N, 6.28; O, 10.76; S, 7.18; Se, 17.69

Anti-**6$^{N\text{-}Me/Se\text{-}Me}$** was synthesised according to the general procedure for selenated compounds. For the reaction 0.03 g *anti*-**5$^{N\text{-}Me}$** (0.05 mmol, 1 eq.) and 0.16 g methyltrifluoromethanesulfonate (0.02 ml, 0.16 mmol, 3 eq.) were used. After purification 0.04 g *anti*-**6$^{N\text{-}Me/Se\text{-}Me}$** (0.04 mmol, 90%) was obtained as slightly beige solid.

^{1}H NMR (300 MHz, Acetonitrile-*d*$_3$):

δ [ppm] = 8.35 (q, *J* = 7.1, 6.1 Hz, 1H), 8.13 (d, *J* = 8.1 Hz, 2H), 8.01 (d, *J* = 8.3 Hz, 2H), 7.77 (m, 4H), 7.46 (d, *J* = 8.3 Hz, 2H), 4.28 (s, 6H), 2.53 (s, 6H).

^{13}C NMR (101 MHz, Acetonitrile-*d*$_3$):

δ [ppm] = 148.69, 138.42, 136.53, 135.51, 134.30, 129.64 (d, *J* = 58.61 Hz), 123.60 (q, J = 320.40 Hz), 114.80, 113.93, 36.34, 11.53.

^{19}F NMR (235 MHz, Acetonitrile-*d*$_3$):

δ [ppm] = −56.36 (s, 3F), −79.41 (s, 6F).

ATR-IR:

$\tilde{\nu}$ [cm^{-1}] = 3080 (w), 2960 (w), 1597 (w), 1585 (w), 1508 (w), 1479 (m), 1458 (m), 1404 (m), 1384 (w), 1354 (w), 1213 (m), 1157 (w), 1139 (w), 1109 (m), 1022 (m), 858 (w), 850 (w), 806 (vs), 754 (s), 684 (w), 634 (vs), 570 (m), 555 (w), 513 (s), 459 (w), 432 (w).

ESI-MS:

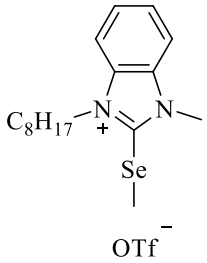
m/*z* (+) = calc. 298.00 $[M]^{2+}$ and 596.01 $[M]^{+}$; found, 284.86 $[M-CH_3]^{2+}$ and 580.84 $[M-CH_3]^{+}$.

m/*z* (−) = calc. 148.95 $[M]^{-}$; found 148.62 $[M]^{-}$.

CHNS:

	C	H	N	S
calc.	36.33	2.60	6.28	7.18
found	36.43	2.63	6.00	8.00

1.6.22. Synthesis of 9$^{Se\text{-}Me}$



Chemical Formula: $C_{18}H_{27}F_3N_2O_3SSe$
Exact Mass: 488.08597 g/mol
Elemental Analysis: C, 44.35; H, 5.58; F, 11.69; N, 5.75; O, 9.85; S, 6.58; Se, 16.20

9$^{Se\text{-}Me}$ was synthesised according to the general methylation procedure for selenated compounds. For the reaction 0.50 g **8** (1.55 mmol, 1 eq.) and 0.51 g methyltrifluoromethanesulfonate (0.34 ml, 3.09 mmol, 2.0 eq.) were used. After purification 0.677 g **9$^{Se\text{-}Me}$** (1.39 mmol, 90%) was obtained as white solid.

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

δ [ppm] = 7.71 (m, 4H), 4.62 (dd, *J* = 8.6, 6.8 Hz, 2H), 4.25 (s, 3H), 2.66 (s, 3H), 1.91 (t, *J* = 7.4 Hz, 2H), 1.39 (m, 10H), 0.86 (t, *J* = 7.2 Hz, 3H).

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

δ [ppm] = 146.37, 134.50, 133.33, 128.11 (d, *J* = 1.3 Hz), 122.20 (d, *J* = 320.9 Hz), 114.23, 49.47, 35.37, 32.45, 30.39, 29.72 (d, *J* = 4.8 Hz), 27.19, 23.33, 14.36, 11.13.

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

δ [ppm] = −78.46 (s, 3F).

ATR-IR:

$\tilde{\nu}$ [cm^{-1}] = 3025 (w), 2926 (m), 2856 (m), 1739 (m), 1610 (w), 1558 (w), 1504 (w), 1475 (m), 1456 (w), 1415 (w), 1398 (w), 1377 (w), 1352 (m), 1255 (m), 1222 (m), 1145 (vs), 1029 (vs), 927 (s), 804 (s), 773 (m), 754 (s), 634 (vs), 588 (w), 570 (m), 516 (s), 437 (m), 405 (w).

ESI-MS:

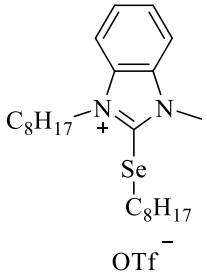
m/*z* (+) = calc. 339.13 $[M]^+$; found 338.91 $[M]^+$.

m/*z* (−) = calc. 148.95 $[M]^-$; found 148.62 $[M]^-$.

CHNS:

	C	H	N	S
calc.	44.35	5.58	5.75	6.58
found	44.17	5.39	5.81	6.58

1.6.23. Synthesis of 9$^{Se\text{-}Oct}$



Chemical Formula: $C_{25}H_{41}F_3N_2O_3SSe$
Exact Mass: 586.19552 g/mol
Elemental Analysis: C, 51.27; H, 7.06; F, 9.73; N, 4.78; O, 8.20; S, 5.47; Se, 13.48

9$^{Se\text{-}Oct}$ was synthesised according to the general octylation procedure for selenated compounds. For the reaction 0.90 g **8** (3.29 mmol, 1 eq.) and 2.73 g octyltrifluoromethanesulfonate (2.27 ml, 9.88 mmol, 3 eq.) were used. After purification 0.58 g **9$^{Se\text{-}Oct}$** (1.08 mmol, 33%) was obtained sticky, slightly yellowish solid.

^{1}H NMR (300 MHz, Chloroform-*d*):

δ [ppm] = 7.83 (m, 1H), 7.64 (m, 3H), 4.61 (dd, *J* = 8.7, 6.7 Hz, 2H), 3.30 (t, *J* = 7.4 Hz, 2H), 1.84 (dq, *J* = 29.3, 7.3 Hz, 4H), 1.33 (m, 20H), 0.87 (t, *J* = 7.5 Hz, 6H).

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

δ [ppm] = 146.38, 134.50, 133.33, 128.10 (d, *J* = 1.3 Hz), 122.18 (d, *J* = 321.0 Hz), 114.23, 49.47, 35.37, 32.45, 30.40, 29.75 (d, *J* = 4.2 Hz), 27.19, 23.33, 14.37, 11.13.

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

δ [ppm] = −78.47 (s, 3F).

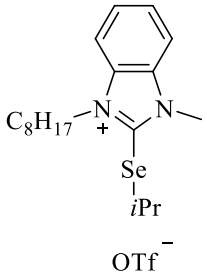
ATR-IR:

$\tilde{\nu}$ [cm^{-1}] = 3029 (w), 2956 (m), 2924 (s), 2856 (m), 1500 (m), 1475 (w), 1413 (w), 1377 (w), 1352 (w), 1253 (vs), 1222 (m), 1155 (vs), 1029 (s), 806 (w), 767 (s), 723 (w), 636 (s), 572 (w), 555 (w), 516 (m), 433 (w).

CHNS:

	C	H	N	S
calc.	51.27	7.06	4.78	5.47
found	49.38	6.64	4.71	6.58

1.6.24. Synthesis of 9$^{Se\text{-}iPr}$



Chemical Formula: $C_{20}H_{31}F_3N_2O_3SSe$
Exact Mass: 516.11727 g/mol
Elemental Analysis: C, 46.60; H, 6.06; F, 11.06; N, 5.43; O, 9.31; S, 6.22; Se, 15.32

9$^{Se\text{-}iPr}$ was synthesised according to the general *iso*-propylation procedure for selenated compounds. For the reaction 0.14 g **8** (0.64 mmol, 1 eq.) and 0.16 ml *iso*-propyltrifluoromethane-sulfonate (0.93 mmol, 2 eq.) were used. After purification 0.17 g **9$^{Se\text{-}iPr}$** (0.42 mmol, 91%) was obtained as sticky, beige oil.

^{1}H NMR (300 MHz, MeCN-*d*$_3$):

δ [ppm] = 7.90 (m, 2H), 7.69 (m, 2H), 4.63 (t, *J* = 7.5 Hz, 2H), 4.17 (s, 3H), 3.97 (p, J = 6.8 Hz, 1H), 1.86 (m, 2H), 1.50 (d, J = 6.8 Hz, 6H), 1.22 (m, 10H), 0.88 (m, 3H).

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

δ [ppm] = 145.57, 134.59, 133.44, 128.28, 121.62 (d, *J* = 320 Hz), 114.48 (d, *J* = 4.6 Hz), 49.55, 43.11, 35.75, 32.45, 30.35, 29.73 (d, *J* = 4.6 Hz), 27.15 24.96, 23.33, 14.37.

^{19}F NMR (235 MHz, MeCN-*d*$_3$):

δ [ppm] = −78.47 (s, 3F).

ATR-IR:

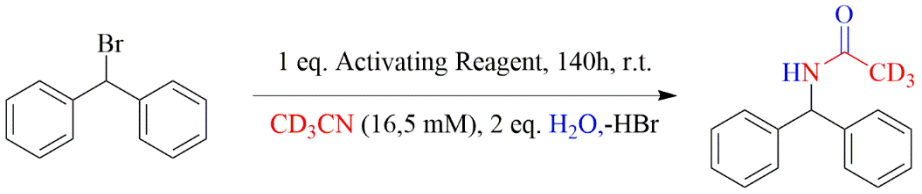
$\tilde{\nu}$ [cm^{-1}] = 3071 (w), 2927 (w), 2858 (w), 1502 (w), 1473 (m), 1413 (w), 1373 (w), 1284 (s), 1222 (vs), 1166 (vs), 1026 (vs), 873 (w), 804 (w), 748 (m), 636 (s), 572 (w), 514 (w).

ESI-MS:

m/*z* (+) = calc. 367.16 $[M]^+$; found 366.72 $[M]^+$.

m/*z* (−) = calc. 148.95 $[M]^-$; found 148.51 $[M]^-$.

2. Catalysis Experiments – Benchmark reaction



1 **2**

Scheme 1: Benchmark reaction.

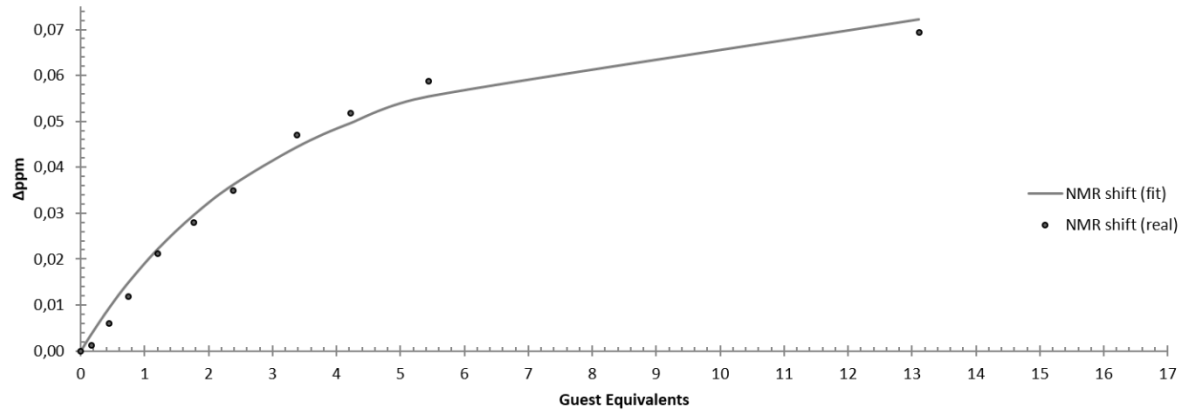
To a NMR tube the respective donor (10.0 µmol, 1.eq or 2.eq) was added followed by evacuation for 45 min. and flushing with argon. Under an argon atmosphere 0.6 ml of a benzhydryl bromide stock solution (16.5 mM, 1eq.; 0.36µL water, 2 eq.) were added and it was mixed for 1 min. All experiments were started simultaneously and the yield was determined by ^{1}H NMR spectroscopy after approximately 6, 12 , 18, 27, 30, 36, 45, 57, 69, 81, 93, 105, 117, 129 and 140h of reaction time.

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. The measured shifts (Δppm) were plotted against the guest-equivalents and the resulting curve was fitted.[2] 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.

Figure 1: Titration Plot of syn-6$^{N\text{-}Oct/Se\text{-}iPr}$ (host) in MeCN-*d3* and N(Oct)$_4$Br as guest molecule.

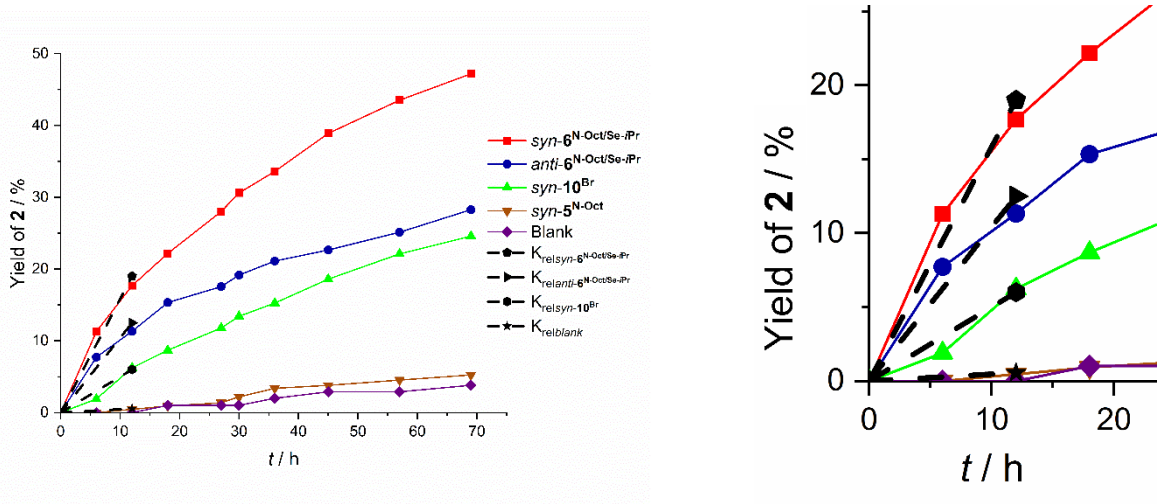


4. Determination k_{rel} values

K_{rel} was determined by a linear fit from the kinetic plot. To this end, the gradient between zero hours and 12h and the corresponding yield of **2** was determined for selected curves. The blank reaction 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 line was (see plot at the end) pasted. The determined initial rates are:

Compound	**k_{rel}**
Blank	1
syn-**10**^{Br}	9
anti-**6**$^{N\text{-}Oct/Se\text{-}iPr}$	23
syn-**6**$^{N\text{-}Oct/Se\text{-}iPr}$	34

Figure 2: Plot with linear fit (left) and zoom into the fit (right).



5. *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 bromide. To this end, the M06-2X density functional[3] was employed with the Gaussian09 suite of programs,[4] in combination with a triple-zeta TZVPP basis set.[5] The optimized structure was confirmed as a minimum by the absence of imaginary frequencies. The complex is shown below (plot by CYLview).[6]

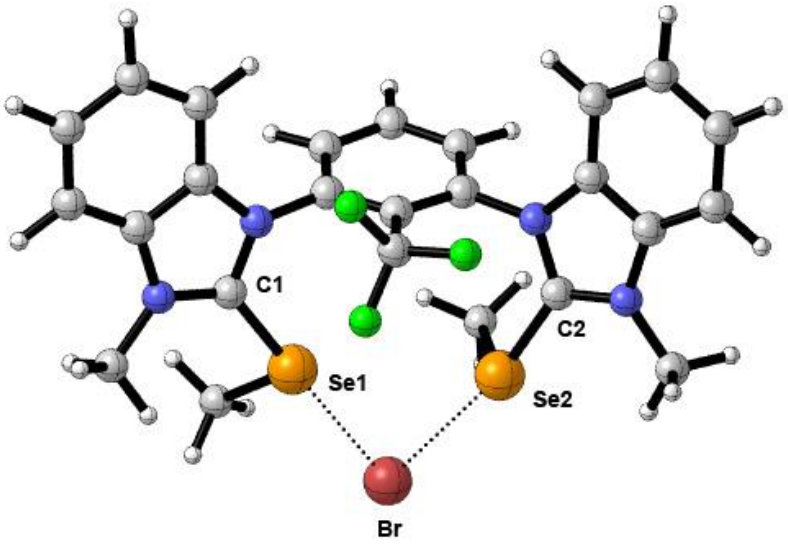


Figure 3: Calculated chalcogen bonding complex

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

Se1-Br = 2.92

C1-Se1-Br = 179

Se2-Br = 3.08

C2-Se2-Br = 169

Se1-Br-Se2 = 75

Coordinates:

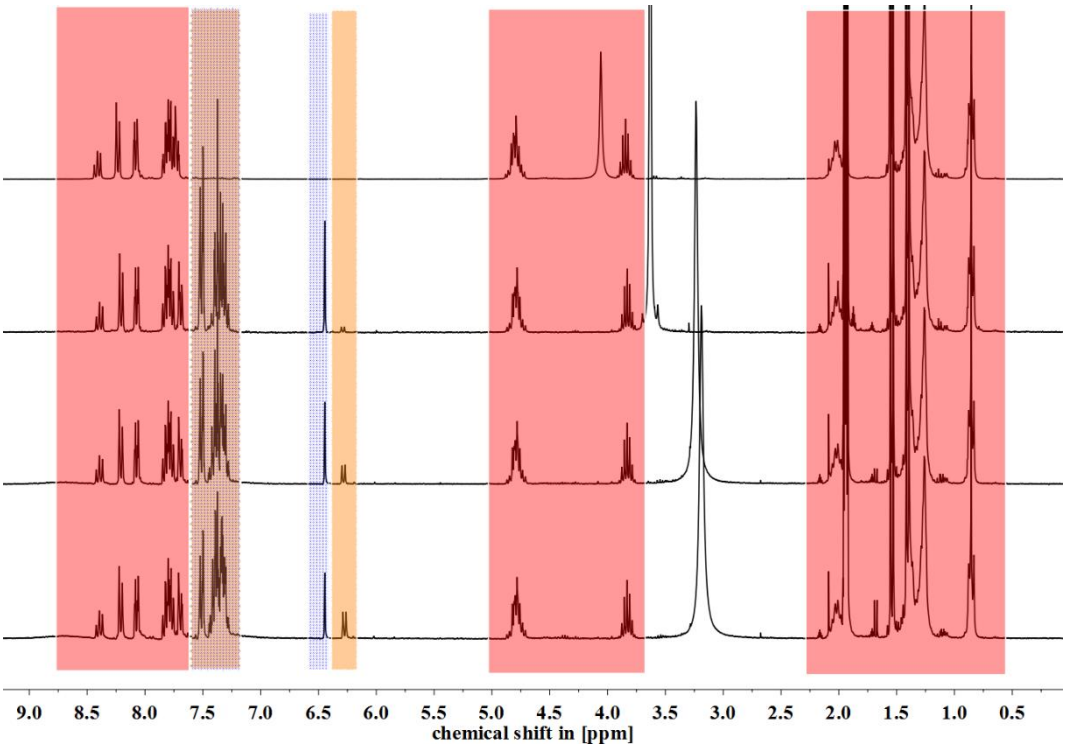
H	-2.05201800	-1.45633600	2.91997400
C	-1.08987000	-1.39301200	2.43001500

C	1.33334500	-1.09523800	1.12867000
C	-1.04521500	-1.27109700	1.05168200
C	0.08802600	-1.41137200	3.15975200
C	1.29554000	-1.22875300	2.50932600
C	0.16895800	-1.19241500	0.36668600
H	0.06016800	-1.51478700	4.23485100
H	2.22209600	-1.15902100	3.06354400
N	2.59152800	-0.80819400	0.52131600
N	-2.28463800	-1.17703300	0.34544200
C	-2.84133200	-0.00794900	-0.06205500
N	-4.05147400	-0.28653500	-0.55582000
C	-3.17888200	-2.22456700	0.12967900
C	-4.31006500	-1.65064100	-0.44090800
C	2.91057800	0.36758200	-0.07247300
N	4.09418300	0.21398300	-0.67273200
C	3.60465200	-1.73717100	0.29563000
C	4.55834000	-1.08333300	-0.47602400
C	-4.94089100	0.66628200	-1.20286400
H	-5.70985700	1.00430700	-0.51093100
H	-4.35171200	1.51120800	-1.54768100
H	-5.40464500	0.17856700	-2.05677200
C	4.83487000	1.23203900	-1.40501000
H	4.79673200	1.01794400	-2.47117100
H	4.38924400	2.20175800	-1.20684200
H	5.86766500	1.22429300	-1.06413000
C	1.47316900	2.00657300	1.77125800
H	0.50226100	1.56625200	1.98013700
H	2.27849500	1.49806400	2.29299800
H	1.45763500	3.06348800	2.01080100
C	-3.32168300	2.73777800	0.72594800
H	-3.76432800	3.34787700	-0.05400600
H	-4.05435400	2.08516900	1.19153500
H	-2.84938800	3.37720400	1.46347200
Se	1.80083600	1.95076800	-0.16149400
Se	-1.85716600	1.67748800	-0.03065500
Br	-0.32870700	4.16356500	0.01170100

C	-5.41489300	-2.41432800	-0.79053000
C	-3.08726100	-3.58569400	0.37481700
C	3.74893800	-3.06248600	0.67686200
C	5.71616900	-1.72105900	-0.89940400
H	-6.29825400	-1.97366300	-1.23003200
H	-2.19963800	-4.02523700	0.80761900
H	6.45817700	-1.21688800	-1.50182100
H	2.99897200	-3.56953600	1.26750500
C	-5.33085700	-3.77301700	-0.54322800
C	-4.18879100	-4.34819400	0.02904000
C	4.90223200	-3.70023300	0.25561200
C	5.86887700	-3.04111100	-0.51555500
H	-6.16721400	-4.40782900	-0.79842200
H	-4.16792000	-5.41473300	0.20143400
H	6.75413900	-3.58013500	-0.82101600
H	5.06197300	-4.73424700	0.52585200
C	0.15474500	-1.33623300	-1.14874900
F	-0.53568300	-2.43810400	-1.46691400
F	1.37244500	-1.48007700	-1.66756400
F	-0.42650000	-0.31502700	-1.76884000

6. *Selected NMR Spectra*

Figure 4: ^{1}H NMR stacked plot of BHB reaction with syn-6$^{N\text{-}Oct/Se\text{-}iPr}$ as activating agent in MeCN-d_3.



Top: syn-6$^{N\text{-}Oct/Se\text{-}iPr}$; Second: Reaction after 6h; Third: Reaction after 69h; Last: Reaction after 140h. red: syn-6$^{N\text{-}Oct/Se\text{-}iPr}$, orange: compound 1 and blue dottet: compound 2.

Figure 5: Selected ^{1}H NMR spectra of blank reaction after 144h in MeCN-d_3.

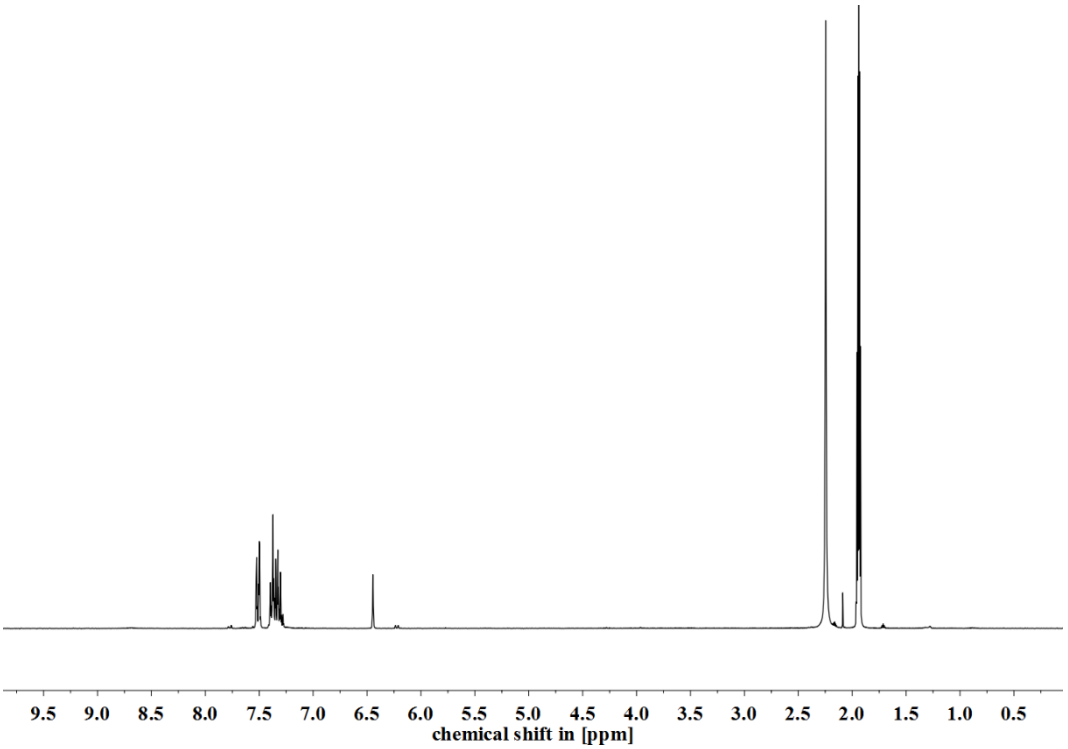


Figure 6: Selected ^{1}H NMR and spectra of syn-6$^{N\text{-}Oct/Se\text{-}Me}$ catalysed reaction (down) after 96h showing decomposition (red) and syn-5$^{N\text{-}Oct}$ donor (up) in MeCN-d_3.

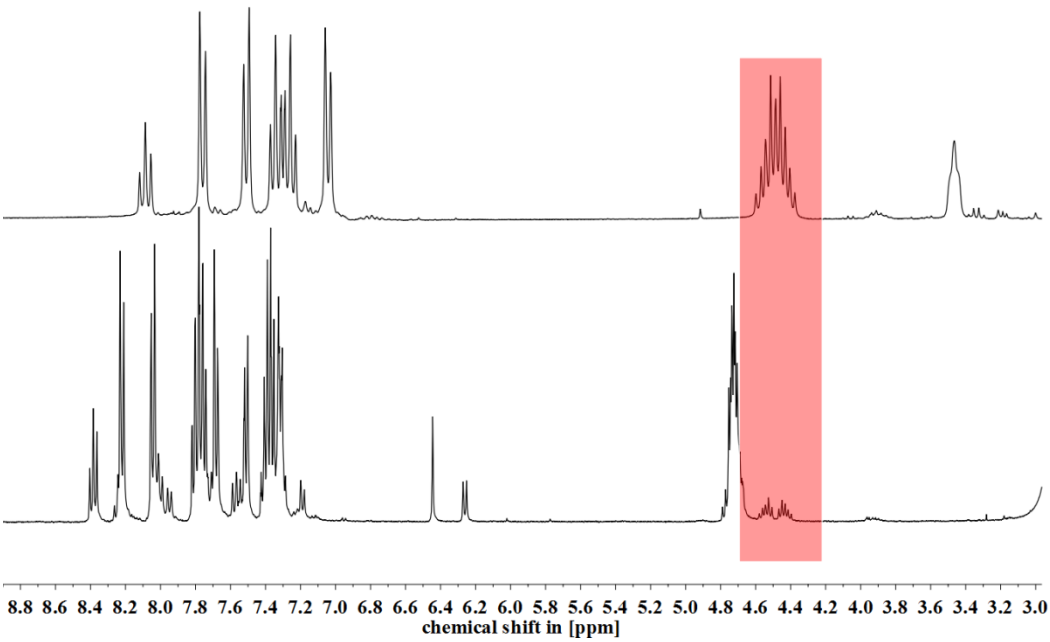


Figure 7: **^{1}H NMR spectra of catalysed reaction with syn-6$^{N\text{-}Oct/Se\text{-}Me}$ showing decomposition of catalyst (red) and formation of MeBr (blue) in MeCN-d_3.**

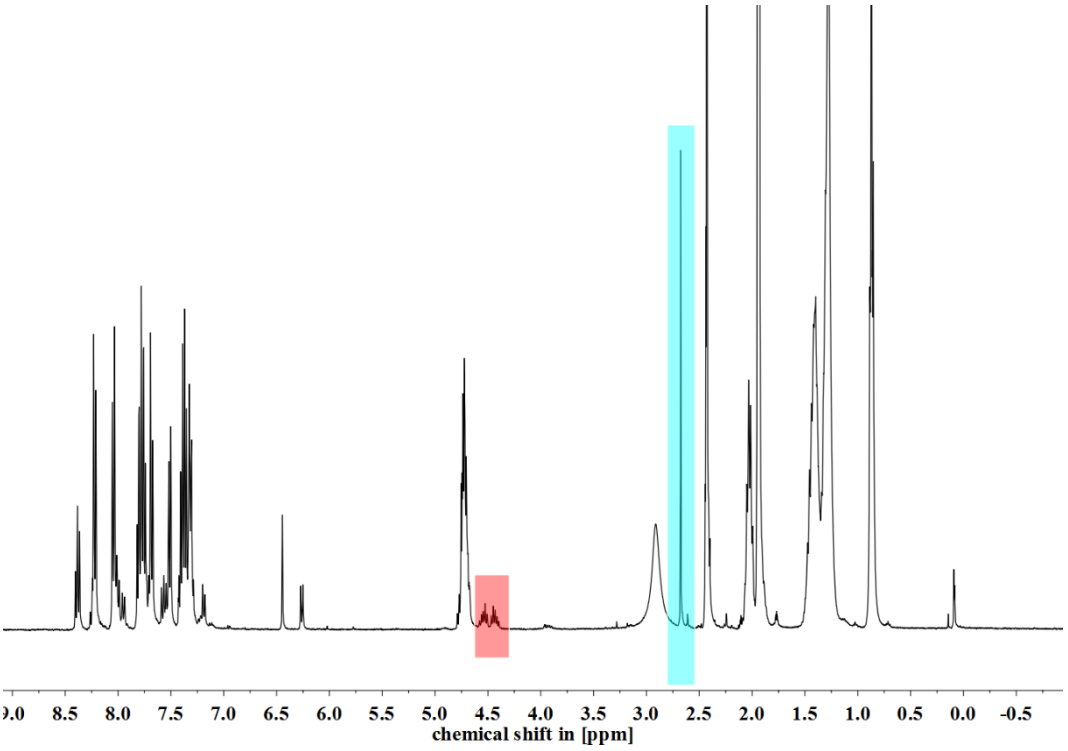


Figure 8: **^{19}F NMR spectra of catalysed reaction with syn-6$^{N\text{-}Oct/Se\text{-}Me}$ showing decomposition of the donor (red: Donor, blue: mono dealkylated ChB-Donor ca. 40%) in MeCN-d_3.**

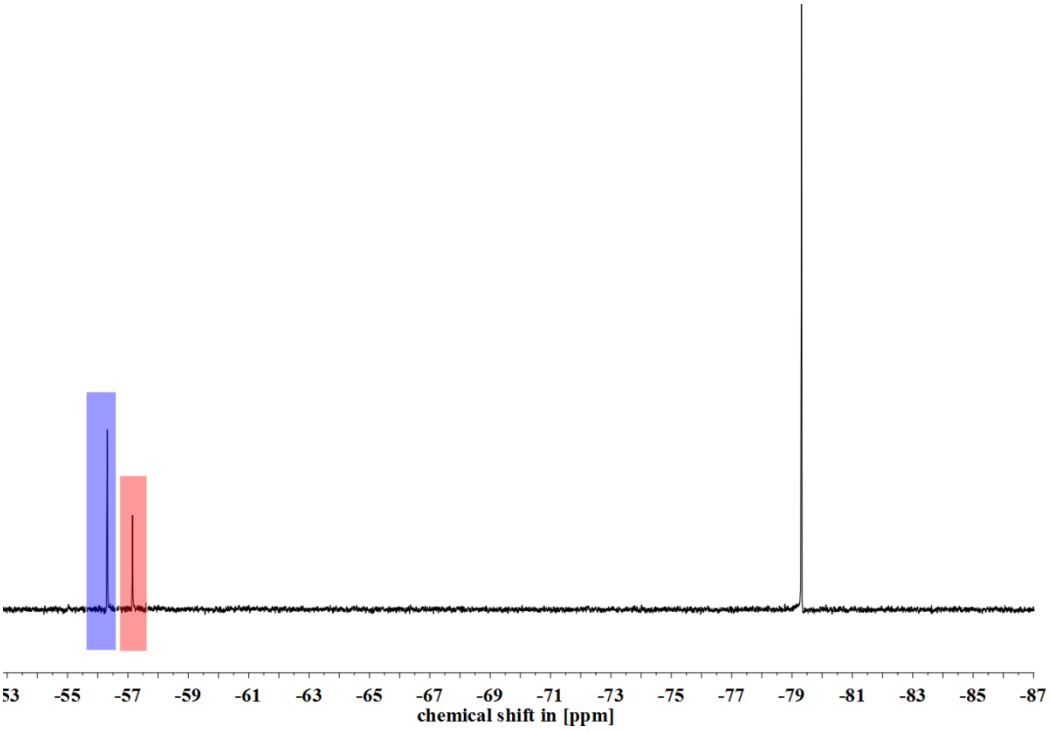


Figure 9: **^{19}F NMR spectra of catalysed reaction with syn-6$^{N\text{-}Me/Se\text{-}Oct}$ donor showing decomposition of the donor (red: Donor, blue: mono dealkylated ChB-Donor. 20%) in MeCN-d_3.**

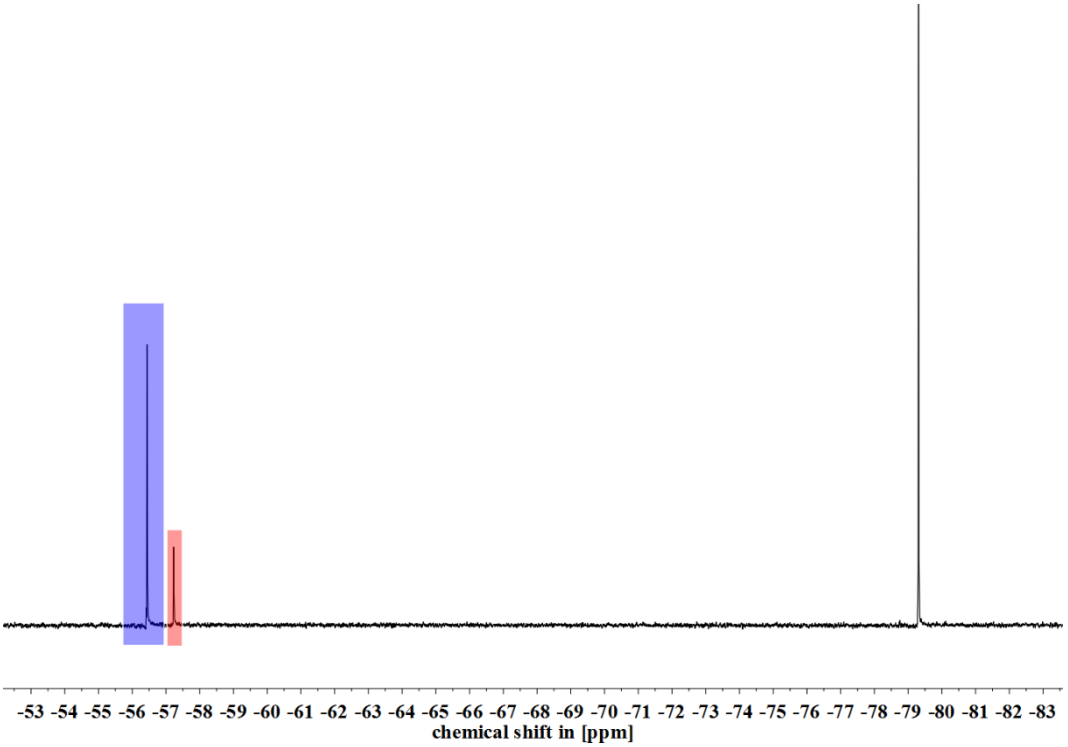
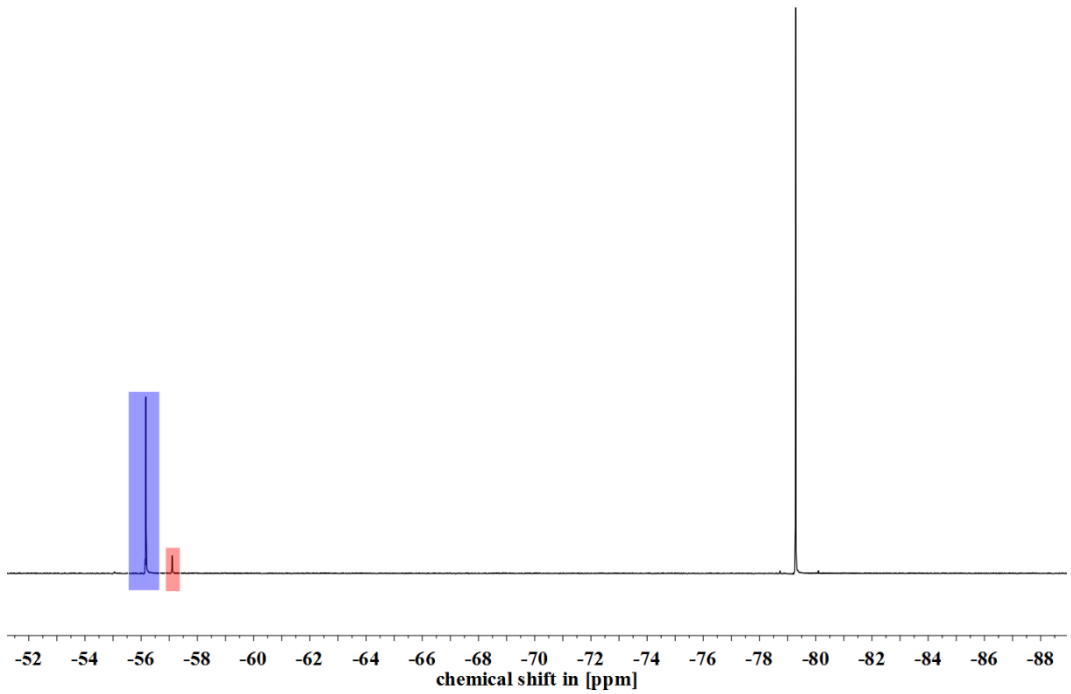


Figure 10: **^{19}F NMR spectra of catalysed reaction with syn-6$^{N\text{-}Oct/Se\text{-}iPr}$ showing decomposition of the donor (red: Donor, blue: mono dealkylated ChB-Donor ca. 4%) in MeCN-d_3.**



7. XRD Data

Table 1. Crystallographic data of *anti*-**6**$^{\text{N-Me/Se-Me}}$

	PW-0075-s
Empirical formular	$C_{27}H_{23F9}N_4O_6S_2Se_2$
Formular weight [g·mol^{-1}]	892.53
Temperature [K]	170(2)
λ [Å]	MoK_α, 0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a [Å]	19.3379(10)
b [Å]	12.3218(7)
c [Å]	27.5669(15)
β [°]	91.825(5)
V [Å^3]	6565.3(6)
Z	8
ρ_{ber} [g·cm^{-3}]	1.806
μ [mm^{-1}]	2.479
F(000)	**3536.0**
2θ for data collection [deg]	5.8 - 25
Index-ranges	***-22 ≤ h ≤ 22,*** ***-14 ≤ k ≤ 14,*** -32 ≤ l ≤ 32
Reflections collected	91875
Independent reflections	10393
R_{int}	0.089
S[a)]	1.024
R_1 [I ≥ 2σ(I)/all data][b)]	0.080/ 0.1036
wR_2 [I ≥ 2σ(I)all data,][c)]	0.1787/ 0.1909
Residual electron density [e Å^{-3}]	1.241/ -1.286
CCDC number	

a) $S = \{\sum[w(F_0^2 - F_c^2)^2]\}/(n-p)\}^{0.5}$, n = number of reflections, p = number of parameters.

b) $R_1 = \sum||F_0| - |F_c|| \sum|F_0|$. [c)] $wR_2 = \{\sum[w(F_0^2 - F_c^2)^2 / \sum[(F_0^2)^s]\}^{0.5}$

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